

Notes X-ray Crystallography

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1997

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X-ray Crystallography Lectures

Updated 1/24/95

Solids

Crystalline....

Materials which internally possess **long-range** three dimensional order.

Examples : Table salt, sugar, gems, quartz, metals

Non-crystalline...

Glass : amorphous, short-range ordered, or random ordered materials "Super cooled liquids"

Liquid crystal : One or two dimensional ordered solids, fibers

The single crystal (xtal)

Typical xtal for X-ray diffraction analysis

Size : 0.3 x 0.3 x 0.3 mm; Volume = 0.027 mm³

Typical unit cell

def.... The parallelepiped volume which, reproduced by close packing in three dimensions, gives the whole crystal.

Size : 12 x 12 x 12 mm; Volume = 1728 mm³

Å = 10⁻¹⁰ meters = 10⁻⁸ cm = 100 pm (picometers)

Therefore in a typical xtal

1.6 x 10¹⁶ unit cells

1.3 x 10¹⁷ molecules for 8 molecules per cell

Techniques for Structure Investigation in Solids

Observation of anisotropic properties

net dipole moments, thermoelectric, piezoelectric, EPR, NMR etc.
Indirect evidence of internal properties

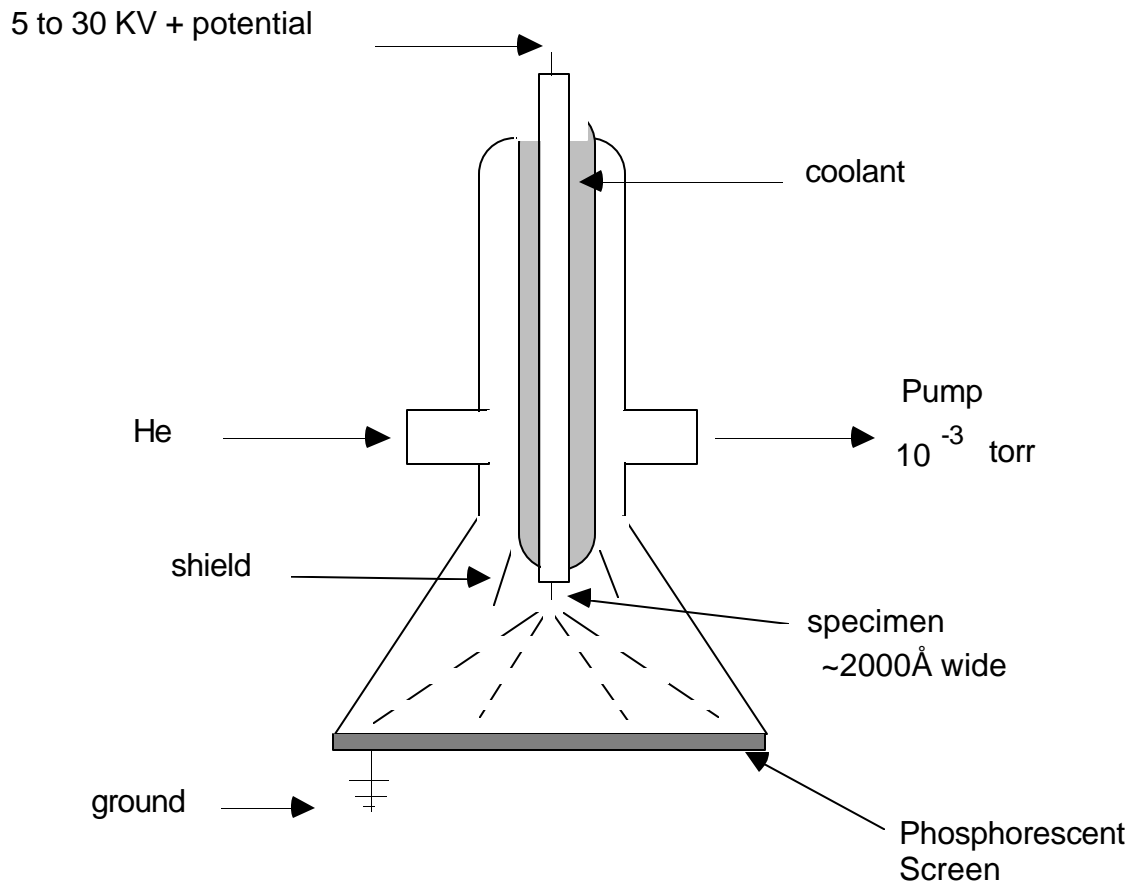
Electron Microscopy

Tunneling; UHV etc, diffraction, LEED, Limited to surface or very thin sheets

Field Ion Microscopy

a positive potential is applied to a thin needle ($\sim 100\text{-}2000\text{\AA}$ thick), at 10^{-3} torr He, protruding atoms ionize the He carrier gas and send a stream of charged He^+ ions toward the phosphorescent screen. Tracing lines of force back to the needle identifies location of atoms.

Schematic:



X-ray and Neutron Diffraction

single-crystal and powder. Investigation of the three-dimensional order of molecules and their structure

$$\begin{array}{l} \text{Energy} \\ \lambda \end{array} \quad = \quad 5 \times 10^{10} \text{ cal/mole} \quad = \quad 10^6 \text{ eV} \\ \quad \quad \quad = \quad 1 \text{ \AA}$$

1914	Max VonLaue	Crystals scatter X-rays
1915	W & W Bragg	Structure of NaCl

Indices for X-rays = 1.0000 X-rays cannot be lensed

Other Structure Identification Techniques

Electron Diffraction

Solids : Limited to very thin films 1000•
2-D crystals, polycrystalline

Gas : Limited to small simple molecules, small amount of data,
good resolution 1 in 1000

Microwave Spectroscopy

Gas : Limited to small molecules with permanent dipoles, isotope
substitutions

Extended X-ray Absorption Fine Structure

Solid, Liquid, Gas : Must contain a heavy atom (at least S). The more
Heavy atoms the more complicated, What and how
Many atoms are coordinated to Heavy atom.
Range from heavy atom ~ 6• .

Crystals

Key to good crystals is time!

It takes time for molecules to deposit onto crystal surfaces.

Important to have very few nucleation sites

Crystallization

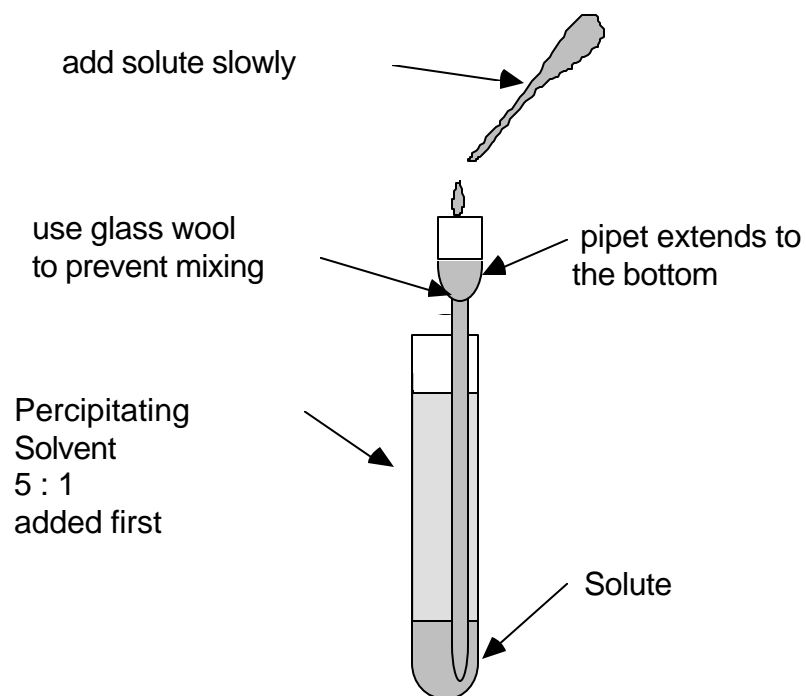
- 1) Purification
very pure, filtered solution
clean dirt free solvents, **new** glassware
- 2) Careful recrystallization
- 3) **Very** slow cooling or **Very** slow evaporation
cooling
allow solution to cool with hot plate
cool solutions in dewars
use temperature gradients (place glassware against cold window)
Evaporation
use clean purge gases, instead of air, to avoid contaminating solution with dust.
- 4) Liquid diffusion and mixed solvents

choose solvents which induce precipitation

Mixed Solvent : Slowly mix the solution with the precipitation solvent at room temperature until the solution turns cloudy then re-dissolved by addition of more of the original solution. Slowly cool the resulting solution.

Liquid Diffusion : Layer the precipitating solvent and the original solution (5 units of solvent to 1 unit of solution) in a tube. Set the tube in a vibration free location and wait.

Schematic :



Solvents:

water/ acetone

CH₂Cl₂/ hydrocarbon

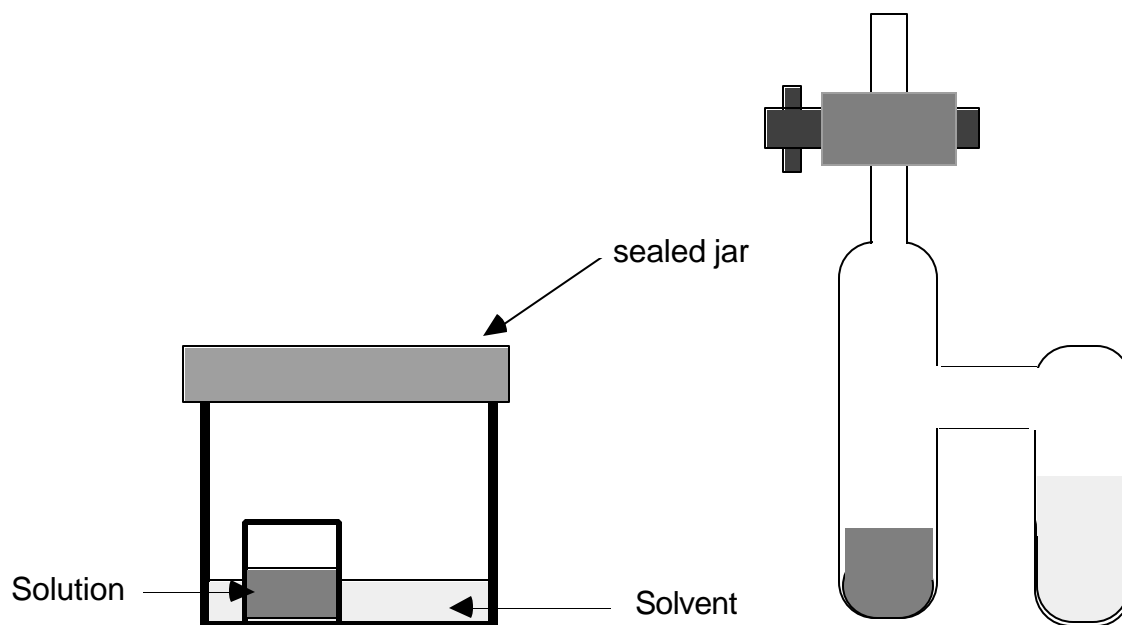
THF/ MeOH

MeOH/ water

MeOH/ benzene

4) Vapor Diffusion

Like liquid diffusion except the precipitating solvent is transferred as a vapor. The solvent **must** be more volatile than the solution.

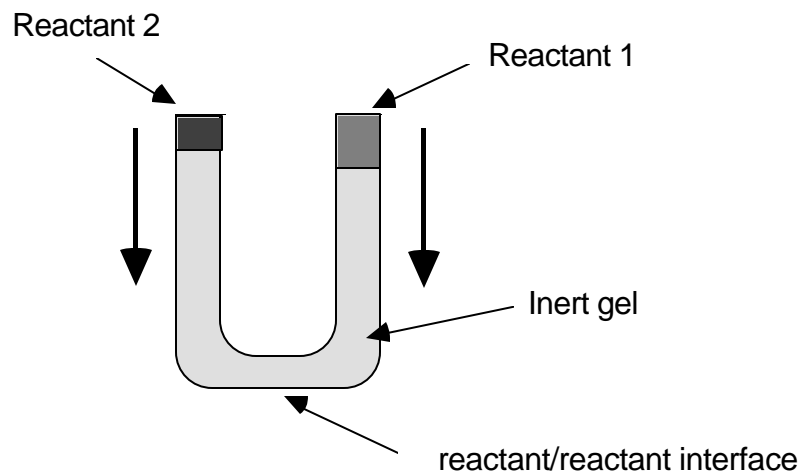


5) Diffusion of reaction solutions

Like liquid or vapor diffusion except the solvent contains one reactant and the solution contains the other. Solvent density can be adjusted to insure a smooth diffusion.

6) Gel

A U-tube is filled with an inert gel. Reaction mixtures are introduced on either side of the tube and allowed to diffuse towards each other.



7) Seed Crystals added to saturated solution

Seed crystals should be fresh and not dried!

The fewer the seeds the larger the resulting crystals.

DON'TS

Do not isolate all of your crystals leave some in their mother liquor and their original container.

Crystal Quality

By Eye Inspection

If you can see shiny faces and make out size and shape of your crystals without the aid of a microscope then they may be suitable for X-ray analysis.

Microscopic Inspection

what to look for:

well defined faces,
no clumping,
non-opaque,
polarizability i.e. uniform extinction of polarized light
no layered crystals
Size max. ~ 0.5mm

Is the structure worth doing?

Average structure takes about 4 days of diffractometer time

What can you get?

Identification

Metric information

atomic coordinates, bond lengths etc.

Relative and absolute configuration

Compound choice

Minimize disorder

Dynamic and static disorder

AVOID : ClO_4^- , BF_4^- , PF_6^- , SiF_6^- , Li^+ , Na^+

USE : AsPh_4^+ , PPN^+ , BPh_4^-

Minimize Inclusion of solvent or effervescence of solvent

Use non-polar solvents, avoid water use DMSO instead,

Use large molecular solvents

Cool Xtals to avoid solvent loss, seal crystals in capillaries

Plan your crystallization before you do the experiment.

Has the structure been done ?

Data Bases

Organic and inorganic compounds which contain at least a C-H bond and which are not a long polymer or protein can be found in the Cambridge Structural Database.

Symmetry

Crystals are solids characterized by long range three dimensional order.

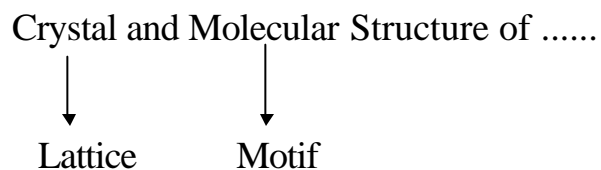
A lattice can be seen in an array of repeat units known as a **motif**.

Lattice:

A conceptual array of points which defines geometric relationships between motifs.

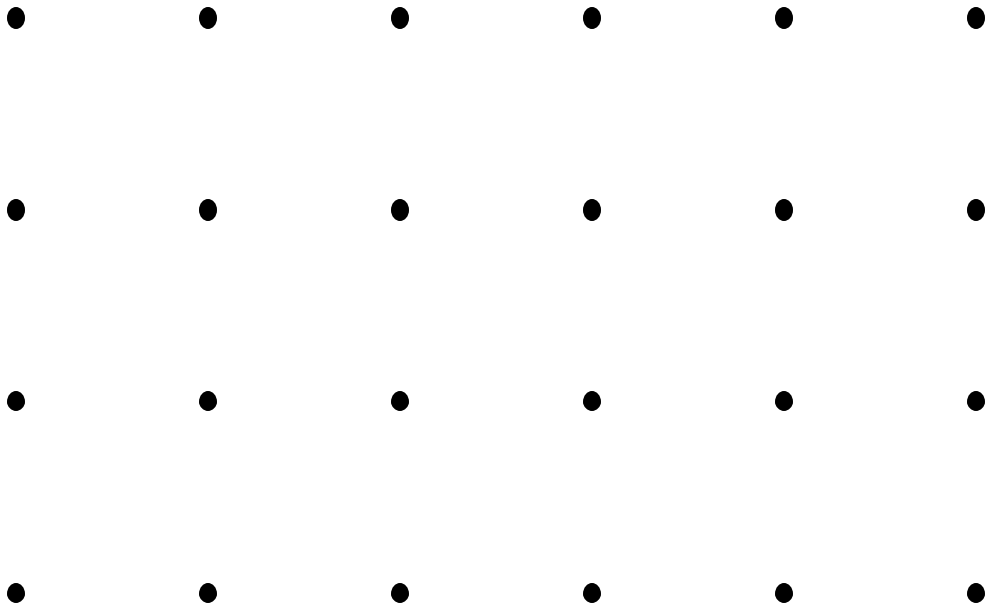
Observations

- 1) the environment about each lattice point is the same.
- 2) the position of the lattice point is arbitrary.
- 3) In the 'real world' the motif is an array of atoms, molecules etc.
- 4) The overall structure is thus a combination of the lattice structure **and**
The structure of the motif.



Lattice Structure

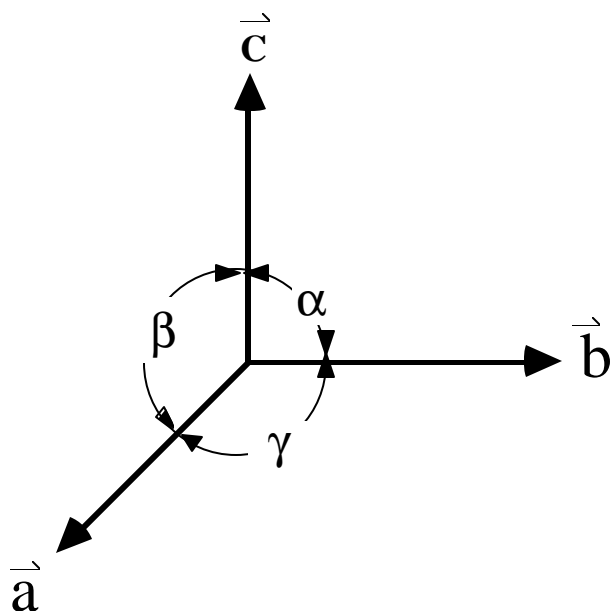
In any lattice there are an infinite number of ways of describing that lattice in terms of vectors between lattice points.



The volume described by a , b and γ is known as the **unit cell**.

The number of lattice points per cell = $4 \times (1/4) = 1$ lattice point

A **primitive cell** is described as a cell which contains only one lattice point.



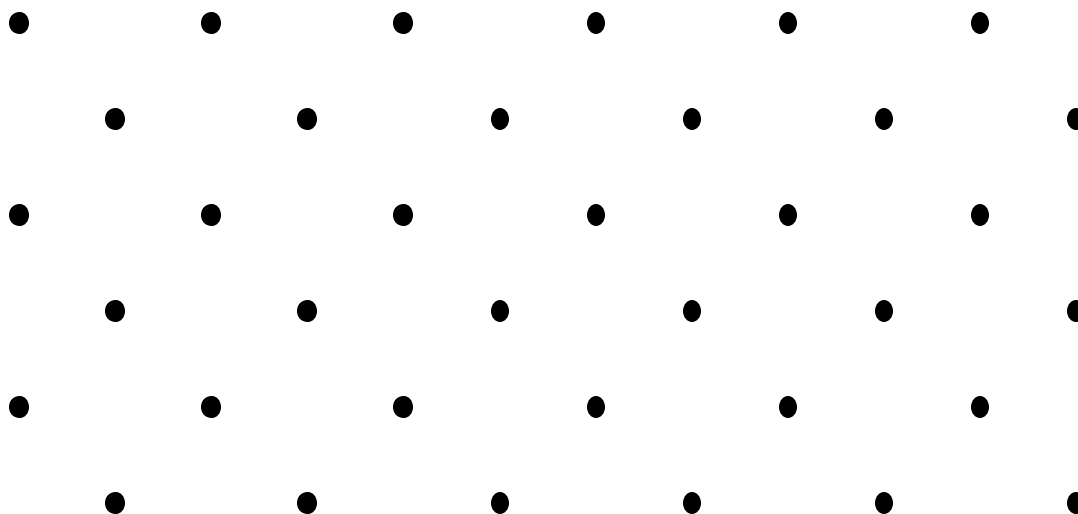
Conventions for choosing unit cell:

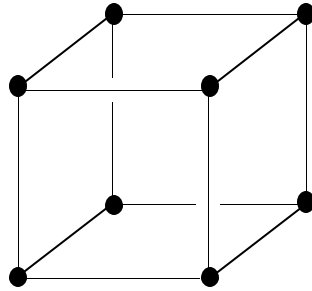
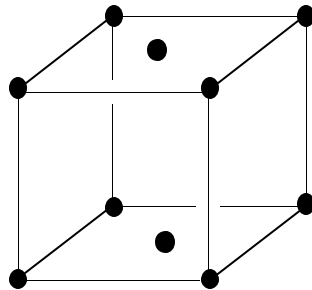
Choose angles α , β , γ near 120° if none then choose angles $\alpha = \beta = \gamma$,
if none then choose angles $= 90^\circ$,
if none then angles $> 90^\circ$

Choose axis so that $a=b=c$ if none $a=b$ or $a=c$ or $b=c$ if none then $a < b < c$

Symmetry criteria:

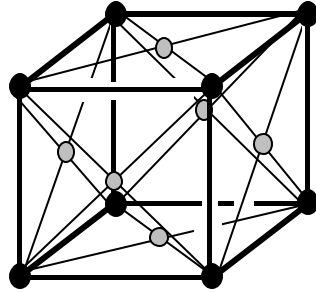
Choose a unit cell which expresses the symmetry of the cell.



CellsPrimitivelattice points = $1 = 8(1/8)$ C-Centeredlattice points = $2 = 8(1/8) + 2(1/2)$ 

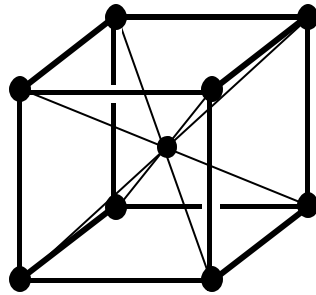
F-Centered

lattice points = $4 = 8(1/8) + 6(1/2)$



I-Centered

lattice points = $2 = 8(1/8) + 1$



Crystal systems

<u>System</u>	<u># of independent cell parameters</u>	<u>Cell restrictions</u>		<u>Types of Centering</u>
1. Triclinic	6	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma$	P
2. Monoclinic	4	$a \neq b \neq c$	$\alpha \neq \gamma \neq 90; \beta = 90;$	P,C
3. Orthorhombic	3	$a \neq b \neq c$	$\alpha = \gamma = \beta = 90;$	P,C,I,F
4. Tetragonal	2	$a = b \neq c$	$\alpha = \gamma = \beta = 90;$	P,I
5. Hexagonal (6)	2	$a = b \neq c$	$\alpha = \beta = 90; \gamma = 120;$	P
6. Trigonal (3)*	2	$a = b \neq c$	$\alpha = \beta = 90; \gamma = 120;$	P
7. Cubic	1	$a = b = c$	$\alpha = \gamma = \beta = 90;$	P,I,F

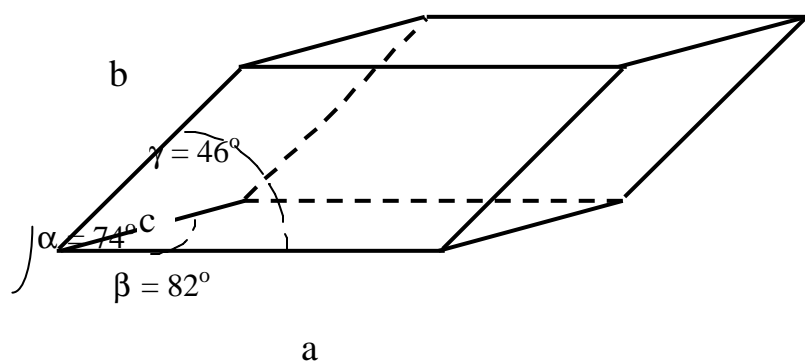
7 = Crystal systems

Bravais Lattices = 14

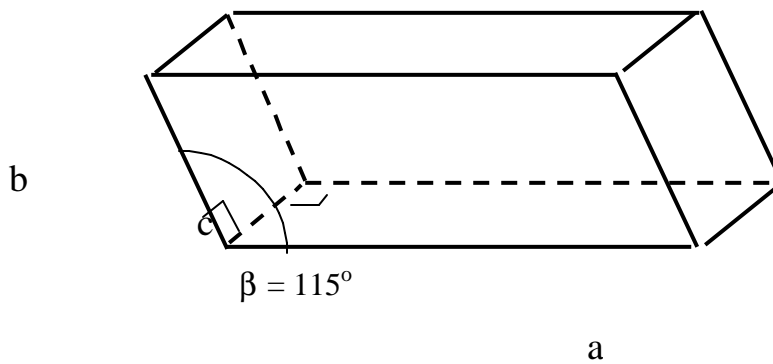
* Rhombohedral 2 $a = b = c$ $\alpha = \gamma = \beta \neq 90;$ R

Cells

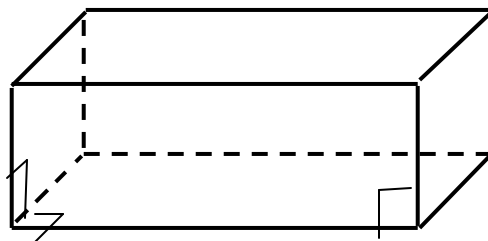
Triclinic $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$



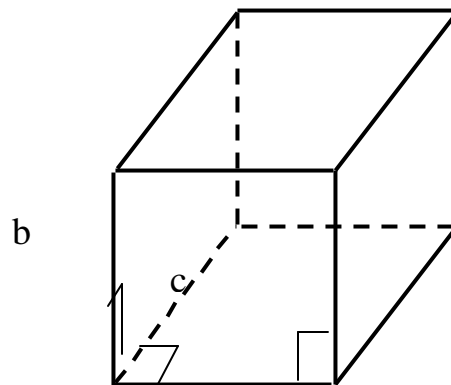
Monoclinic $a \neq b \neq c$ $\alpha = \beta = 90^\circ$ $\gamma \neq 90^\circ$



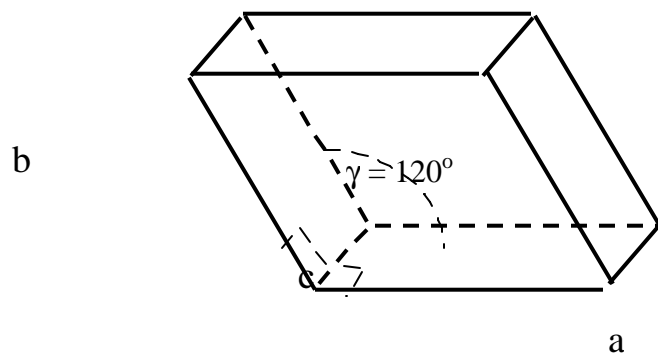
Orthorhombic $a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$



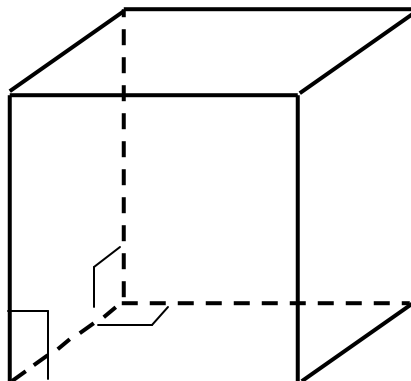
Tetragonal $a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$



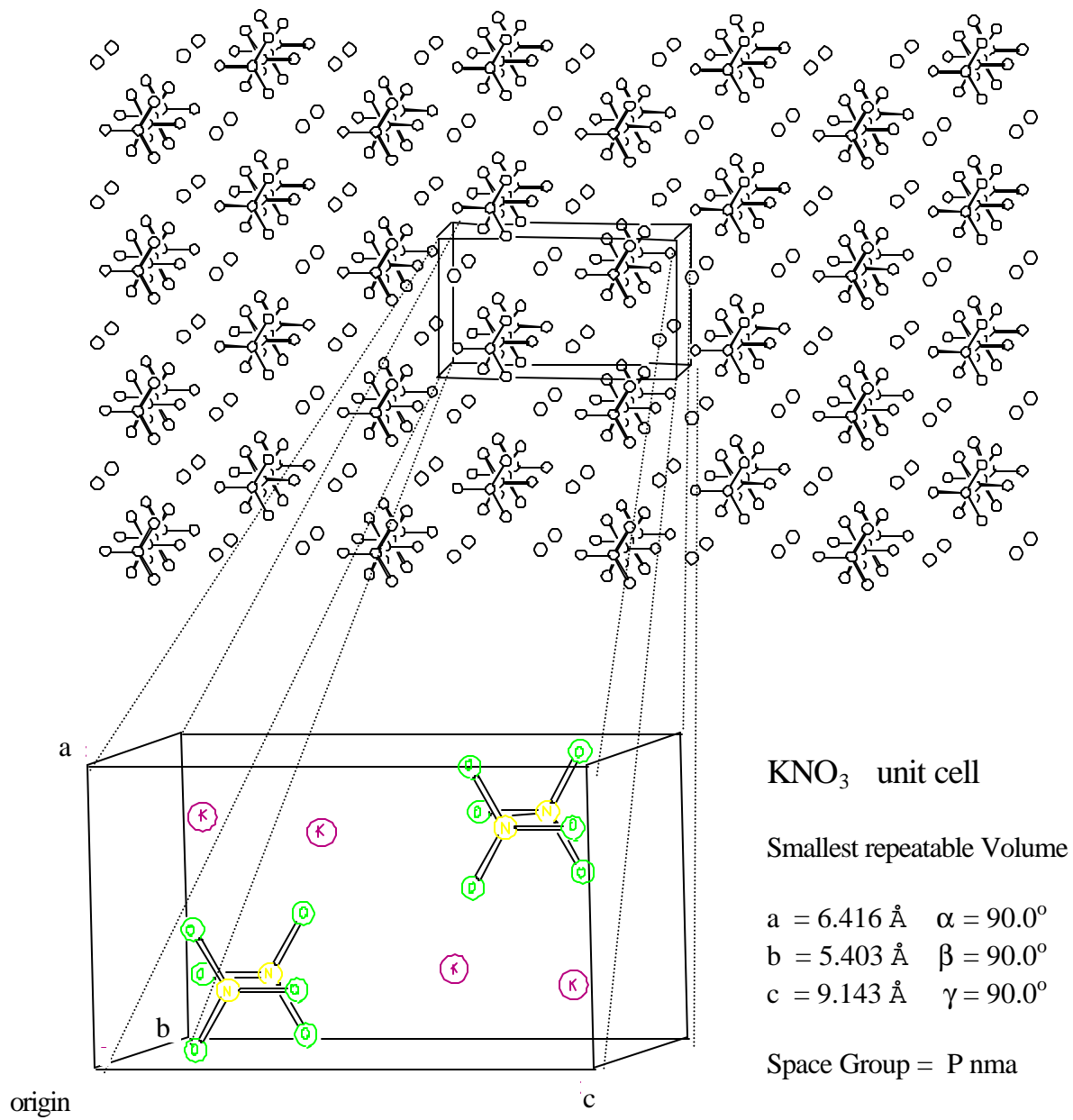
Hexagonal/Trigonal $a = b \neq c$ $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$



Cubic $a = b = c$ $\alpha = \beta = \gamma$



KNO₃ motif & unit cell



Space Symmetry

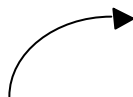
In space all symmetry operations are present. The only requirement is that you must fill all space. This requirement puts limits on the axis operations that are allowed.

Therefore only rotations of $360/n$ where $n = 1,2,3,4$ and 6 are allowed.

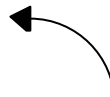
Notation

Rotation	Schönfliess	Hermann
Identity	C_1	1
2-fold	C_2	2
3-fold	C_3	3
4-fold	C_4	4
6-fold	C_6	6

clockwise



counter-clockwise



symbols

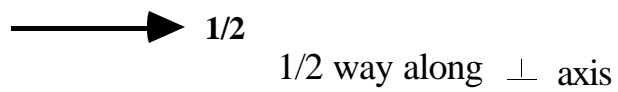
perpendicular to the plane of the paper



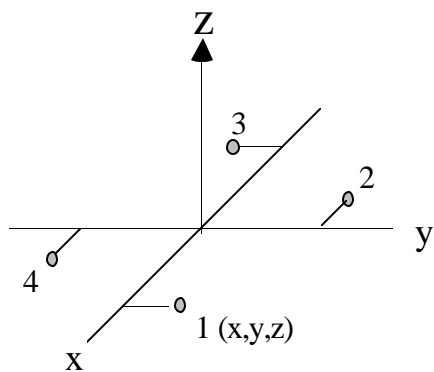
in the plane



parallel but not in the plane



Rotation continued



$$1) \quad x, y, z$$

$$2) \quad \bar{y}, x, z$$

$$3) \quad \bar{x}, \bar{y}, z$$

$$4) \quad y, x, \bar{z}$$

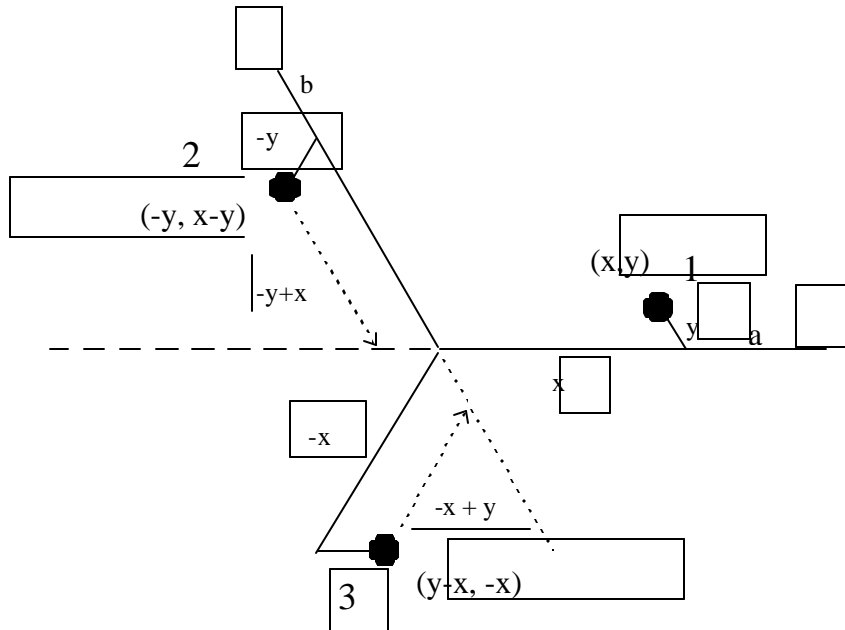
$$\boxed{\bar{y} = -y}$$

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} \begin{pmatrix} 0 & \bar{1} & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \bar{y}, x, z$$

R_4

Rotation (continued) : 3-fold

Positions (x, y) ; $(-y, x-y)$, $(y-x, -x)$



Point 1

From the **b** axis ($a=0$) to point **1** go x distance along **a**,
the **a** axis ($b=0$) to point **1** go y distance along **b**
position = (x, y)

Point 2

From the **b** axis ($a=0$) to point **2** go $-y$ distance along $-(\mathbf{a}+\mathbf{b})$,
the **a** axis ($b=0$) to point **2** go $-y$ distance along $-(\mathbf{a}+\mathbf{b})$ and x distance along **b**
position = $(-y, x-y)$

Point 3

From the **b** axis ($a=0$) to point **3** go $-x$ distance along $-(\mathbf{a}+\mathbf{b})$ and y distance along **a**
the **a** axis ($b=0$) to point **3** go $-x$ distance along $-(\mathbf{a}+\mathbf{b})$
position = $(y-x, -x)$

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} \begin{pmatrix} 0 & \bar{1} & 0 \\ 1 & \bar{1} & 0 \\ 0 & 0 & 1 \end{pmatrix} = \bar{y}, x-y, z$$

R_3

mirror

notation

Schönflies

Hermann

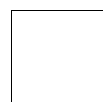
 σ

m

symbols

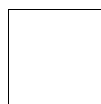
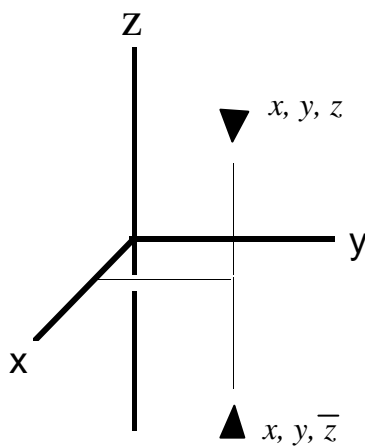
 \perp to the plane of paper

in the plane



|| but not in the plane

1/4

1/4 along the \perp axis

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \bar{1} \end{pmatrix} = \mathbf{R}_m$$

combinations

2-fold & \perp mirror

2/m = two upon m

$$\mathbf{R}_2 = \begin{pmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \bar{1} \end{pmatrix} = \mathbf{R}_m$$

$$\mathbf{R}_2 \times \mathbf{R}_m = \begin{pmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & \bar{1} \end{pmatrix} = \mathbf{R}_{2/m}$$

Combination of mirrors

$$\mathbf{R}_{m-a} \times \mathbf{R}_{m-b} = \mathbf{R}_{2 \mid c}$$

$$\begin{pmatrix} \bar{1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\mathbf{R}_{m-a} \times \mathbf{R}_{m-c} = \mathbf{R}_{2 \mid b}$$

$$\mathbf{R}_{m-b} \times \mathbf{R}_{m-c} = \mathbf{R}_{2 \mid a}$$

inversion

notation

\mathbb{O}

Schönfliess

Hermann

inversion

i

$1 \bar{\quad}$ (1-bar)

$x, y, z \xrightarrow{\bar{1}} \bar{x}, \bar{y}, \bar{z}$

$$2/m = \bar{1}$$

$$m = \bar{1} 2$$

$$2 = \bar{1} m$$

Schönfliess notation for $2/m$

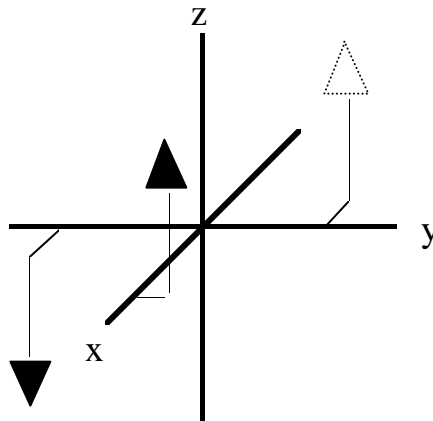
operators : E, C_2 , i, σ_h =

d) improper rotations

a rotation by $360/n$ followed by inversion

$\bar{1}$ = inversion , $\bar{2}$ = m, $\bar{3}$, $\bar{4}$, $\bar{6}$

$\bar{4}$



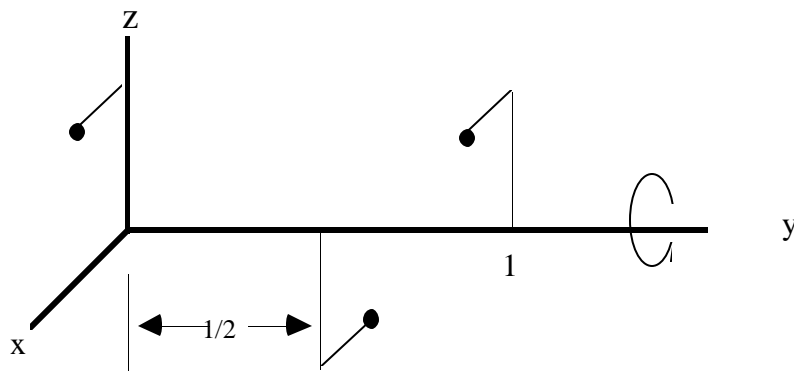
c) screw axis

rotation followed by translation

notation

N_m (N sub m) N-fold rotation followed by m/N translation

2_1



$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} \begin{pmatrix} \bar{1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \bar{1} \end{pmatrix} + \begin{pmatrix} 0 \\ 1/2 \\ 0 \end{pmatrix} = \bar{x}, 1/2 + y, \bar{z}$$

symbols

\perp plane of paper

2



3



4



6



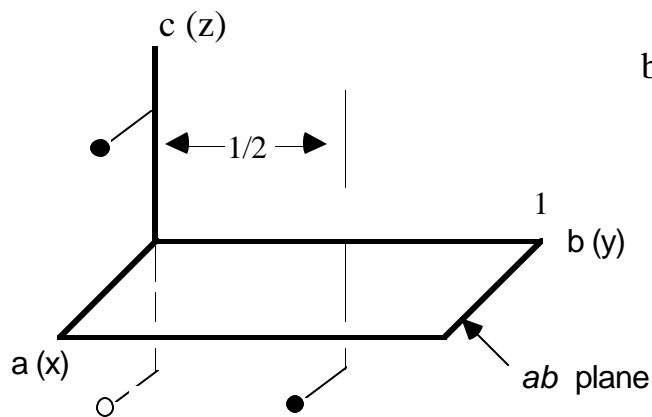
\parallel plane of paper



f) glide planes

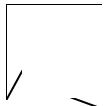
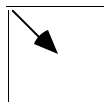
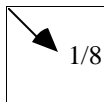
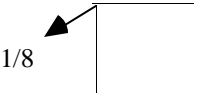
m reflection and translation**m** action

- a reflect across ab or ac plane and translate $1/2$ along a
- b reflect across ba or bc plane and translate $1/2$ along b
- c reflect across ca or cb plane and translate $1/2$ along c
- n reflect across ab , ac , or bc plane and translate $1/2$ along the diagonal of that plane. $(a+b)/2$, $(a+c)/2$ or $(b+c)/2$
- d reflect across abc plane and translate $1/4$ along the diagonal of that plane. $(a+b+c)/4$



$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + \begin{pmatrix} 0 \\ 1/2 \\ 0 \end{pmatrix} = x, 1/2 + y, \bar{z}$$

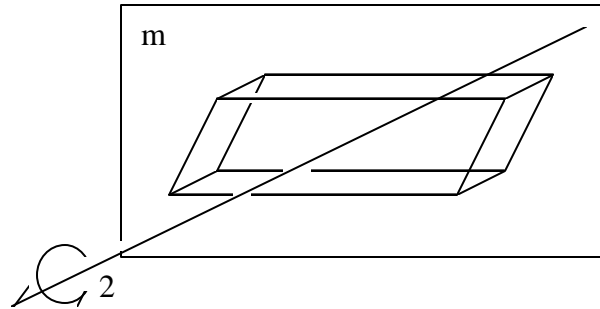
notations

symbol	explanation
-----	for a, b and c glides the reflection plane is normal to plane of the paper and the translation is in the paper
.....	for n glides the reflection plane is normal to plane of the paper and the translation is in the paper
.....>..	for d glide the reflection plane is normal to plane of the paper and the translation is in the paper
.....	for a, b, and c glides the reflection plane <u>and</u> translational direction are normal to the plane of the paper.
 translation direction	for a,b, and c glides, both reflection plane and direction are in the plane of the paper.
	for n glide, both reflection plane and direction are in the plane of the paper.
 translational direction	
	for d glide, both reflection plane and direction are in the plane of the paper.

Point groups

point groups which describe the symmetry of lattice (space symmetry less translations)

monoclinic



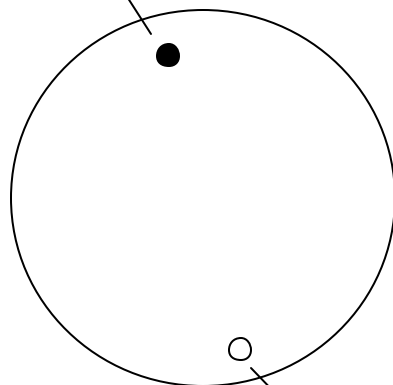
The point group for the lattice describes the highest symmetry possible for the lattice; however point groups of lower symmetry can be fitted into the lattice as long as their effect on the axis and the angles agree with the lattice geometry.

<u>system</u>	<u>point group</u>
1. Triclinic	$\bar{1}$
2. Monoclinic	$2/m$
3. Orthorhombic	mmm
4. Tetragonal	$4/m$ or $4/mmm$
5. Hexagonal	$6/m$ or $6/mmm$
6. Trigonal	3 or $3/m$
7. Cubic	$m\bar{3}m$ or $m\bar{3}$

Point Group Notation

Notation $\bar{1}$

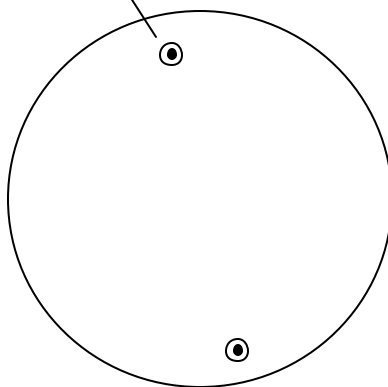
object above plane



object below plane

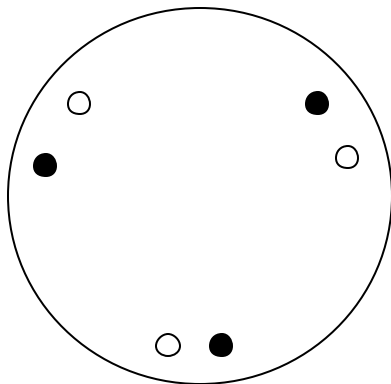
 $2/m$

object on top of object

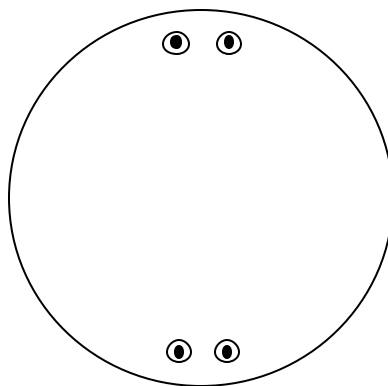


List all symmetry operators and determine the Schönflies notation

32



mmm



Space groups

There are only 230 ways (space groups) to describe how identical objects can be arranged in orderly arrays in an infinite three dimensional lattice network.

Notation

Form

L **ijk**

L = lattice (3D) or net (2D) type
 capital letter for 3D lattice
 small letter for 2D net
ijk = symmetry elements of
 space group (3D)
 or plane group (2D) for the different
 symmetry directions
 where **i** =primary, **j** = secondary
 and **k** = tertiary directions

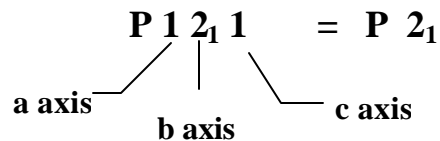
Example: Triclinic, Monoclinic and Orthorhombic space groups

(a) Triclinic no symmetry direction

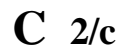
space groups **P 1** and **P 1** —

- (b) Monoclinic symmetry directions are coincident with the a, b, c axis however two of the directions coincide with just the identity operator. By convention these axis are a and c .

example:



The space group symbol tells us that the lattice is primitive and that there is a 2-fold screw axis coincident with the b axis.

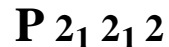


\mathbf{C} = c - centered cell

$\mathbf{2}/c$ = 2-fold axis along b and a

c glide (reflection and translation along c) in the ac plane

orthorhombic examples



\mathbf{P} = primitive

$\mathbf{2}_1$ = 2 fold screw axis along a

$\mathbf{2}_1$ = 2-fold screw axis along b

$\mathbf{2}$ = 2-fold rotation around c

$$\mathbf{P} \ 2/m \ 2/n \ 2_1/a = \mathbf{P} \ mna$$

P = primitive

2/m = 2-fold rotation around *a* and mirror in *bc* plane

2/n = 2-fold rotation around *b* and *n* glide in *ac* plane

2₁/a = 2-fold screw along *c* and *a* glide in *ab* plane

Name the space group

Primitive cell

symmetry:

a glide in *ac* plane; *b* glide in *ab* plane ; *c* glide in *bc* plane
2 fold screw along *a*, *b*, and *c*.

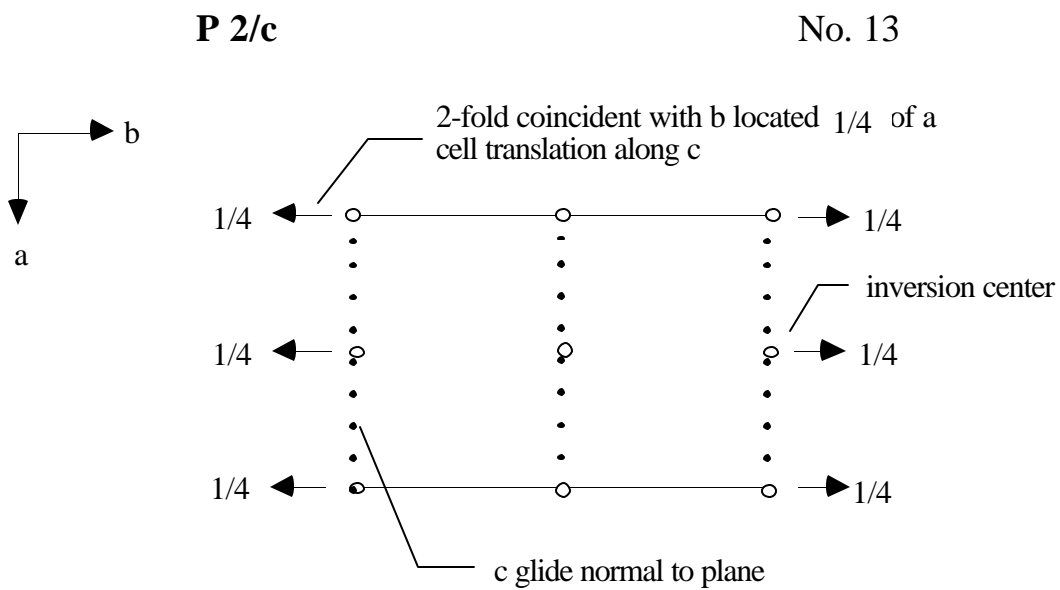
Tables

International Tables for X-ray Crystallography

Volume 1 (1952)

Volume A (1985)

example of standard cell projections



general positions

$$x, y, z ; x, \bar{y}, \bar{z} ; x, \bar{y}, 1/2 - z ; x, y, 1/2 + z$$

symmetry operators

1 = identity

$$\mathbf{R}_1 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \mathbf{t}_1 = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} \mathbf{R}_1 + \mathbf{t}_1 = x y z$$

2-fold

$$\mathbf{R}_2 = \begin{pmatrix} \bar{1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \mathbf{t}_2 = \begin{pmatrix} 0 \\ 0 \\ 1/4+1/4 \end{pmatrix}$$

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} \mathbf{R}_2 + \mathbf{t}_2 = \bar{x} y \ 1/2 - z$$

inversion

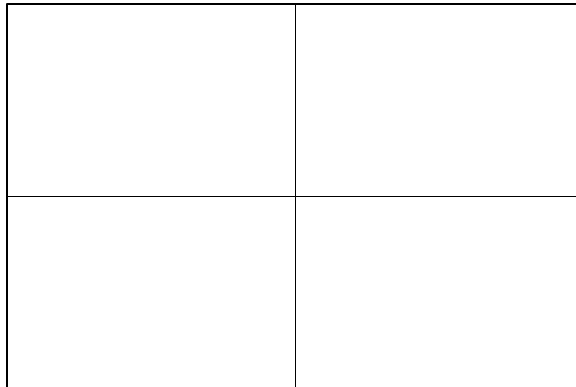
$$\mathbf{R}_i = \begin{pmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & \bar{1} \end{pmatrix} \quad \mathbf{t}_i = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} \mathbf{R}_i + \mathbf{t}_i = \bar{x} \bar{y} \bar{z}$$

c glide

$$\mathbf{R}_c = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \mathbf{t}_c = \begin{pmatrix} 0 \\ 0 \\ 1/2 \end{pmatrix}$$

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} \mathbf{R}_c + \mathbf{t}_c = x \bar{y} \quad 1/2 + z$$



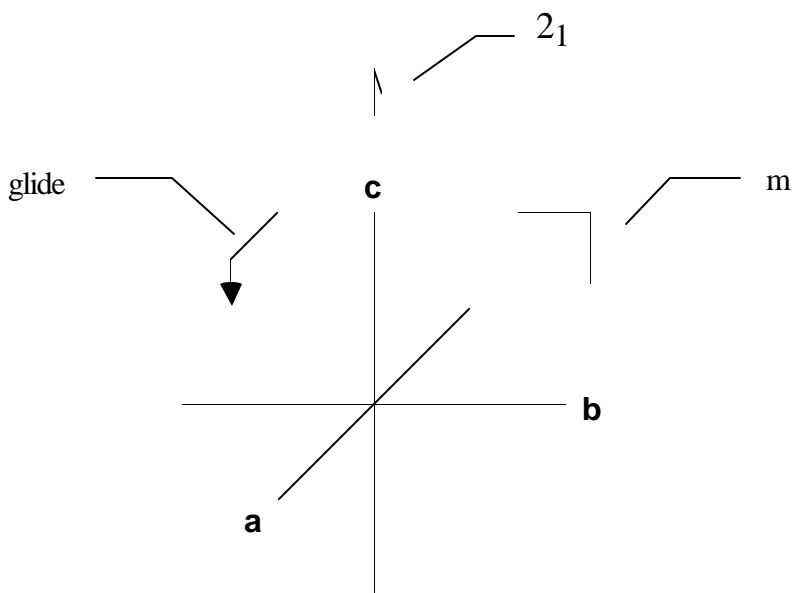
Comments

There are more than one way to describe each of the 230 unique space groups. To clarify and standardize the nomenclature certain conventions have been established.

conventions

triclinic	$a < b < c$ $\alpha, \beta, \gamma > 90$
monoclinic	b axis is unique $\beta > 90$
orthorhombic	$c < a < b$
tetragonal, trigonal and, hexagonal	c axis is the major axis

example of the same orthorhombic space group, standard and non-standard settings



convention	space group	comment
abc	P mc2₁	standard
cab	P 2₁ma	right handed
bca	P b2₁m	right handed
acb	P m2₁b	left handed
bac	P cm2₁	left handed
cba	P 2₁am	left handed

2-D plane groups

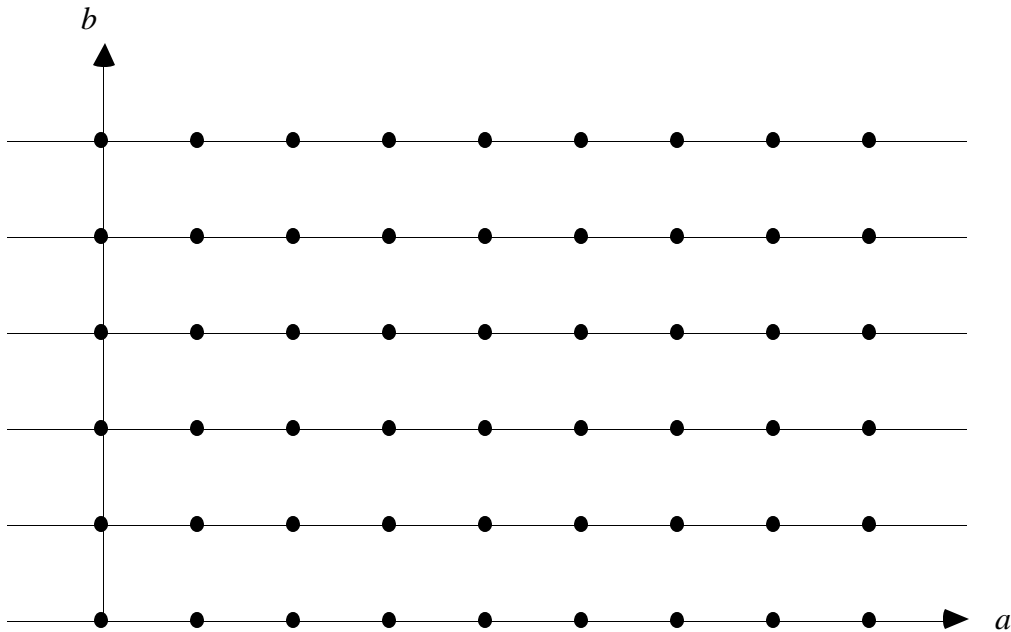
	<u>system</u>	<u>type</u>	<u>point grp.</u>	<u>plane groups</u>
(1)	oblique	p	1,2	p1, p2
(2)	rectangular	p, c	m, 2mm	pm, pg, cm, pmm, pmg, pgg, cmm,
(3)	square	p	4, 4mm	p4, p4m, p4g
(4)	hexagonal	p	3, 3m 6, 6mm	p3, p3m1, p31m, p6, p6m

summary

4 systems, 5 nets, 12 pnt grps, 17 plane grps

Indices

Families of rational lines



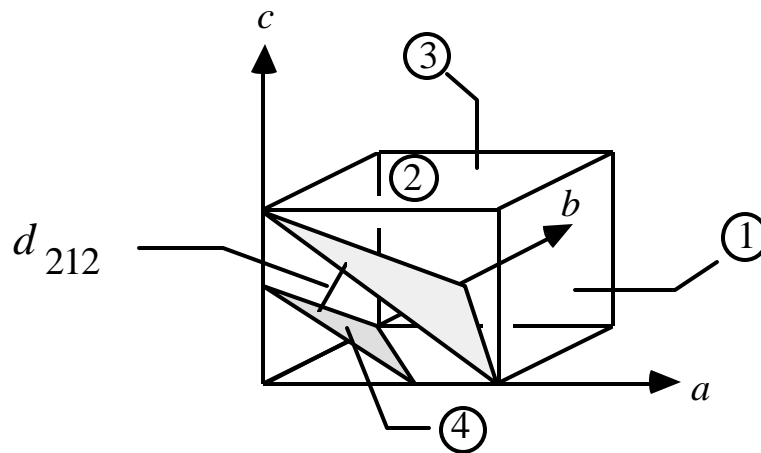
- i) Rational lines come in parallel sets
- ii) for every set of lines every lattice point is a member of that set

set	comments	h, k
1	intersects a at 8 , b at 1	$(0, b / 1)$ or $(0, 1)$
2	intersects a at 1 , b at 8	$(a / 1, 0)$ or $(1, 0)$
3	intersects a at 1 , b at $1/2$	$(a / 1, b / 2)$ or $(1, 2)$
4	intersects a at $1/2$, b at 1	$(a / 2, b / 1)$ or $(2, 1)$

General indices

Rational lines will generate fractional intercepts which are the ratio of whole numbers. Rational lines are the reciprocal of the fractional intercepts

Rational Planes



① $a/1, 0, 0$ or $(1,0,0)$

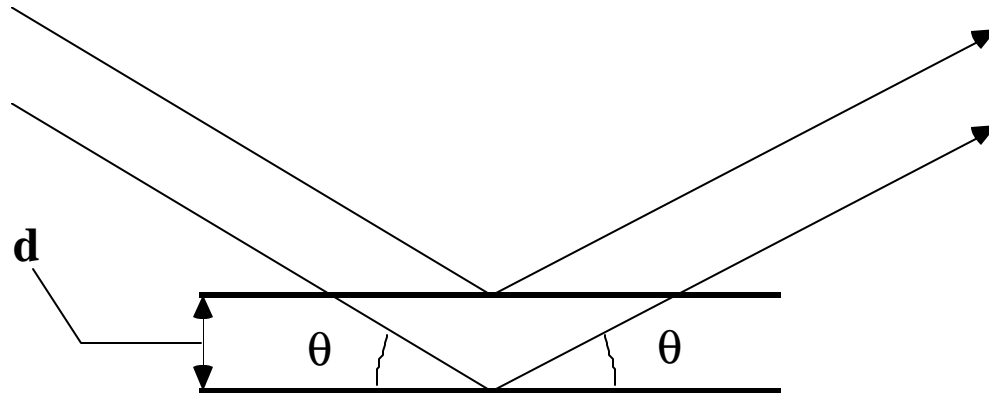
② $(0,1,0)$

③ $(0,0,1)$

④ $a/2, b/1, c/2$
 $(2,1,2)$

Diffraction

Braggs Law



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

If d is constant then λ can be selected by adjusting θ (diffraction gratings).
 Conversely if λ is constant then d can be determined by adjusting θ .

Therefore Bragg's law is satisfied for d_{hkl} at a value θ_{hkl}

$$\lambda = 2d_{hkl} \sin \theta_{hkl}$$

X-ray scattering occurs when an incident x-ray interacts with an electron, causing it to oscillate. An oscillating particle acts as a source of radiation, which in turn radiates in all directions. Radiation from evenly spaced oscillators interact to cause the phenomenon of diffraction.

Reciprocal space

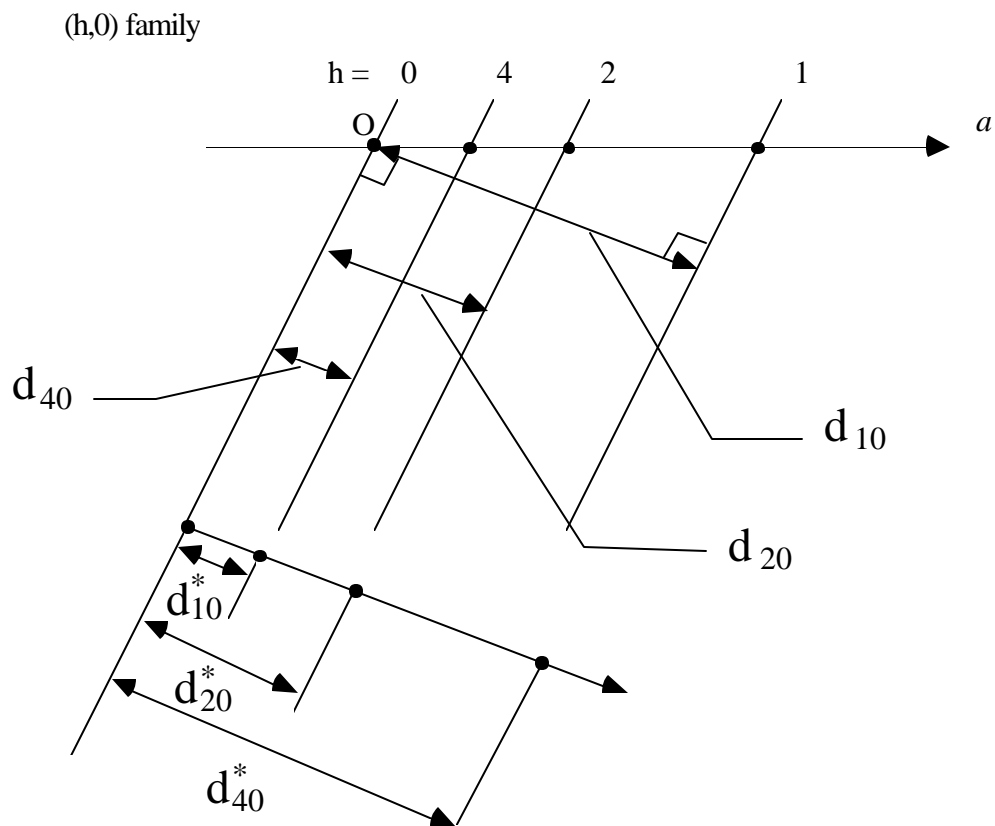
Braggs Law $\lambda = 2\mathbf{d}_{hkl} \sin\theta_{hkl}$

$$1/\mathbf{d}_{hkl} = 2\sin\theta_{hkl}/\lambda$$

$$\mathbf{d}^*_{hkl} = 1/\mathbf{d}_{hkl} = 2\sin\theta_{hkl}/\lambda$$

Reciprocal Lattice

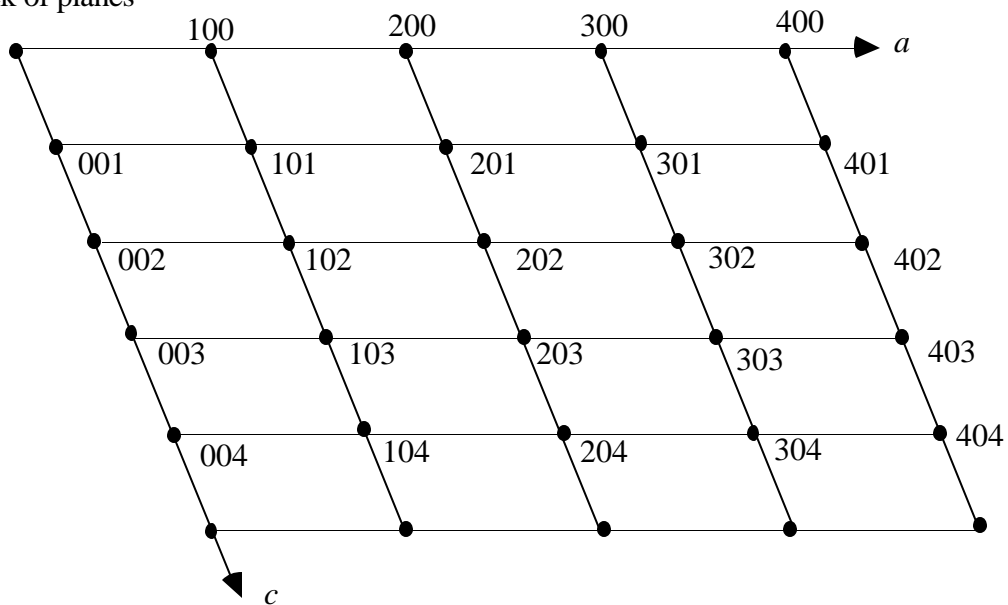
- (1) Select any point in the real lattice as the origin
- (2) Draw normal from the origin to the (hkl) plane with length = $1/d_{hkl}$
- (3) End point of the normal is a point in reciprocal lattice



Facts

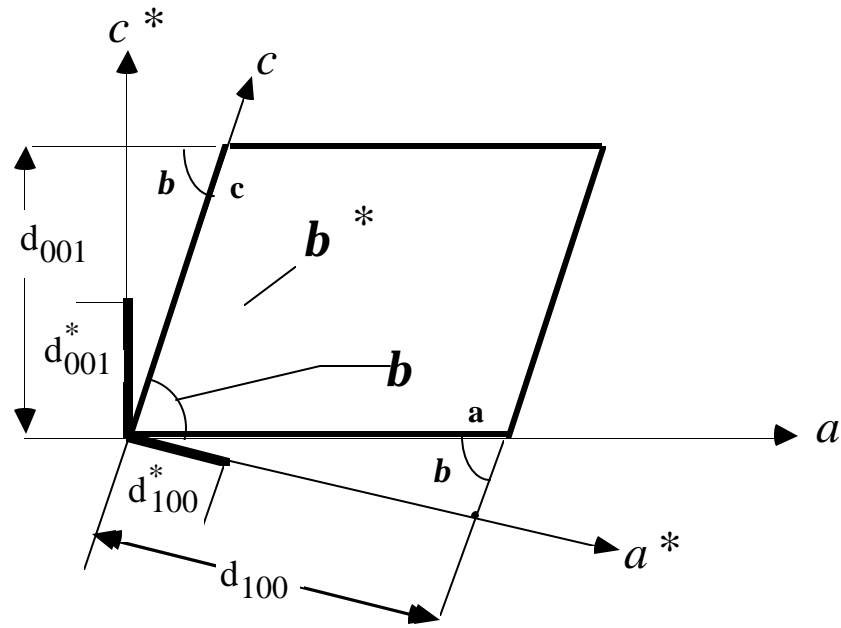
A three-dimensional stack of planes in real space can be represented by a net of reciprocal lattice points in reciprocal space.

h0l stack of planes



Real space vs Reciprocal space

Monoclinic



$$d_{100} = a \sin b$$

$$a^* = d_{100}^* = \frac{1}{d_{100}} = \frac{1}{a \sin b}$$

$$c^* = \frac{1}{c \sin b}$$

$$b^* = \frac{1}{b \sin a} = \frac{1}{b}$$

$$b^* = 180 - b$$

Notes

Every real cell $a, b, c, \mathbf{a}, \mathbf{b}, \mathbf{c}$ has a corresponding r.l. cell which exists in the same crystal.

definitions:

$$\mathbf{a}^* = \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \times \mathbf{b} \times \mathbf{c}} = \frac{\mathbf{b} \times \mathbf{c}}{V}$$

$$\mathbf{b}^* = \frac{\mathbf{a} \times \mathbf{c}}{V}$$

$$\mathbf{c}^* = \frac{\mathbf{a} \times \mathbf{b}}{V}$$

$$\mathbf{G}_{hkl} = h \mathbf{a}^* + k \mathbf{b}^* + l \mathbf{c}^*$$

where \mathbf{G} has magnitude d_{hkl}^* and direction normal to the set of rational planes (hkl)

$$d_{hkl}^{*2} = h^2 a^{*2} + k^2 b^{*2} + l^2 c^{*2} + 2kl b^* c^* \cos \alpha^* + 2hl a^* c^* \cos \beta^* + 2hka^* b^* \cos \gamma^*$$

$$V = abc(1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma)$$

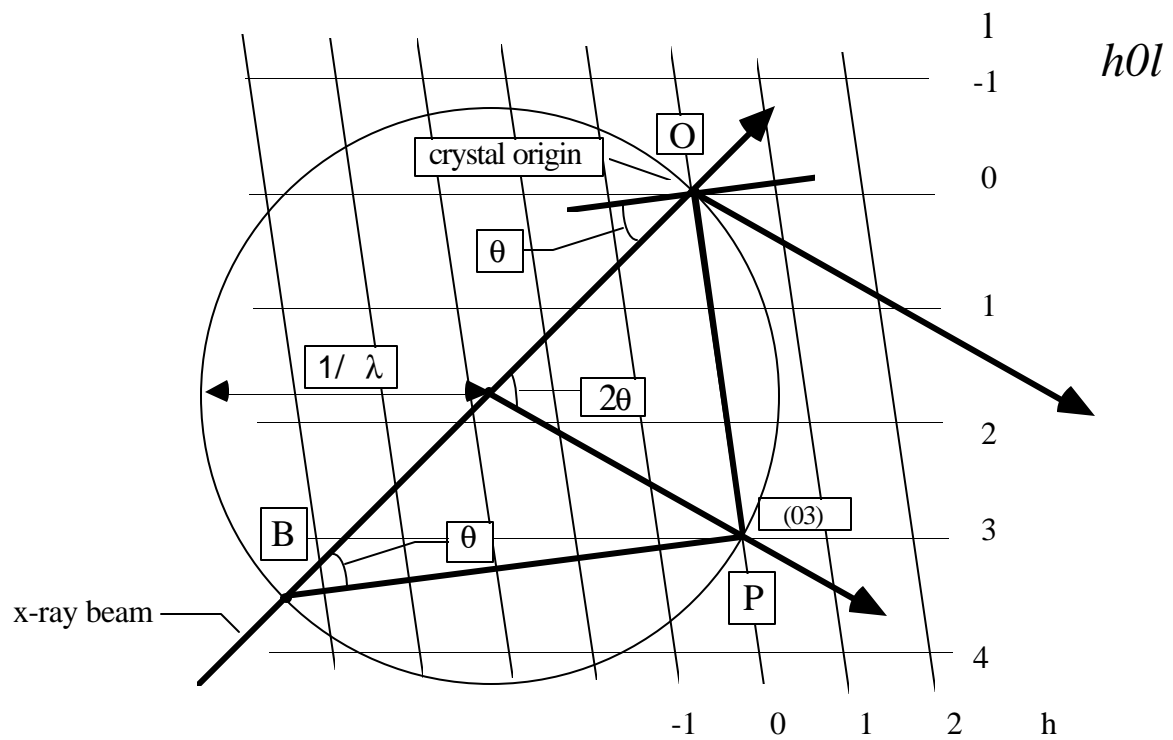
Number of r.l. points (reflections) in a given volume (V)

$$N = (4/3)\pi(2/\lambda)^3 V = (33.6 \times V)/\lambda^3$$

conclusions

- a) The reciprocal lattice is just as "real" as the direct lattice. Where one lattice is the Fourier transform of the other.
- b) The direct lattice has a fixed orientation in space relative to the crystal and so does the reciprocal lattice.

Ewald's construction



$$\sin \theta = \frac{OP}{OB} \quad OP = \frac{1}{d_{hkl}} \quad OB = \frac{2}{\lambda}$$

$$\sin \theta = \frac{\lambda}{2 d_{hkl}} \quad \lambda = 2 d_{hkl} \sin \theta$$

Notes

Any r.l. point with $d^* > 2/\lambda$ will not cross the sphere of reflection and cannot satisfy Bragg's law.

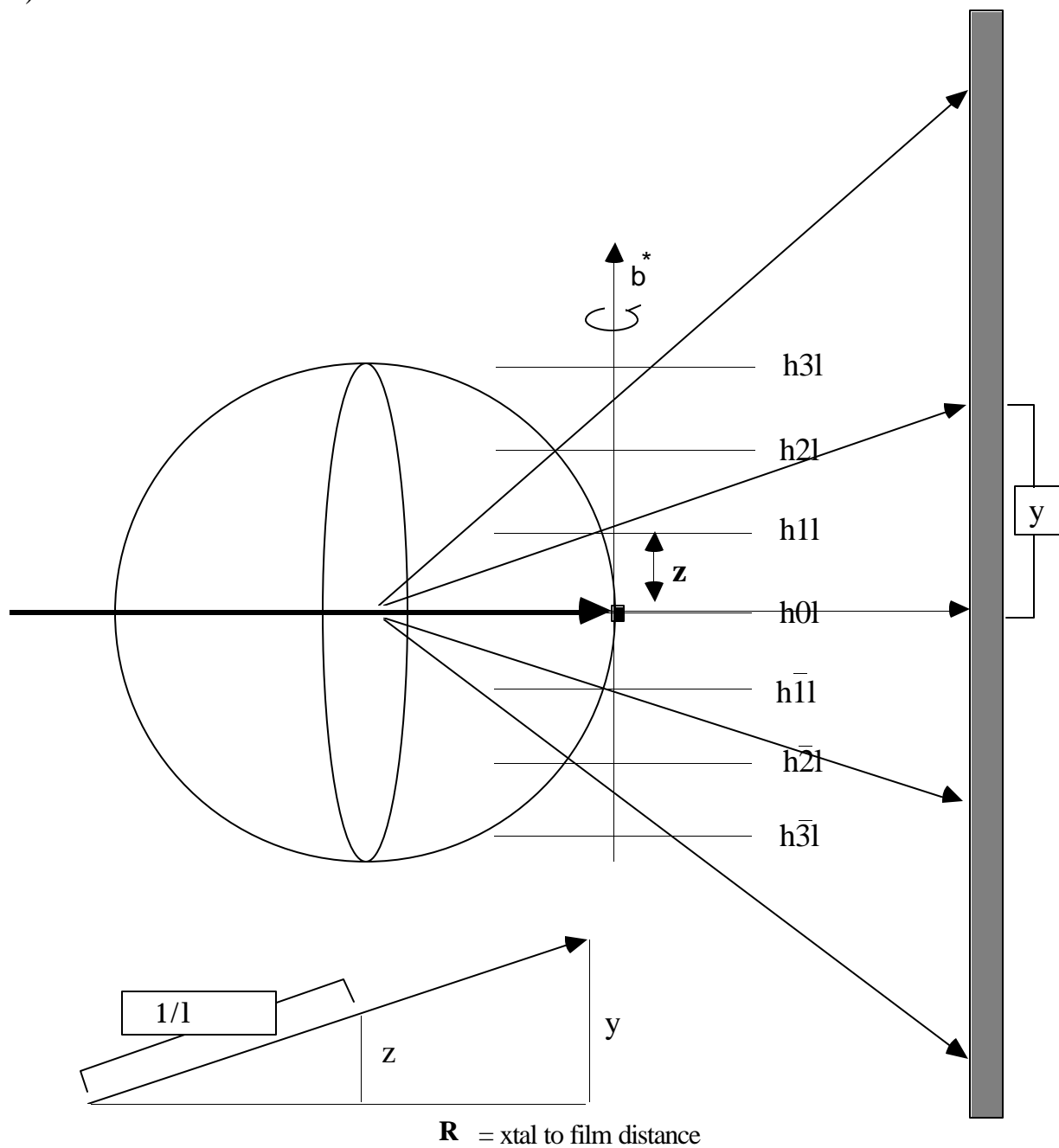
Limits on the minimum value of d . for monochromatic radiation generated by bombarding specific targets metals.

Target	λ	$1/\lambda$	$d(\text{\AA})$
Cr	2.29	0.437	1.15
Cu	1.542	0.6485	0.771
Mo	0.7017	1.407	0.355
W	0.213	4.69	0.106

Increasing the atomic number of the target material increases the number of r.l. points which can be observed.

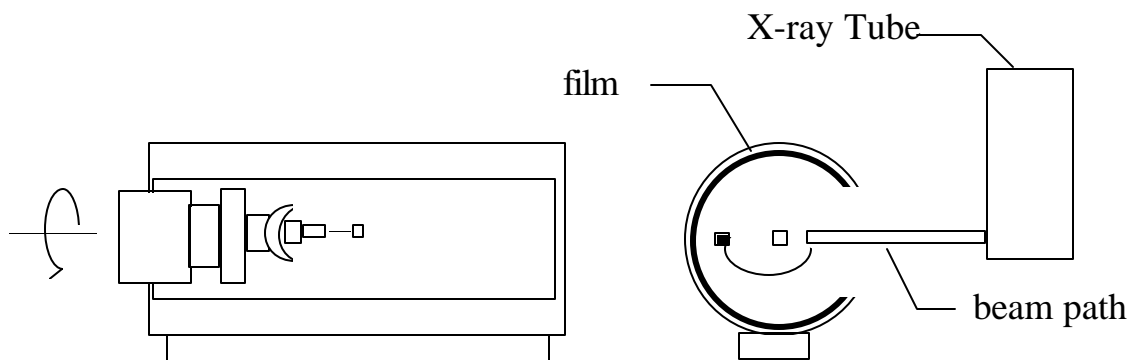
X-ray measurements

1) Film



$$z = 1/\lambda [\sin(\tan^{-1}(y/R))] = d_{010}^*$$

Flat film gives a distorted view so the film is curved



i) rotation and oscillation photographs

tells us

the cell length coincident with the crystal rotation axis
information on symmetry of the crystalline lattice (oscillation)

Information contained in the layer lines is difficult to decipher because information is compressed.

solution : spread the layer line out over more space in a uniform fashion.

ii) Weissenburg photograph

- a) selected only one layer at a time by blocking out the remaining layers with a metal shield.
- b) rotate and translate the camera at the same time to spread the layer line out across the entire length and width of the photo

The weissenburg photograph tells us :

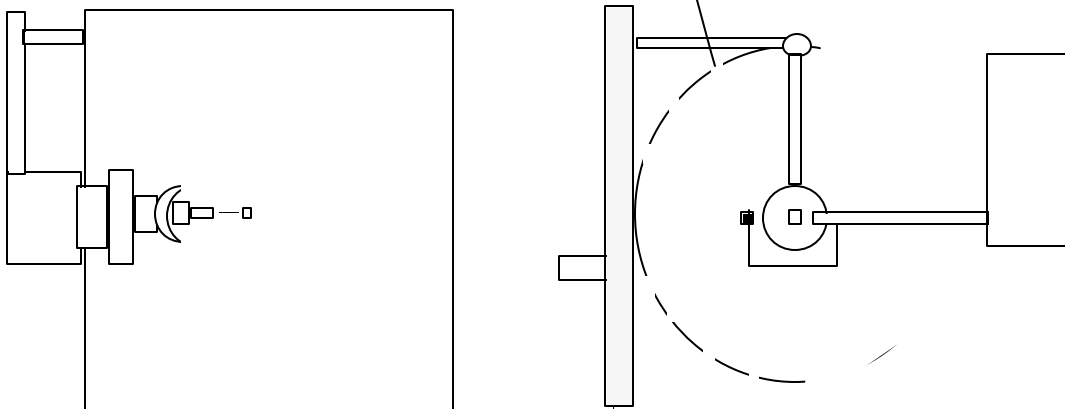
- a) The remaining cell lengths and cell angles
- b) Detailed information about the indices

iii) Precession photograph

a flat camera is moved along with the crystal in such a way as to keep the r.l. nets and the film parallel.

i.e. diffracted X-rays are always kept normal to the film

This photograph gives an undistorted view of the r.l. net
imaginary sphere



b) Counter techniques

mechanical cradle is utilized to bring the diffracted x-rays to a detector.

The camera and related mechanism is replaced by a step motor driven goniometer capable of bringing any diffracted ray to a set geometric position. In term a scintillation counter is driven by a step motor to that position and is used to detect the presence and information content of that x-ray.

Information available from diffracted X-rays

a) geometric

From: rulers or mechanical cradle

2θ , crystal system, lattice parameters

gives us the crystal structure

b) Intensity

From : estimation, densitometers, counters

symmetry of the lattice, space group, position of the electrons

gives us the molecular structure

Structure determination is therefore a two-fold experiment

1) determine the crystal structure and 2) determine the molecular structure.

Lattice symmetry determination

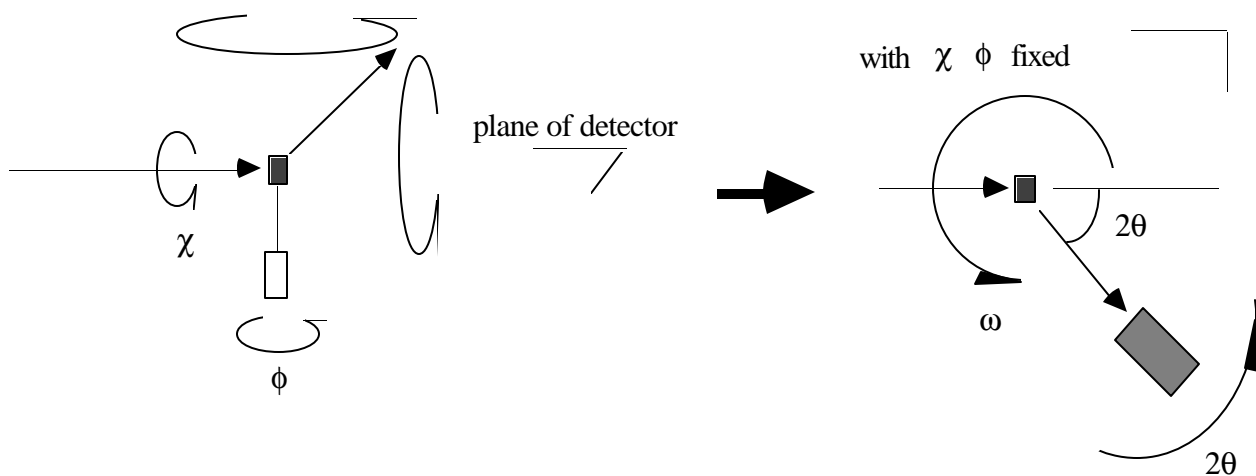
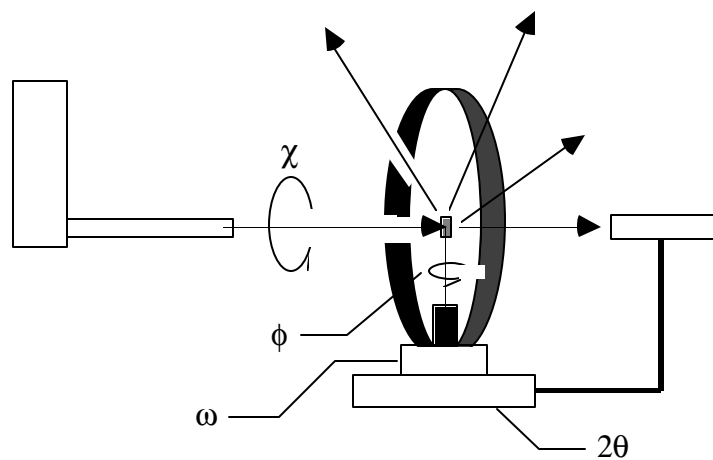
Mirror symmetry (or lack of symmetry) in the crystal lattice can be identified by mirror symmetry (or lack of symmetry) in the intensity distribution of the oscillation photographs of the axis a^* , b^* , c^* .

Orthorombic cell has symmetry: mmm . The oscillation photographs will display mirror symmetry in the a^* , b^* and c^* axis.

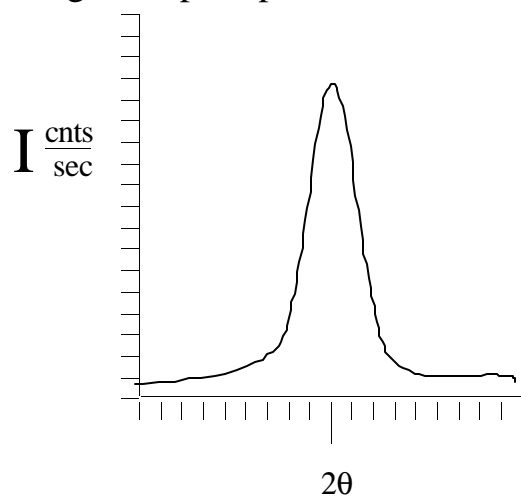
Monoclinic systems (with b axis unique) has symmetry: $2/m$ and will show mirror symmetry for the b^* axis photograph but no mirror symmetry in the a^* and c^* axis.

Triclinic systems has no mirror symmetry (1-bar) and will show no mirror symmetry in the axial photographs.

Four-circle diffractometers



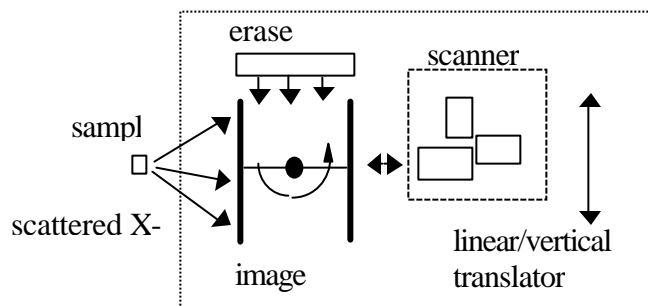
Scanning ω with 2θ fixed gives a peak profile:



Area Detectors

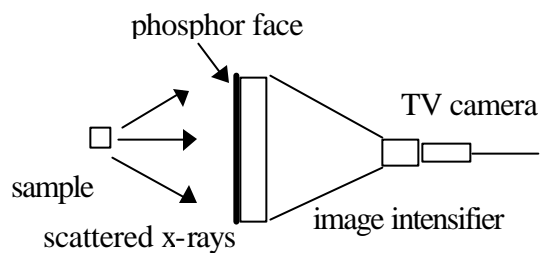
- 1) Film
 - fine grained x-ray film
 - film reader (microdensitometer)

- 2) Imaging Plates
 - thin plastic (0.5mm) sheets coated with phosphor crystals (BaFBr + Eu)
 - X-rays promote electrons from the Eu atoms to F sites where they are “captured”
 - Exposure to red light (600nm) cause the electron to return to Eu which produces a blue light (400nm). The light is detected by a position sensitive detector.



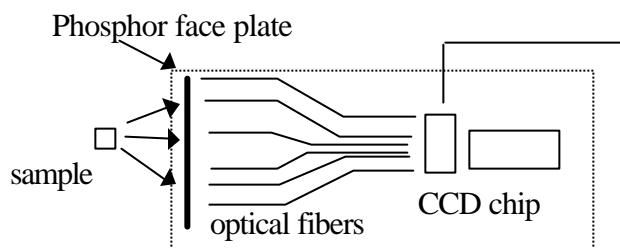
3) Television Detectors

- Television camera, image intensifier and phosphor plate
- X-rays produce light images on a phosphor plate. The images are intensified and scanned by a television camera



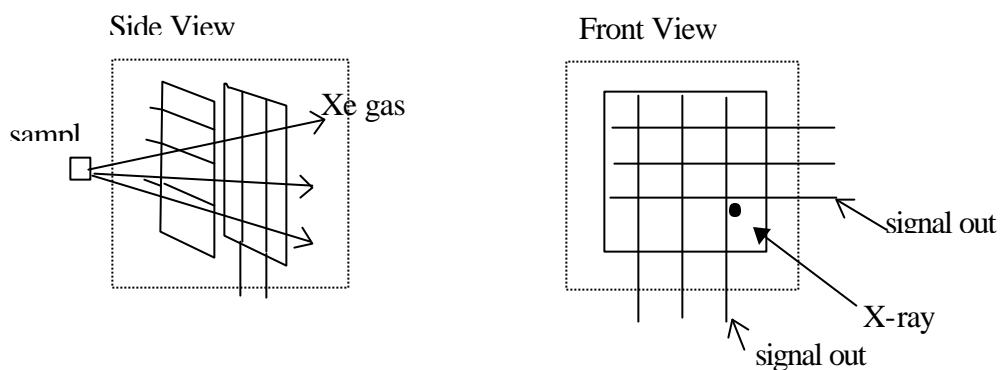
4) Charge Coupled Devices (CCD)

- Similar to the television camera
- X-rays produce light images on a phosphor plate. The images are “transferred” by fiber optics to a CCD chip. The chip is sensitive to light and position.



5) Multi-wire Proportional Counters

- Xe gas filled chambers containing alternating planes of anode (vertical) and cathode (horizontal) wires.
- X-ray events trigger currents between the wires at specific locations close to the near intersections of individual anode and cathode wires.



How many data points are unique?

$$N = [(4/3)\pi(2/\lambda)^3]V$$

for a typical cell $V = 1000 \cdot \lambda = 0.71073 \cdot$

$$N = 93,593 \text{ possible reflections}$$

Not all of these reflections are unique!

Every cell has an inversion center.

$$N = 94,000/2 = 47,000 \text{ reflections}$$

other restrictions

symmetry which equates reflections

e.g. Monoclinic systems = $2/m = 94,000/4 = 24,000$ refl.
Orthorhombic = $mmm = 94,000/8 = 12,000$ refl.

Diffractometer and intensity restrictions

for Mo X-rays max. $2\theta = 50^\circ$; divide N by 5

So for an orthorhombic cell $V = 1000 \cdot$ Mo radiation

$$N = 94,000/(8 \cdot 5) = 2350 \text{ unique collectable reflections}$$

Time factor

If you collect one reflection every 2 mins then

Time to collect 2350 reflections = $4700 \text{ mins} = 78 \text{ hr.} = 3 \text{ days}$

Space Group

A systematically absent reflection is defined as a reflection which has zero intensity at odd intervals due to translational symmetry operations.

Systematic absences arise from:

screw axis glide planes centering

and not from

mirror inversion rotations

Intensity	I(hkl)		
	primary	secondary	tertiary
orthorhombic	(a)	(b)	(c)
glides	0kl	h0l	hk0
screw	h00	0k0	00l

Example

monoclinic

no absences seen for $I(0kl)$, $I(hk0)$, $I(h00)$, $I(00l)$

		h	k	l	reflection
$h0l$	$l = 2n+1$	1	0	1	not seen
		2	0	1	not seen
		1	0	2	seen

c glide normal to the b axis

$0k0$	$k = 2n+1$	0	1	0	not seen
		0	2	0	seen
		0	3	0	not seen

 2_1 screw along the b axis**P $2_1/c$**

Examples

conditions

h00	$h = 2n+1$	2_1 along a axis
0k0	$k = 2n+1$	2_1 along b axis
00l	$l = 2n+1$	2_1 along c axis

P $2_12_12_1$

0kl	$k = 2n+1$	b glide normal to a axis
0k0	$k = 2n+1$	due to b glide
h0l	$h = 2n+1$	a glide normal to b axis
h00	$h = 2n+1$	due to a glide
hk0	$h+k = 2n+1$	n glide normal to c axis

P ban

0kl	$k = 2n+1$	b glide normal to a axis
0k0	$k = 2n+1$	due to b glide
h0l	$l = 2n+1$	c glide normal to b axis
00l	$l = 2n+1$	due to c glide
hk0	no conditions	-----

P bcm or P bc 2_1

0kl	no conditions	
h0l	$h = 2n+1$	a glide normal to b axis
h00	$h = 2n+1$	due to a glide

hk0 no conditions

P mam or Pma 2 or P 2am or P 2a 2

centering

hkl	$h+k = 2n+1$	C
	$h+l = 2n+1$	B
	$k+l = 2n+1$	A
	$h+k+l = 2n+1$	I
	h+k and h+l and	
	$k+l = 2n+1$	F

Example

conditions

hkl	$h+k = 2n+1$	C centering
0kl	$l = 2n+1$	c glide normal to a axis
00l	$l = 2n+1$	due to c glides
h0l	$l = 2n+1$	c glide normal to b axis
hk0	$h = 2n+1$	a glide normal to c axis
h00	$h = 2n+1$	due to a glide

C cca

What to look for

Centering	absences in I(hkl)
glide planes	absences in I(hk0), I(h0l), I(0kl)
screw axis	absences in I(h00), I(0k0), I(00l)
no conditions	assume mirror or rotation

Data Reduction

- (1) reduce intensities to structure factors

$$|F_{hkl}| = k\sqrt{I_{hkl}}$$

- (2) correct for Lorentz and polarization effects

$$L = \frac{1}{\sin(2\theta)}$$

$$L = 19 \text{ to } 1$$

$$p = \frac{1 + \cos^2(2\theta)}{2}$$

$$p = 1.0 \text{ to } 0.7$$

$$|F_{hkl}| = \sqrt{\frac{k' I_{hkl}}{Lp}}$$

The observed F_{hkl} values are known as F_{observed} or F_o

(3) Absorption Correction

$$\frac{I}{I_0} = e^{-\mu t}$$

μ = absorption coefficient

t = path length

(4) Merge equivalent reflections, sort and flag reflections which are **unobserved**

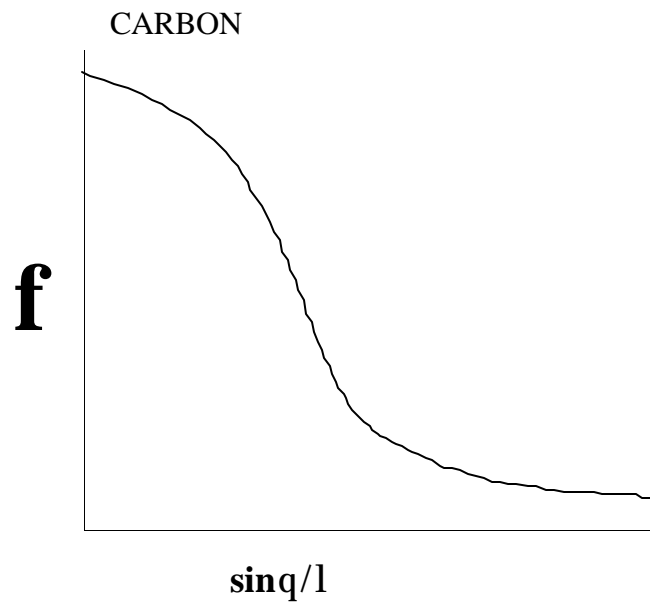
$$I_{\text{obs}} = 3\sigma(I)$$

Structure Factor

Definition

The structure factor F_{hkl} is the resultant of j waves scattered in the direction of the reflection hkl by j atoms in the unit cell. Each wave will have amplitude proportional to f_j (scattering factor of the atom) and a phase (δ) with respect to the wave scattered by hypothetical electrons at the origin of the cell.

f_j = is the individual scattering factor of each atom as a function of $\sin\theta/\lambda$

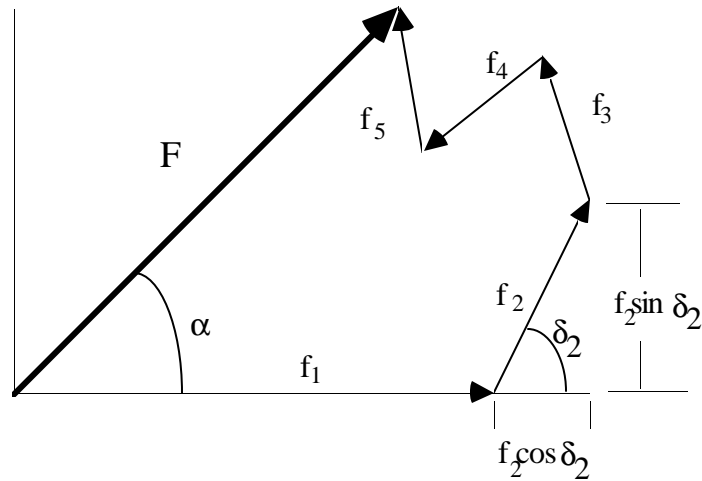


therefore if θ and λ are known then f can be calculated
(with respect to the origin. i.e. all electrons at the origin.)

$$\delta_j = 2\pi(hx_j + ky_j + lz_j)$$

Superposition of waves

waves as a vector



$$|F| = [(\sum f_j \cos \delta_j)^2 + (\sum f_j \sin \delta_j)^2]^{1/2}$$

$$|F| = (A^2 + B^2)^{1/2}$$

$$\alpha = \tan^{-1}(B/A)$$

α is the **phase angle** for F_{hkl}

$$|F|^2 = A^2 + B^2 = \mathbf{F}\mathbf{F}^*$$

$$\mathbf{F}\mathbf{F}^* = (A+iB)(A-iB)$$

$$\mathbf{F} = A+iB$$

$$\delta = 2\pi(hx_j + ky_j + lz_j)$$

$$\mathbf{F}_{hkl} = \sum_{j=1}^n f_j [\cos 2\pi(hx_j + ky_j + lz_j) + i \sin 2\pi(hx_j + ky_j + lz_j)]$$

$$\alpha = \tan^{-1} \left(\frac{\sum f_j \sin 2\pi(hx_j + ky_j + lz_j)}{\sum f_j \cos 2\pi(hx_j + ky_j + lz_j)} \right)$$

$$\mathbf{F}_{hkl} = |F|_{hkl} \exp(i\alpha_{hkl})$$

If x, y, z 's are known for atoms j then the structure factors \mathbf{F}_{hkl} can be calculated.

The calculated values are known as $\mathbf{F}_{\text{calculated}}$ or \mathbf{F}_c

Motion

isotropic motion

$$f_j = f_{o,j} \exp(-\beta \sin^2\theta/\lambda^2)$$

anisotropic motion

$$f_j = f_{o,j} \exp[1/4(\beta_{11}h^2a^{*2} + \beta_{22}k^2b^{*2} + \beta_{33}l^2c^{*2} + 2\beta_{12}hka^*b^* + 2\beta_{13}hla^*c^* + 2\beta_{23}klb^*c^*)]$$

note: $\beta = 8\pi^2 \overline{U^2}$

Friedels Law

$$I_{hkl} = I_{\bar{h}\bar{k}\bar{l}}$$

$$F_{hkl} = A_{hkl} + iB_{hkl} \quad F_{\bar{h}\bar{k}\bar{l}} = A_{hkl} - iB_{hkl}$$

$$F_{hkl}^2 = (A_{hkl} + iB_{hkl})(A_{hkl} - iB_{hkl}) = F_{\bar{h}\bar{k}\bar{l}}^2$$

Verification of extinction conditions

2_1 along b $0k0$ $k = 2n$ (for observation)

$$x, y, z \rightarrow -x, \frac{1}{2}+y, -z$$

$$\cos(a+b) = \cos(a)\cos(b) - \sin(a)\sin(b)$$

$$\sin(a+b) = \sin(a)\cos(b) + \cos(a)\sin(b)$$

$$\cos(k\pi) = 1 \quad k = 2n ; -1 \quad k = 2n+1$$

$$\sin(k\pi) = 0$$

$$F(hkl) = \sum f \cos[2\pi(hx+ky+lz)] + if \sin[2\pi(hx+ky+lz)]$$

$$\begin{aligned} F(0k0) &= f \cos(2\pi ky) + if \sin(2\pi ky) + f \cos[2\pi k(\frac{1}{2}+y)] + if \sin[2\pi k(\frac{1}{2}+y)] \\ &= f \cos(2\pi ky) + if \sin(2\pi ky) + \\ &\quad f \cos[2\pi k(\frac{1}{2})] \cos(2\pi ky) - f \sin[2\pi k(\frac{1}{2})] \sin(2\pi ky) + \\ &\quad if \sin[2\pi k(\frac{1}{2})] \cos(2\pi ky) + if \cos[2\pi k(\frac{1}{2})] \sin(2\pi ky) \end{aligned}$$

k odd

$$\begin{aligned} &= f \cos(2\pi ky) + (-1) f \cos(2\pi ky) + if \sin(2\pi ky) + (-1) if \sin(2\pi ky) - \\ &\quad (0) f \sin(2\pi ky) + (0) if \cos(2\pi ky) \end{aligned}$$

$$= 0$$

k even

$$\begin{aligned} &= f \cos(2\pi ky) + (+1) f \cos(2\pi ky) + if \sin(2\pi ky) + (+1) if \sin(2\pi ky) - \\ &\quad (0) f \sin(2\pi ky) + (0) if \cos(2\pi ky) \end{aligned}$$

$$= 2f \cos(2\pi ky) + 2[if \sin(2\pi ky)]$$

$$\neq 0$$

Relationship between the structure factor and the electron density

$$F_{hkl} = \iiint_{hkl} \rho(xyz) e^{2\pi i(hx+ky+lz)} dV$$

Fourier series:

$$\rho(xyz) = \frac{1}{V} \sum_h \sum_k \sum_l F_{hkl} e^{-2\pi i(hx_j+ky_j+lz_j)}$$

describes the periodic wave function

separating F_{hkl} into magnitude and phase α_{hkl}

$$\rho(xyz) = \frac{1}{V} \sum_h \sum_k \sum_l |F_{hkl}| e^{i\alpha_{hkl}} e^{-2\pi i(hx_j+ky_j+lz_j)}$$

$$\rho(xyz) = \frac{1}{V} \sum_h \sum_k \sum_l |F_{hkl}| e^{-2\pi i(hx_j+ky_j+lz_j - \alpha'_{hkl})}$$

expanding the term and including some known equivalents (Friedel's) we calculate the trigonometric form of the equation:

$$\rho(xyz) = \frac{1}{V} \sum_h \sum_k \sum_l |F_{hkl}| \cos 2\pi(hx_j+ky_j+lz_j - \alpha')$$

$$\text{where } \alpha' = \alpha_{hkl}/2\pi$$

If $|F_{hkl}|$ **and** the phase angle α are known one can calculate ρ electron density map

the X-ray experiment provides the $|F_{hkl}|$ **however** the phase angles α are **unknown**

"To get the **Answer**, you need the **Answer**"

Phase

Problem

Prove the phase (α_{hkl}) for centrosymmetric space groups is either 0 or π .
one dimensional case

relationships $\sin(x) = -\sin(-x); \quad \cos(x) = \cos(-x)$

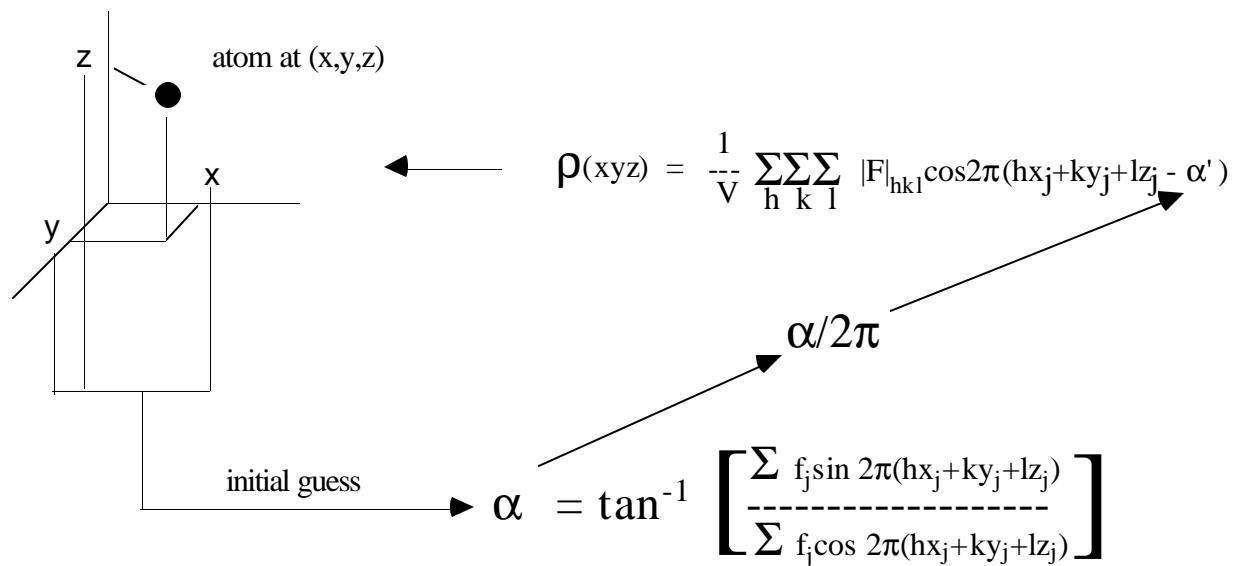
coordinated $x, y, z; \quad -x, -y, -z$

$$\begin{aligned} A_{hkl} &= \cos 2\pi xh + \cos 2\pi(-x)h + \cos 2\pi yk + \cos 2\pi(-y)k + \cos 2\pi zl + \cos 2\pi(-z)l \\ &\quad \text{since } \cos(x) = \cos(-x) \\ &= 2\cos 2\pi xh + 2\cos 2\pi yk + 2\cos 2\pi zl \end{aligned}$$

$$\begin{aligned} B_{hkl} &= \sin 2\pi xh + \sin 2\pi(-x)h + \sin 2\pi yk + \sin 2\pi(-y)k + \sin 2\pi zl + \sin 2\pi(-z)l \\ &\quad \text{since } \sin(x) = -\sin(-x) \\ &= \sin 2\pi xh - \sin 2\pi xh + \sin 2\pi yk - \sin 2\pi yk + \sin 2\pi zl - \sin 2\pi zl \\ &= 0 \end{aligned}$$

$$\alpha_h = \tan^{-1}(B_h/A_h) = (0/2\cos 2\pi xh) = \tan^{-1}(0) = 0 \quad \text{or} \quad \tan^{-1}(0) = \pi$$

Phase Problem



solutions to the phase problem

- (1) Heavy Atom Methods
 - a) Patterson Synthesis
 - b) Isomorphous replacement
- (2) Direct Methods

Patterson Function

The square of the structure factors F_{hkl} are phaseless expressions.

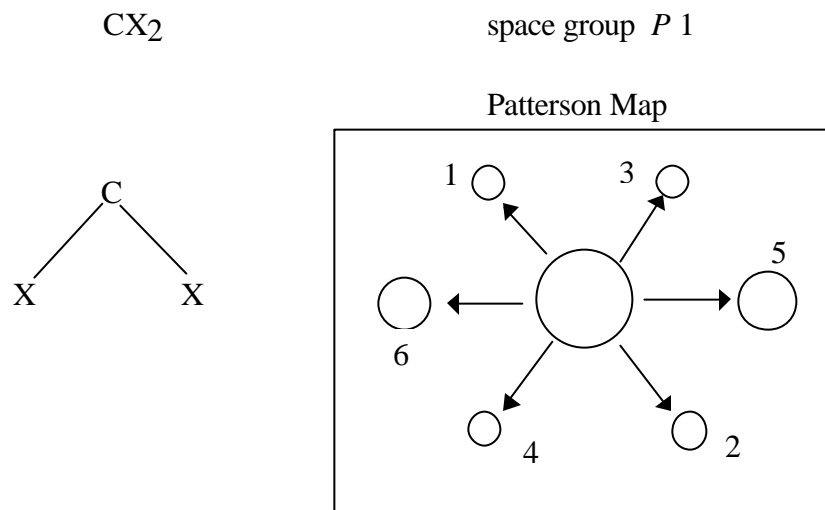
$$\mathbf{P}(xyz) = \frac{1}{V} \sum_h \sum_k \sum_l |F_{hkl}|^2 e^{-2\pi i(hx + ky + lz)}$$

by Friedels Law

$$|F_{hkl}|^2 = |F_{\bar{h}\bar{k}\bar{l}}|^2$$

$$\mathbf{P}(xyz) = \frac{1}{V} \sum_h \sum_k \sum_l |F_{hkl}|^2 \cos 2\pi(hx + ky + lz)$$

Height of a peak in the Patterson map = $(Z_i \times Z_j)$



$Z_i Z_j$

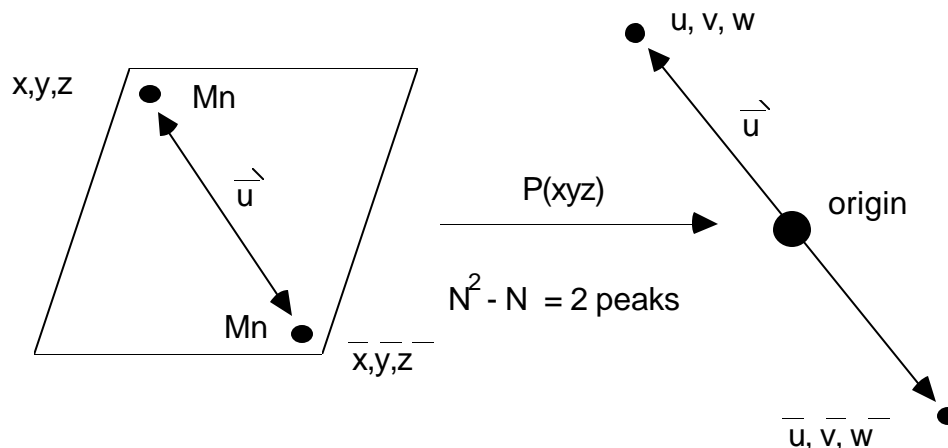
vectors	X=O	X=C	X=S
1,2	48	36	96
3,4	48	36	96
5,6	64	36	256
origin	164	108	548

Observations

- (1) Patterson map is centrosymmetric
- (2) Map is overcrowded
- (3) Atoms of similar *Z* produce maps with little variation

$$\frac{Z_{\text{heavy atoms}}^2}{Z_{\text{light atoms}}^2} - 1$$

Mn(TPPCl) Space Group $P\bar{1}$ $Z = 2$



→

$$u = x - (\bar{x}); v = y - (\bar{y}); \bar{w} = z - (\bar{z}) \quad 2x, 2y, 2z = u, v, w, = \text{Mn} \rightarrow \text{Mn}$$

peak	u	v	w	
1	0	0	0	origin peak
2	0.38	0.36	0.52	Mn----Mn peak

Mn co-ordinates

x	y	z
0.19	0.18	0.26
-0.19	-0.18	-0.26

Harker Line : Two of the variables (u,v,w) are fixed (0,1/4,1/3,1/2, etc.)

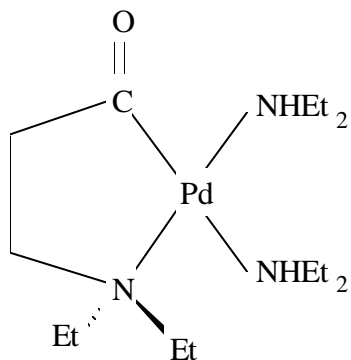
$$u, v, w = (0, 1/2+2y, 1/2)$$

Harker Plane : one of the variables (u,v,w) is fixed (0,1/4,1/3,1/2, etc.)

$$u, v, w = (2x, 1/2, 1/2+2z)$$

Harker planes and Harker lines are more intense.

Example Space group $P 2/c$



- ① x, y, z
- ② $\bar{x}, \bar{y}, \bar{z}$
- ③ $\bar{x}, 1/2+y, 1/2-z$
- ④ $x, 1/2-y, 1/2+z$

General interatomic vectors

	x, y, z	$\bar{x}, \bar{y}, \bar{z}$	$\bar{x}, 1/2+y, 1/2-z$	$x, 1/2-y, 1/2+z$
x, y, z	0,0,0	$2\bar{x}, 2\bar{y}, 2\bar{z}$	$2\bar{x}, 1/2, 1/2-2z$	$0, 1/2-2y, 1/2$
$\bar{x}, \bar{y}, \bar{z}$	$2x, 2y, 2z$	0,0,0	$0, 1/2+2y, 1/2$	$2x, 1/2, 1/2+2z$
$\bar{x}, 1/2+y, 1/2-z$	$2x, 1/2, 1/2+2z$	$0, 1/2-2y, 1/2$	0,0,0	$2x, 2\bar{y}, 2z$
$x, 1/2-y, 1/2+z$	$0, 1/2+2y, 1/2$	$2\bar{x}, 1/2, 1/2-2z$	$2\bar{x}, 2y, 2z$	0,0,0

Peak	u	v	w
1	0.0	0.0	0.0
2	0.0	0.05	1/2
3	0.42	1/2	0.23
4	0.42	0.46	0.28

use $0, 1/2 \pm 2y, 1/2$ $\pm 2x, 1/2, 1/2 \pm 2z$

$$v = 1/2 \pm 2y = 0.05 \quad u = \pm 2x = 0.42 \quad w = 1/2 \pm 2z = 0.23$$

$$\pm 2y = -0.45 \quad \pm 2z = -0.27$$

$$\pm y = 0.23 \quad \pm x = 0.21 \quad \pm z = 0.135$$

Coordinate for Pd $\pm 0.21x/a$ $\pm 0.23y/b$ $\pm 0.14x/c$

Patterson Map (Continued)

Follow up:

- 1) place heavy atom and calculate rough α hkl 's
- 2) use rough α hkl 's to calculate rough \mathbf{r} (x,y,z) map
- 3) find more atomic coordinates from map and use to calculate better α hkl 's
- 4) repeat until all atoms are found.

Isomorphous Replacement Method

- method requires a pair (or series) of isomorphous crystals.

- isomorphous crystals are crystalline solids with essentially identical cell dimensions and atomic arrangements but with a variation in the nature of one or more atoms present.

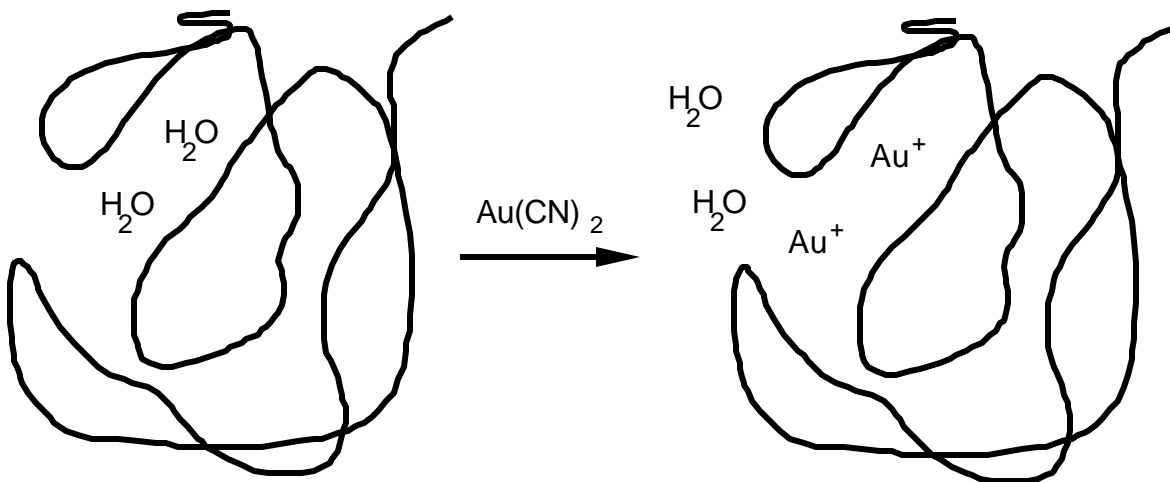
- examples



colorless crystal

purple crystal

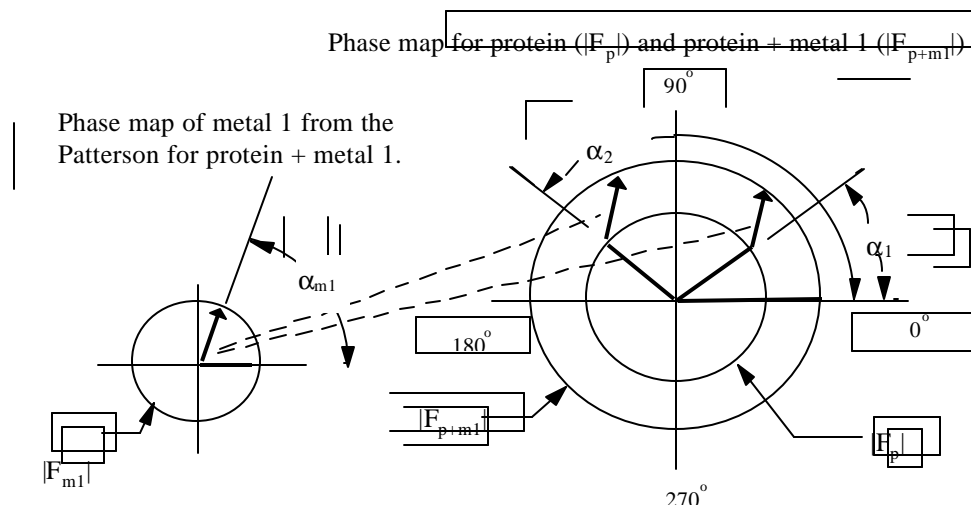
- protein



Isomorphous Replacement Method (continued)

Estimate phase angle for \mathbf{F}_p from known phase α_{m1} and α_{m2} and amplitudes $|F_{m1}|$ and $|F_{m2}|$.

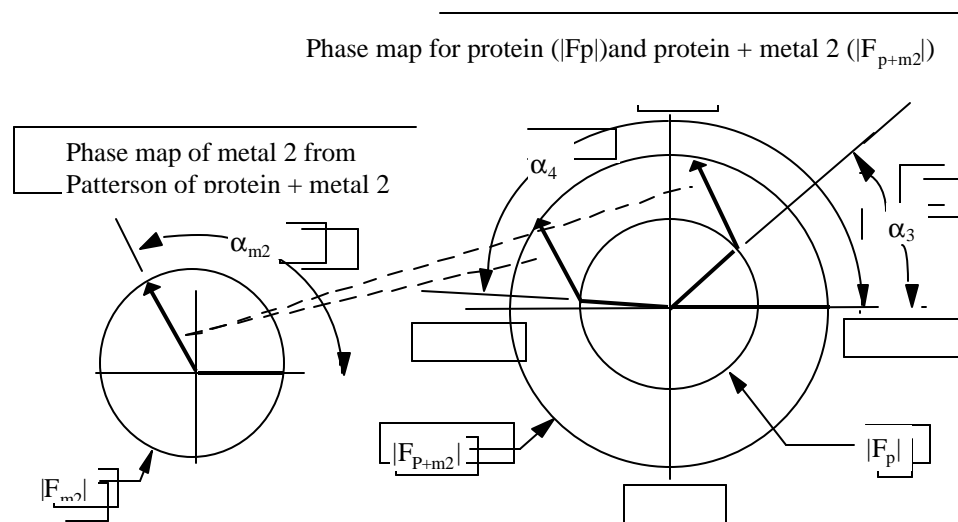
First metal derivative.



Known $\alpha_{m1} = 69^\circ$ and amplitude of $\mathbf{F}_{m1} = |F_{m1}|$.

Predicted phase angles for \mathbf{F}_p $\alpha_1 = 38^\circ$ $\alpha_2 = 136^\circ$.

Second metal derivative



Known $\alpha_{m2} = 119^\circ$ amplitude of $\mathbf{F}_{m2} = |F_{m2}|$

Predicted phase angles for \mathbf{F}_p $\alpha_3 = 41^\circ$ $\alpha_4 = 175^\circ$

The four angles suggested by the maps are 38° , 136° , 41° and 175° .

Therefore it is predicted that the phase angle of \mathbf{F}_p is about 39°

Non-Linear Least-Squares Refinement

$$D = \sum_{hkl} w_{hkl} (|F_o| - k |F_c|)^2$$

$w \propto 1/\sigma(F)$ **scale factor**

$$|F_c| = \sqrt{A^2 + B^2}$$

parameters (x,y,z) $f_c e^{-\beta \sin^2 \theta / \lambda^2}$

isotropic	b_{iso}	
anisotropic	b_{ij}	(6)

D is minimized by taking $\frac{\partial D}{\partial p_j}$ for each parameter (p_j)

$$0 = \sum w (F_o - |kF_c(p_1, p_2, p_3 \dots p_n)|) \frac{\partial |kF_c(p_1, p_2, p_3 \dots p_n)|}{\partial p_j}$$

Expressing F_c as a Taylor series (neglecting powers > 1)

$$|kF_c(p_1, p_2, p_3 \dots p_n)| = |kF_c(c_1, c_2, c_3 \dots)| + \frac{\partial |kF_c|}{\partial p_1} \Delta p_1 + \dots$$

Which after substitution produces $n \times n$ matrix

$$\mathbf{A} \mathbf{x} = \mathbf{V}$$

$$A_{ij} = \sum w \left(\frac{\partial(kF_c)}{\partial p_i} \right) \left(\frac{\partial(kF_c)}{\partial p_j} \right)$$

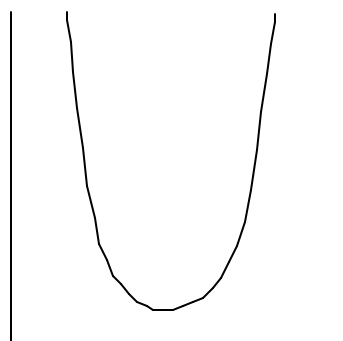
$$x_j = \Delta p_j$$

$$V_i = \sum w \Delta F \left(\frac{\partial(kF_c)}{\partial p_i} \right)$$

$$\mathbf{x} = \mathbf{A}^{-1} \mathbf{V}$$

For 25 atoms (x,y,z and 6 β 's) $25 \times 9 = 225$ parameters + scale factor = 226
 \mathbf{A} will be $226 \times 226 = 51076$ elements (only 1/2 unique)

Least Squares (continued)



restrained refinement

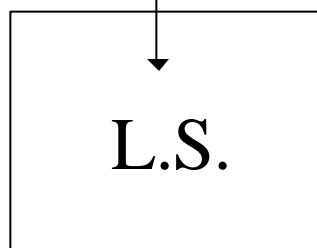
$$\Sigma (d_{\text{ideal}} - d_{\text{obs}})^2$$



constrained refinement

Treat as rigid body :
reduces the 18
parameter phenyl
ring to 3 parameters

x, y, z



"black box"

x+Δx, y+Δy, z+Δz

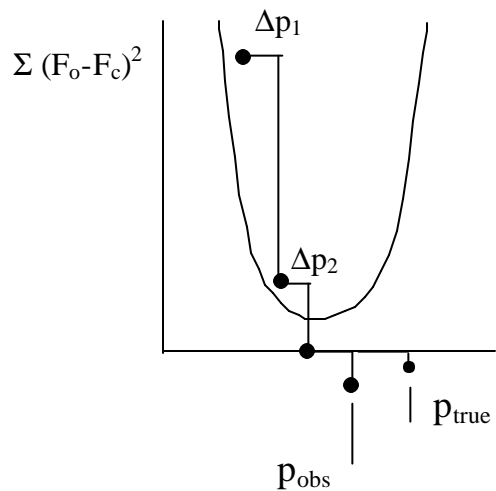
Δx

Δy

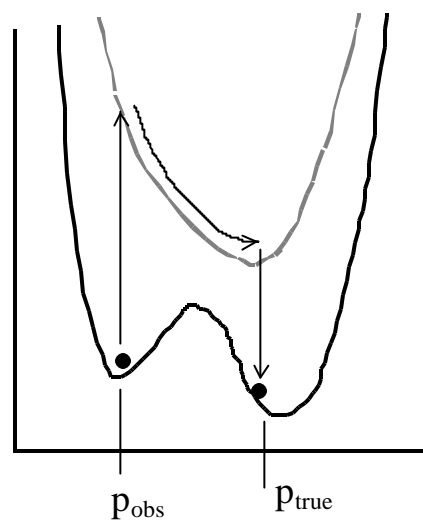
Δz

Stop when $\Delta p < \text{fixed value}$
(radius of convergence)

Steepest Descent (SD)
PROLSQ



Simulated annealing
X-PLOR


 $\exp(-E/KbT)$

When is L.S. refinement done?

Terminate refinement when Δp_j are small compared to the e.s.d.'s (~10%).

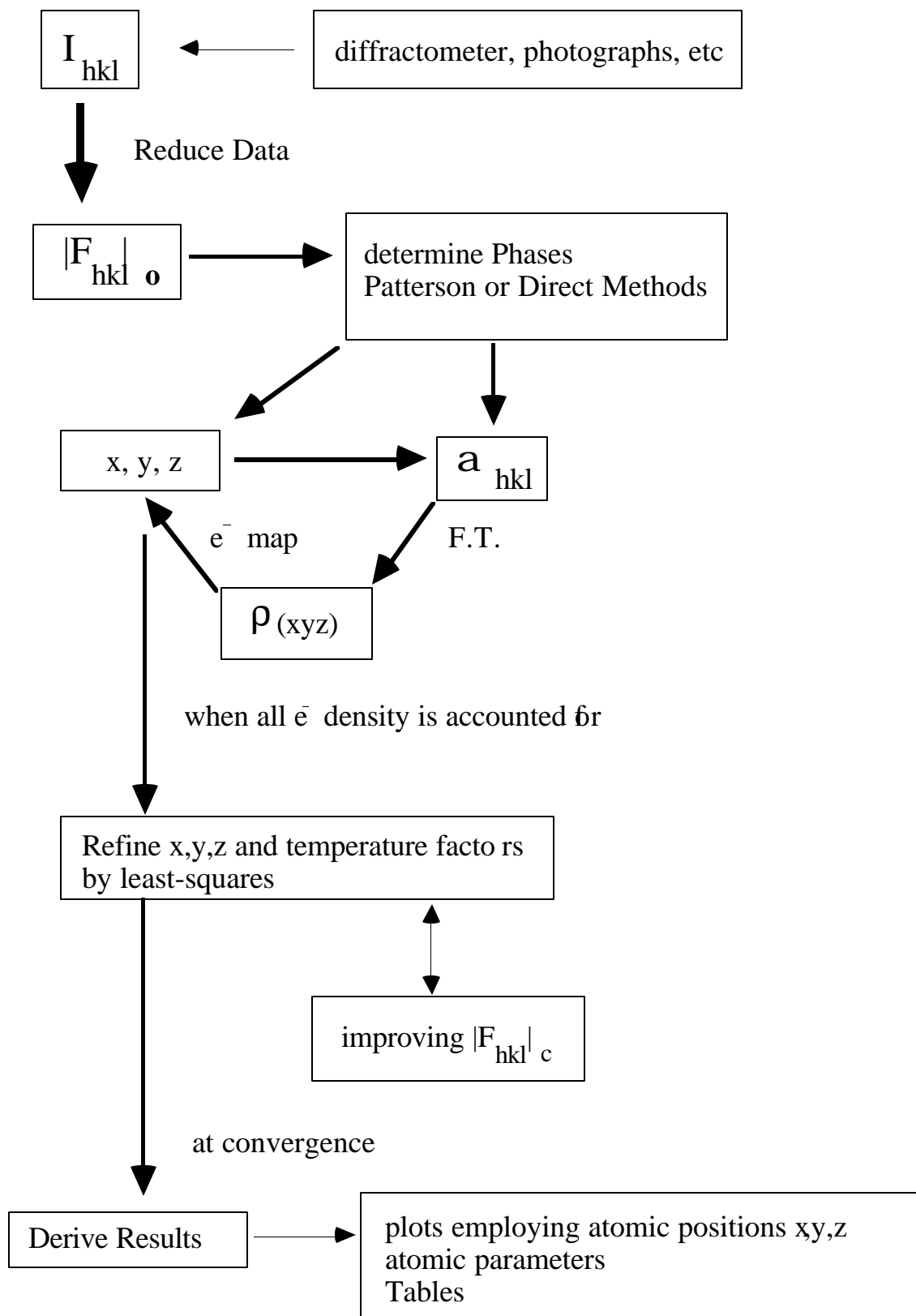
Residuals

$$R = \frac{\sum (|F_o| - |kF_c|)}{\sum (|F_o|)}$$

$$R_w = \left(\frac{\sum w (|F_o| - |kF_c|)^2}{\sum w (|F_o|)^2} \right)^{1/2}$$

R factor is an indication of Quality . Alone **R** value is meaningless

For any least-squares - ratio between Data points and parameters should be 6-10.

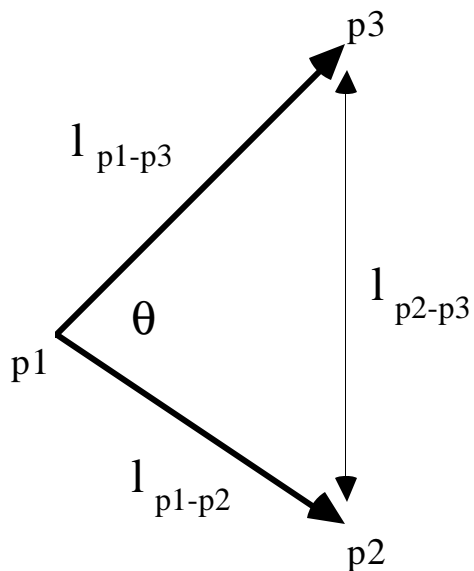


Derived Results atomic coordinates (x,y,z)

$$x = x/a \quad y = y/a \quad z = z/a; \quad \Delta x = x_1 - x_2 \quad \Delta y = y_1 - y_2 \quad \Delta z = z_1 - z_2$$

$$l_{p1-p2} = [(\Delta xa)^2 + (\Delta yb)^2 + (\Delta zc)^2 + 2\Delta x\Delta yab\cos\gamma + 2\Delta x\Delta zaccos\beta + 2\Delta y\Delta zbccos\alpha]^{1/2}$$

(law of cosines in three dimensions)



$$\cos \theta = \frac{l_{p1-p3}^2 + l_{p1-p2}^2 - l_{p2-p3}^2}{2(l_{p1-p3}l_{p1-p2})}$$

estimated standard deviations (e.s.d) σ

If all parameters (p_j) are independent of one another then

$$\sigma_l = \left[\sum_{j=1}^n \left(\frac{\partial l}{\partial p_j} \right)^2 \right]^{1/2}$$

bond lengths (angles) are given in the form $1.54(3)^\circ = 1.54 \pm .03^\circ$

Comparison of bond lengths (angles)

When are two stated bond lengths different within experimental error?

Pair-wise comparison (null hypothesis method)

Assume that **P** (percentage) of finding a measured value more than $\pm \lambda \sigma_{\Delta l}$ from its true value is :

P (in %)	λ
20	1.28
10	1.65
5	1.96
1	2.56
.1	3.29
.01	3.99

For two bond lengths to be considered **different** lengths, the difference in their bond lengths must be greater than $2.56 \times \sigma_{\Delta l}$. This is stated as : The difference in the two bond lengths **are** significant. For two bond lengths to be considered the **same** length the difference in their bond lengths must be less than $1.96 \times \sigma_{\Delta l}$. This is stated as: The difference in the two bond lengths **are not** significant. For difference between $2.56 \times \sigma_{\Delta l}$ and $1.96 \times \sigma_{\Delta l}$ the term **possibly** significant is used.

Example

Comparison between bond length **2.006(6) •** and **2.019(5) •**

1) calculate $\sigma_{\Delta l}$. $\sigma_{\Delta l} = [\sigma_{l1}^2 + \sigma_{l2}^2]^{1/2}$

$$\sigma_{\Delta l} = [(0.006)^2 + (0.005)^2]^{1/2} = 0.008 \bullet$$

2) calculate $\Delta l = [2.019 - 2.006] = 0.013 \bullet$

3) calculate $1.96 \times \sigma_{\Delta l} = 0.016 \bullet$ and $2.56 \times \sigma_{\Delta l} = 0.021 \bullet$

4) compare to table.

0.013 • is less than 0.016 • thus the difference in the two lengths are **not significant**.
The two bond lengths are the same within experimental error

For **2.006(6) •** and **2.028(5) •** the difference (0.022•) is **significant**.

For **2.006(6) A** and **2.022(5) •** the difference (0.016•) is **possibly significant**.

χ^2 test.

Use the test to decide when you can average a collection of bond lengths (angles)

Numbers may be averaged when there is greater than **5%** chance that they are equal.

$$\sigma_{\text{sample}} = \left[\frac{\sum_m (l_m - \bar{l})^2}{m-1} \right]^{1/2}$$

$$\chi^2 = \frac{(m-1)\sigma_{\text{sample}}^2}{\sigma_{\text{refinement}}^2} = \frac{\sum_m (l_m - \bar{l})^2}{\sigma_{\text{refinement}}^2}$$

example

Can we average these bond lengths?

1.985(5) Å, 1.982(5) Å, 1.985(5) Å, and 1.987(5) Å.

1) calculate $\sigma_{\text{sample}} = 0.0034$ Å

2) calculate $\sigma_{\text{refinement}} = \sigma_{\text{lengths}} = \sqrt{\sum \sigma_i^2 / m} = 0.005$ Å

3) calculate $\chi^2 = 1.44$

4) look up the answer from a χ^2 table. For 4-1=3 degrees of freedom the table tells us that there is greater than a 50% chance that the numbers are equal.

thus $\bar{l}_{\text{mean}} = 1.985(3)$ Å

if $\sigma_{\text{refinement}} = 0.002$ then $\chi^2 = 9$. For 3 degrees of freedom the table suggests that there is about 2.5% chance that the bonds are equal. Since this is less than 5% we assume that the bonds **cannot** be averaged.

A Critical Review

P.G. Jones, Chem. Soc. Rev., **1984**, 157.

i) **R values & Accuracy**

Do not use the **R** value alone to decide on the quality of the structure.

Examine the **e.s.d.** s of the coordinates.

High **e.s.d.** s are a sign that too many reflections have been omitted or the data is of poor quality. Look for $2\theta_{\max}$ for Mo $\sim 50^\circ$ and Cu $\sim 100^\circ$ and high data to parameter ratio ~ 8 .

ii) **e.s.d.** s

e.s.d. s are based on σ_F and ignore the systematic error in the instrumentation. The inclusion of the error tends to increase the **e.s.d.** s

i.e. The **e.s.d.** s are inherently low.

iii) Incorrect space groups

Ambiguity in assign space groups (i.e. $P 2$, $P m$, $P 2/m$) or assignment of lower symmetry space group.

Look for simple mathematical equalities in the cell parameters. ($a=\sqrt{b}$, $a=b$, $a=2b$ etc).

Is there more than one molecule in the asymmetric unit.

iv) Absorption correction.

$I/I_0 = \exp(-\mu t)$ where μ is element dependent and t is the path length

though the crystal.

A correction should be applied if $\mu t > 0.5$ ($I/I_0 = 0.60$)

v) Thermal ellipsoids

Thermal parameters are sinks for all types of errors. The usual shape should resemble a rugby football. unusual shapes (discs, plates etc.) point to problems.

Thermal motion effects the location of the atomic positions and may lead to problems in bond lengths and angles.

vi) Problems with "light" atoms

C & N (-C=N-)

N & O , F & O etc.

Location of Hydrogen. (idealized positions)

vii) non-centrosymmetric structures.

Friedel's Law -> not always obeyed. Breaks down in the presence of "heavy" atoms (absorption). Anomalous scattering correction will help.