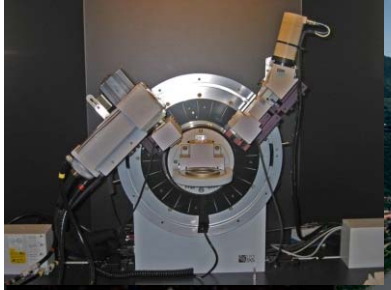
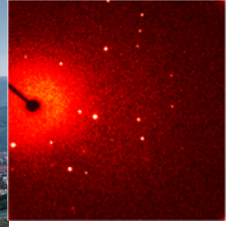
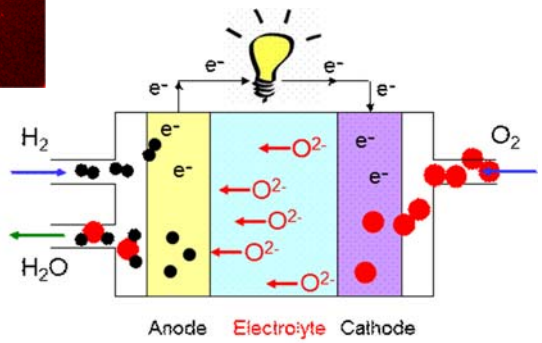
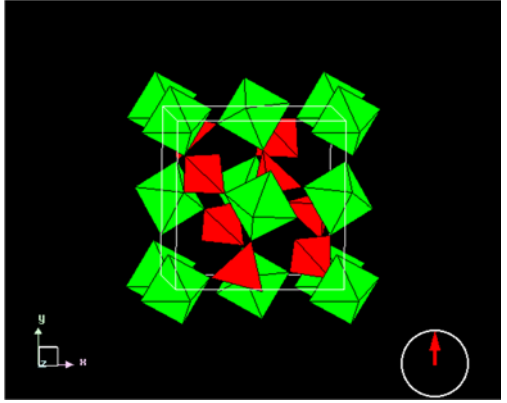
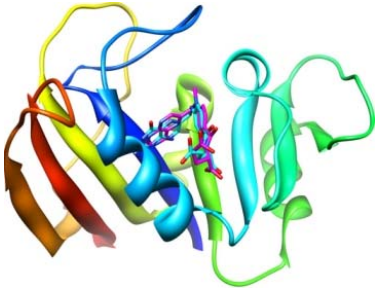


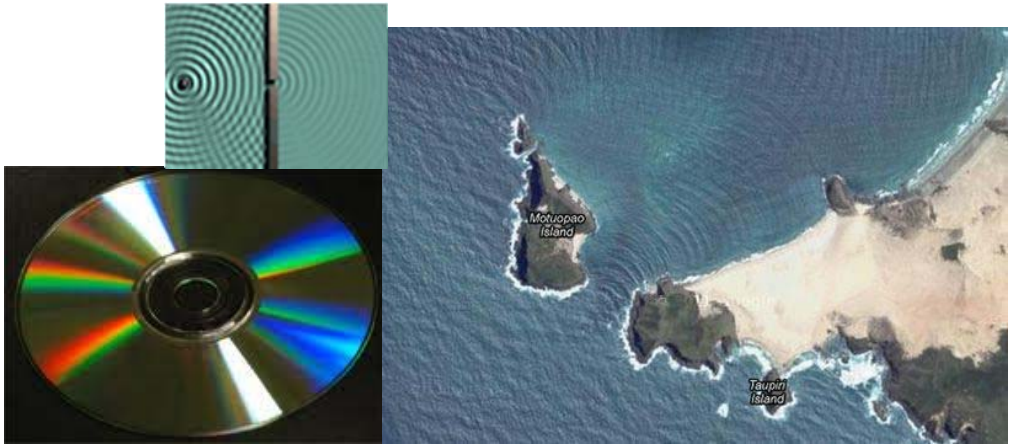




Nove fizickohemijske metode

Ivana Radosavljevic Evans
Durham University, UK

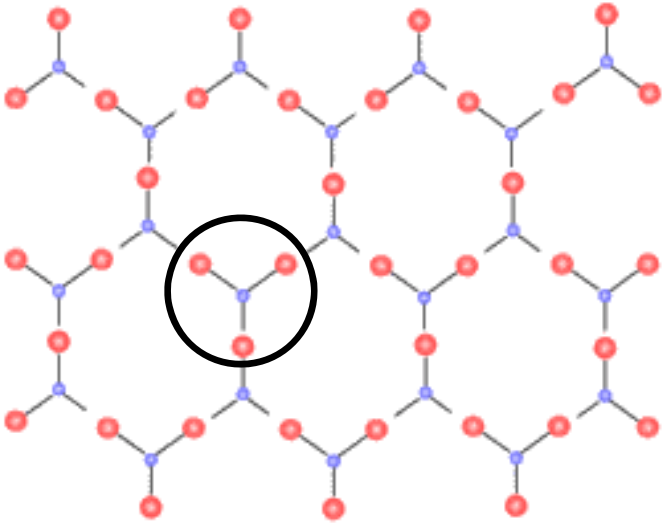
Nove fizickohemijske metode:

Metode zasnovane na sinhrotronskom zracenju

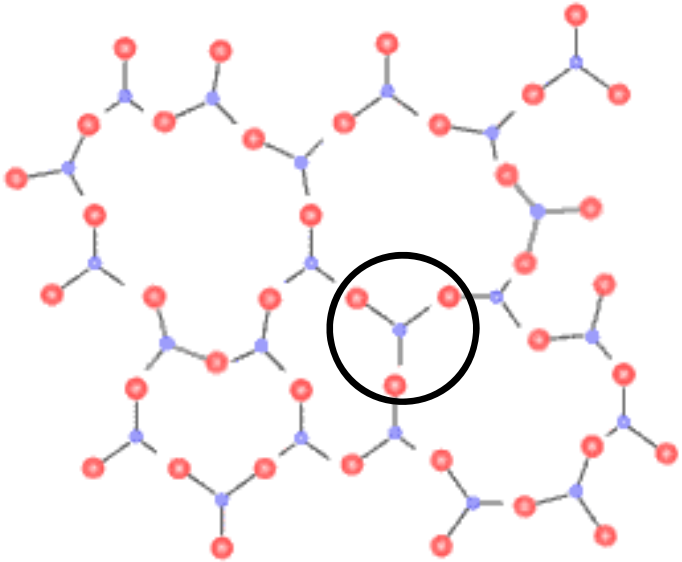
- Plan predavanja:
  - Difrakcione metode strukturne karakterizacije materijala
  - Oblasti primene difrakcije sinhrotronskog X-zracenja
  - Eksperimentalni aspekti difrakcije sinhrotronskog X-zracenja
  - Prednosti (i mane) u odnosu na laboratorijski XRD
  - Primeri studija neorganskih funkcionalnih materijala
- Preporuceni prag znanja:
  - Osnovne kristalografske definicije
  - Kristalografska simetrija, prostorne grupe
  - Difrakcija kao fizicka pojava
  - Bragg-ov zakon
  - Rasejanje sa jedinicne celije: strukturni faktor

Solids

Crystalline



Amorphous



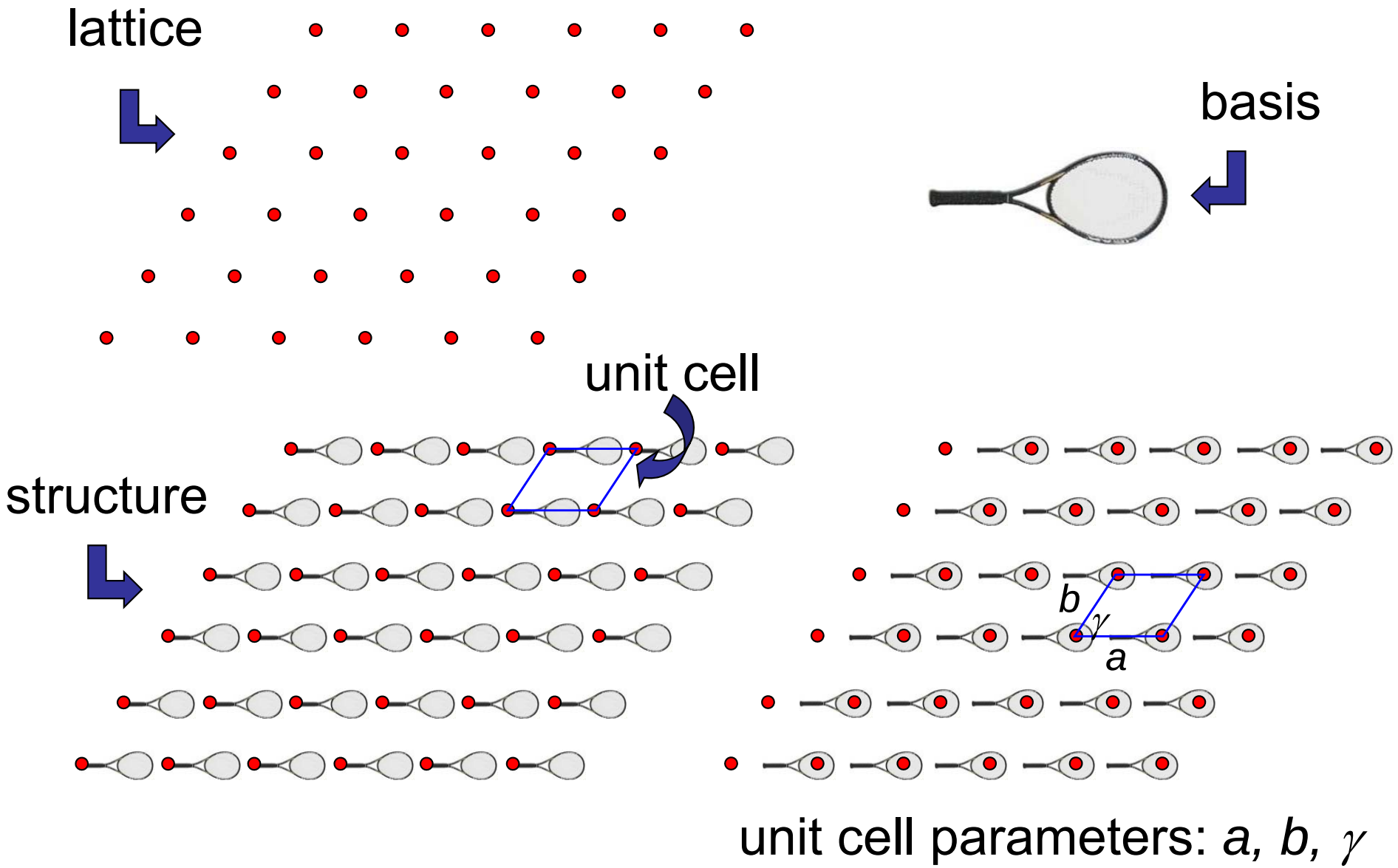
SiO_2 : Si

O

Crystallographic Definitions

- **Lattice** – an infinite array of points in space where each point has identical surroundings
- **Basis** – a motif associated with each lattice point
- **Crystal Structure** – the periodic arrangement of atoms in a solid
- **Unit Cell** – the smallest component from which the entire crystal can be built up, with purely translational displacements

Crystallographic Definitions

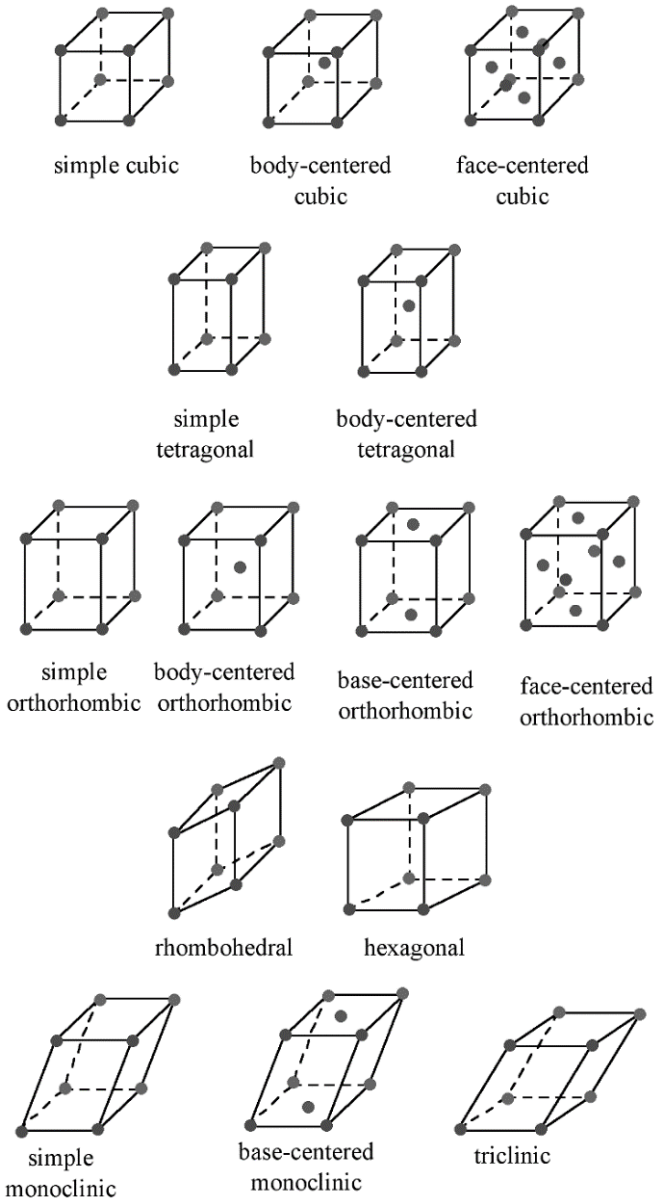


unit cell parameters: *a*, *b*, γ

Crystallographic Definitions

- 3D
  - 14 Bravais lattices (unit cells)
  - 7 crystal systems

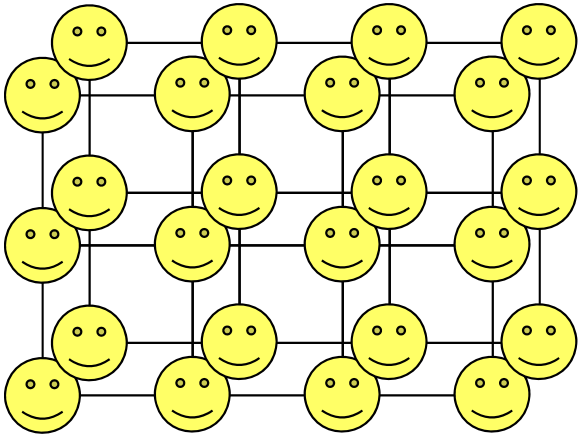
Crystal system	Lattice parameters	Min. symmetry
Cubic	a=b=c $\alpha=\beta=\gamma=90^o$	Four C_3 axes
Tetragonal	a=b≠c $\alpha=\beta=\gamma=90^o$	C_4
Orthorhombic	a≠b≠c $\alpha=\beta=\gamma=90^o$	Three C_2 axes
Rhombohedral	a=b=c $\alpha=\beta=\gamma\neq90^o$	C_3
Hexagonal	a=b≠c $\gamma=120^o$	C_6
Monoclinic	a≠b≠c $\alpha=\gamma=90^o$; $\beta\neq90^o$	C_2 or m
Triclinic	a≠b≠c $\alpha\neq\beta\neq\gamma\neq90^o$	None



Symmetry in the Solid State

- Molecular symmetry:
  - Symmetry of isolated objects
  - Point group symmetry
  - 32 crystallographic point groups

- Crystallographic symmetry:
  - Symmetry of periodic arrays
  - Space group symmetry
  - 230 space groups



Molecular Symmetry

Sym. element	Sym. operation	Symbol*
Identity	Nothing	E
Rotation axis (C_1, C_2, C_3, C_4, C_5, C_6…)	Rotation	C_n
Inversion centre	Inversion	i
Mirror plane	Reflection	σ
Improper axis	Rotation + reflection	S_n

- Examples:
  - Formula: XeF_4, XeF_2Cl_2, …, CHFClBr
  - Point group: D_{4h}, D_{2h}, …, C_1

*Schönflies notation

Crystallographic Symmetry

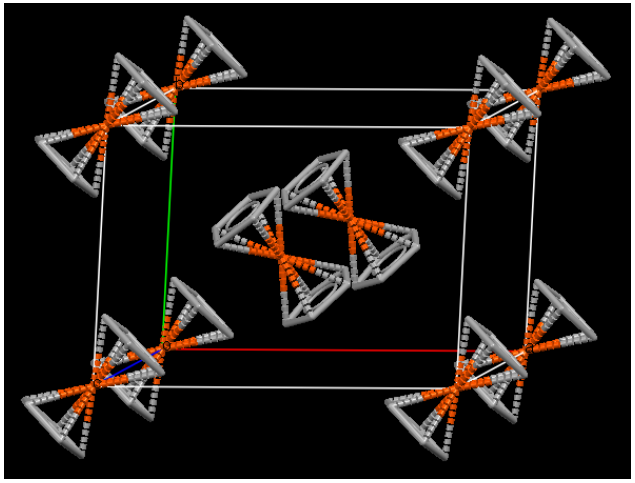
Sym. element	Sym. operation	Symbol*
Identity	Nothing	E
Rotation axis (C_1, C_2, C_3, C_4, C_6)	Rotation	1,2,3,4,6
Inversion centre	Inversion	-1
Mirror plane	Reflection	*m*
Improper axis	Rotation + inversion	-1,-2,-3,-4,-6
Screw axis	Rotation + translation	N_p
Glide plane	Reflection + translation	*a*, *b*, *c*, *n*, *d*

*Hermann-Mauguin notation

Molecular vs. Crystallographic Symmetry

- Q: Can molecules with 5-fold symmetry form crystals?
  - Yes!

- Ferrocene (CSD refcode FEROCE01)
  - Molecular symmetry: D_{5d}
  - Space group symmetry: $P2_1/a$



Space Groups

- Crystal = 3D periodic array
- Full description of crystal symmetry:

Non-translational component + Translational component

Point groups
- Take away linear
- Retain only those with 2,3,4 and 6-fold axes

⇓

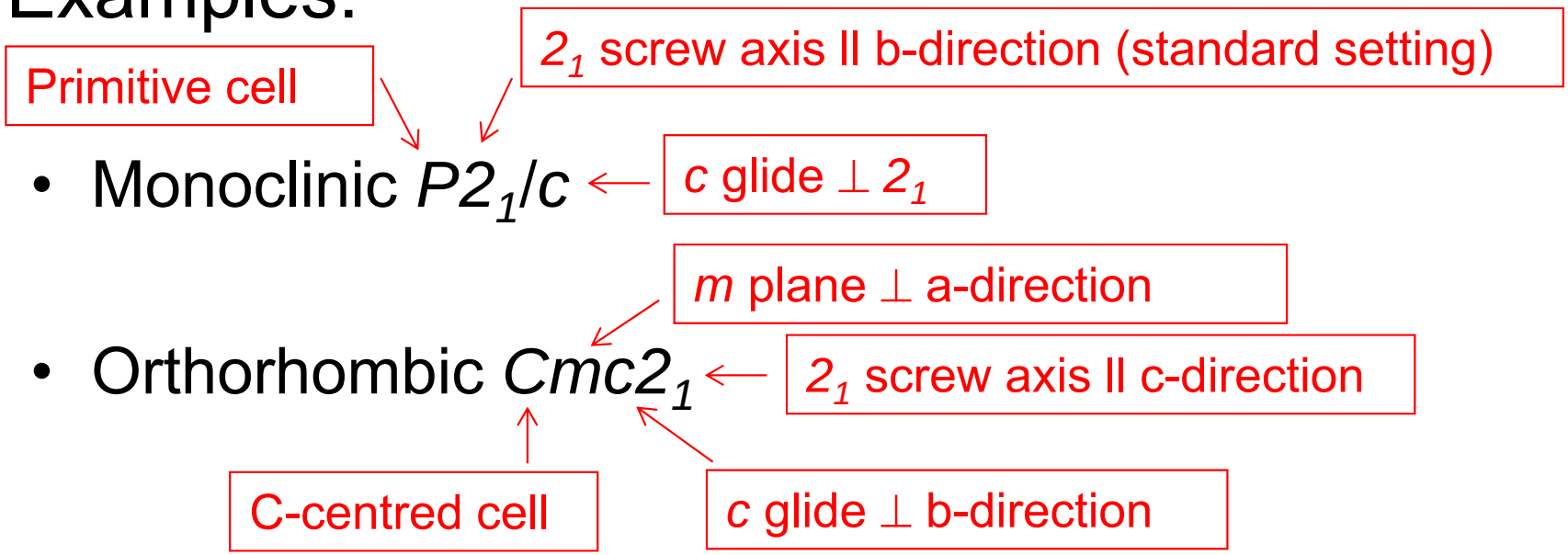
- 32 crystallographic point groups

Translations
- Unit cell translations
- Cell centring translations (F, I, C, B, A)
- Translational symmetry elements

230 space groups

Space Groups

- Notation:
  - Condensed listing of the symmetry elements present
  - First letter indicates the absence (P) or presence (I, F, A, B, C) of unit cell centring
  - Space group symbol notation conventions depend on the crystal system
- Examples:



International Tables for Crystallography

- Key information (to be able to use):
  - Short symbol
  - Crystal system
  - Positions: multiplicity, site symmetry, coordinates
  - Reflection conditions
- Other important information (to note):
  - Space group diagrams (graphical symbol list in Intro)
- Examples: $P2_1/c$ ($^{\#}$ 14) and *Pnma* ($^{\#}$ 53)

International Tables for Crystallography

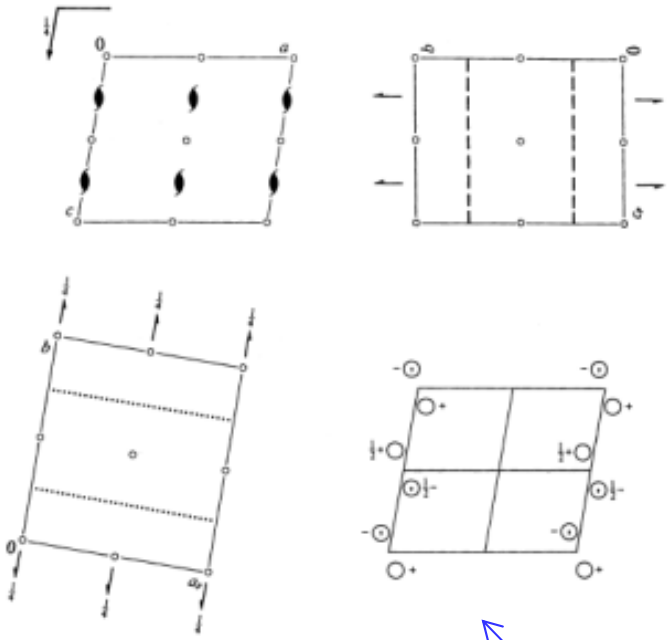
symbol

crystal system

$P2_1/c$ C_{2h}^5 $2/m$ Monoclinic

No. 14 $P12_1/c1$ Patterson symmetry $P12/m1$

UNIQUE AXIS b, CELL CHOICE 1



Origin at $\bar{1}$

Asymmetric unit $0 \le x \le 1;\quad 0 \le y \le \frac{1}{4};\quad 0 \le z \le 1$

Symmetry operations

(1) 1 (2) $2(0,\frac{1}{4},0)$ $0,y,\frac{1}{4}$ (3) $\bar{1}$ $0,0,0$ (4) c $x,\frac{1}{4},z$

space group diagrams (for illustration only!)

CONTINUED No. 14 $P2_1/c$

positions

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (3)

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates				Reflection conditions
							General:
4	e	1	(1) x,y,z	(2) $x,y+\frac{1}{2},z+\frac{1}{2}$	(3) $x,\bar{y},z$	(4) $x,\bar{y}+\frac{1}{2},z+\frac{1}{2}$	$h0l$: $l=2n$ $0k0$: $k=2n$ $00l$: $l=2n$
							Special: as above, plus
2	d	$\bar{1}$	$\frac{1}{2},0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$			hkl : $k+l=2n$
2	c	$\bar{1}$	$0,0,\frac{1}{2}$	$0,\frac{1}{2},0$			hkl : $k+l=2n$
2	b	$\bar{1}$	$\frac{1}{2},0,0$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$			hkl : $k+l=2n$
2	a	$\bar{1}$	$0,0,0$	$0,\frac{1}{2},\frac{1}{2}$			hkl : $k+l=2n$

Symmetry of special projections

Along [001] $p2gm$
$\mathbf{a}' = \mathbf{a}_p$ $\mathbf{b}' = \mathbf{b}$
Origin at $0,0,z$

Along [100] $p2gg$
$\mathbf{a}' = \mathbf{b}$ $\mathbf{b}' = \mathbf{c}_p$
Origin at $x,0,0$

Along [010] $p2$
$\mathbf{a}' = \frac{1}{2}\mathbf{c}$ $\mathbf{b}' = \mathbf{a}$
Origin at $0,y,0$

reflection conditions

Maximal non-isomorphic subgroups

I [2] $P1c1$ (Pc, 7) 1; 4
[2] $P12_11$ ($P2_1$, 4) 1; 2
[2] $P\bar{1}$ (2) 1; 3

IIa none

IIb none

Maximal isomorphic subgroups of lowest index

IIc [2] $P12_1/c1$ ($\mathbf{a}' = 2\mathbf{a}$ or $\mathbf{a}' = 2\mathbf{a}, \mathbf{c}' = 2\mathbf{a}+\mathbf{c}$) ($P2_1/c$, 14); [3] $P12_1/c1$ ($\mathbf{b}' = 3\mathbf{b}$) ($P2_1/c$, 14)

Minimal non-isomorphic supergroups

I [2] $Pnna$ (52); [2] $Pmna$ (53); [2] $Pcca$ (54); [2] $Pbam$ (55); [2] $Pccn$ (56); [2] $Pbcm$ (57); [2] $Pnnm$ (58); [2] $Pbcn$ (60); [2] $Pbca$ (61); [2] $Pnma$ (62); [2] $Cmce$ (64)

II [2] $A12/m1$ ($C2/m$, 12); [2] $C12/c1$ ($C2/c$, 15); [2] $I12/c1$ ($C2/c$, 15); [2] $P12_1/m1$ ($\mathbf{c}' = \frac{1}{2}\mathbf{c}$) ($P2_1/m$, 11); [2] $P12/c1$ ($\mathbf{b}' = \frac{1}{2}\mathbf{b}$) ($P2/c$, 13)

Asymmetric Unit

- The smallest portion of the structure which must be specified (coordinates) before space group symmetry defines the entire structure
- Crystallographically unique (independent) atoms
- Can be equal to/more/less than one molecule (in molecular solids)
- Can be equal to/more/less than the formula unit (in extended solids)

Example: Benzene

- Structure details
  - CSD refcode BENZEN
  - Orthorhombic
  - Space group *Pbca*
  - Asymmetric unit: 3 C, 3 H

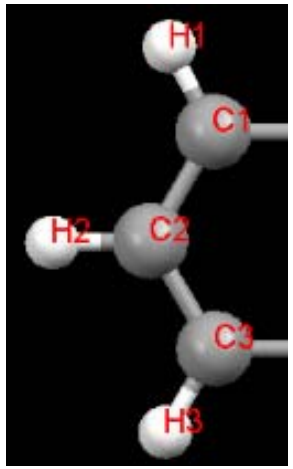
Proc. R. Soc. Lond. A 1964 **279**, 98-110

A crystallographic study of solid benzene by neutron diffraction

By G. E. Bacon*, N. A. Curry and S. A. Wilson
Atomic Energy Research Establishment, Harwell

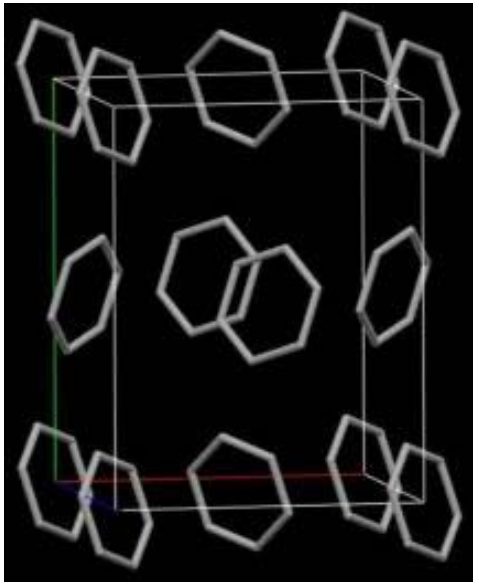
(*Communicated by R. Spence, F.R.S.—Received* 17 *September* 1963—*Read* 6 *February* 1964)

A study by neutron diffraction of crystals of solid benzene at −55 and −135 °C has extended the earlier picture of the molecular structure provided by Cox's X-ray work at −3 °C. Neutron reflexions in four crystal zones have been examined, leading to values of the atomic co-ordinates and thermal parameters. Superimposed upon the random motion of the carbon



Pbca

symmetry



Diffraction by Crystalline Solids

- Crystalline materials = long-range 3D periodic atomic arrays
  - Interatomic distances ~ 0.5 – 2.5 Å

- Waves of comparable wavelengths will be diffracted
  - X-rays = EM radiation, λ ~ 0.1 – 100 Å
  - Neutrons
  - Electrons

  } $\lambda = h / mv$

⇓

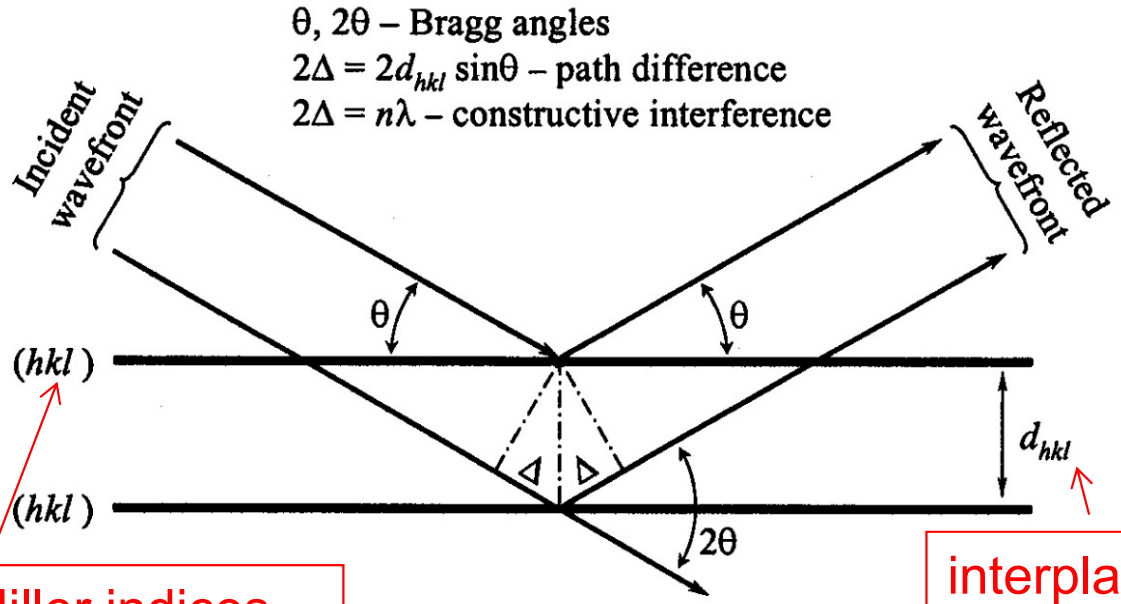
- X-rays, neutrons and electrons are diffracted by crystals

⇓

- X-ray, neutron and electron diffraction patterns contain information about 3D arrangement of atoms in crystals

Bragg's Law

- Simplistic, but useful view of diffraction
  - Atoms arranged in parallel planes in a crystal
  - Incident X-rays reflected off the planes
  - Peaks in diffraction patterns referred to as "reflections"



$2\Delta = n\lambda$

(n=order of diffraction*)

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

Miller indices

interplanar spacing, d-spacing

*n=1, because n^{th} order diffraction from (hkl) planes with spacing d can be treated as 1^{st} order diffraction from (nh, nk, nl) planes with spacing d/n

Structure Factor

- Peak intensities, I_{hkl}: $I_{hkl} \propto |F_{hkl}|^2$
  - $|F_{hkl}|$ ~ the collective scattering power of the atoms in the unit cell
  - Other factors: absorption, thermal vibrations, site occupancies, …

- Structure factor, F_{hkl}

$$F_{hkl} = \sum_{1}^{N} f_n e^{2\pi i(hx_n + ky_n + lz_n)}$$

Electronic property of the atom
Information about atom types

Structural property of the unit cell
Information about atomic positions

*x_n, y_n *and* z_n are atomic fractional coordinates: $x_n = x/a$, $y_n = y/b$, $z_n = z/c$