Survey of Materials. Lecture 2

Atomistic structure

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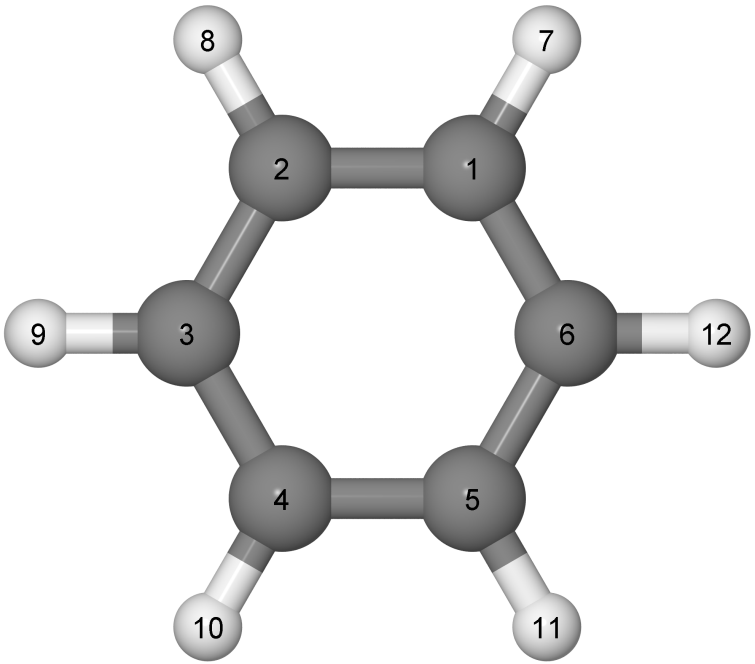
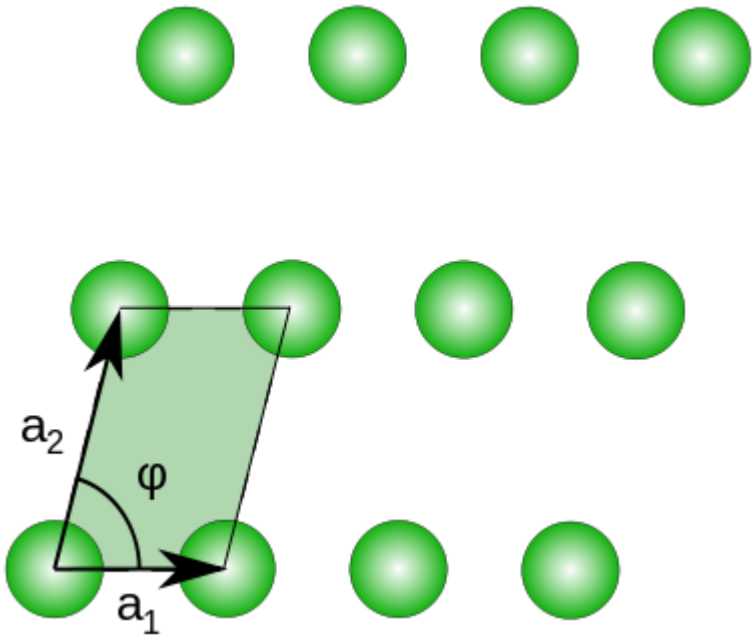
Outline

- 2D crystallography
- 3D crystallography
- Structure characterization (CIF, coordination, voids, APF)

2D crystallography

Space group = point group + translation symmetry

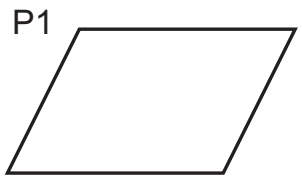


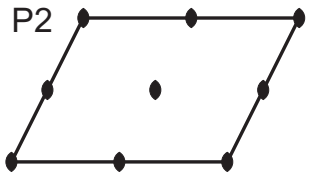


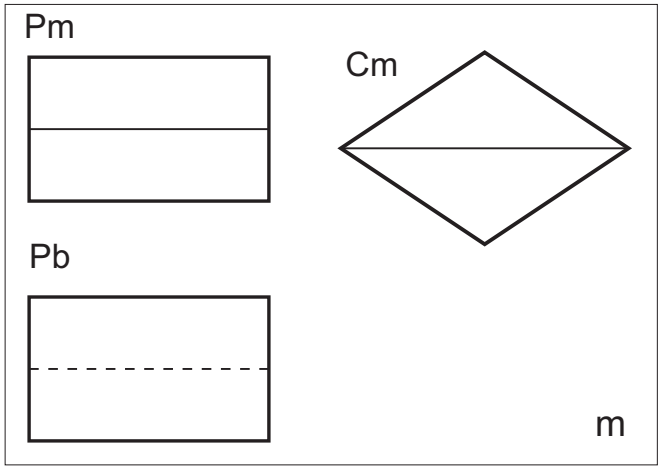
- Determine all 2D point groups
- Determine all 2D Bravais lattices

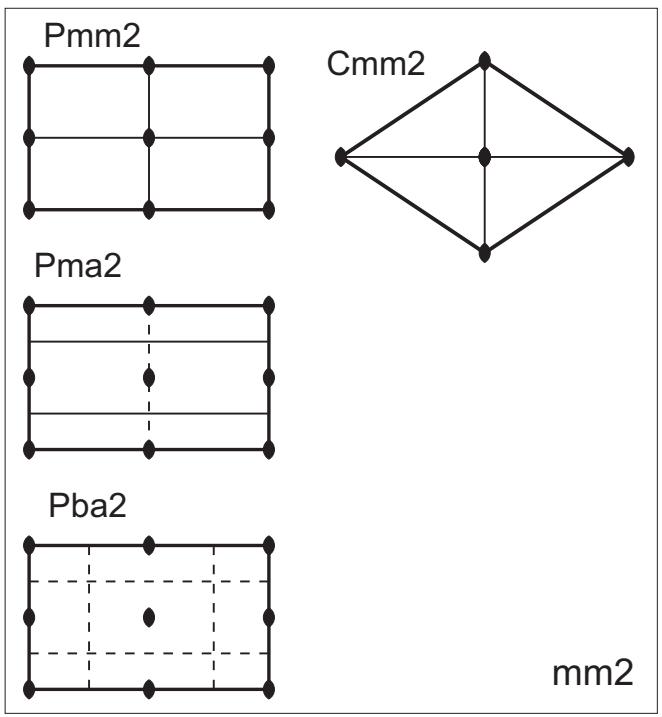
2D crystallography

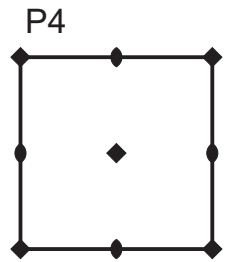
2D space groups (17), point groups, Bravais lattices, and crystal systems (4)

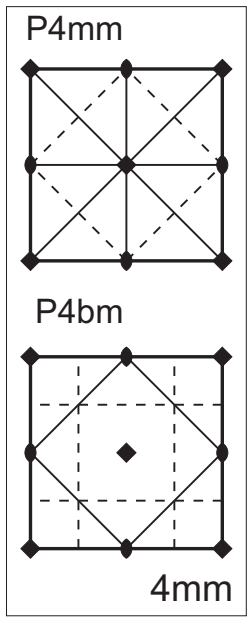


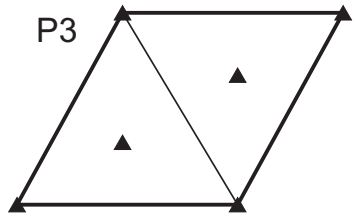


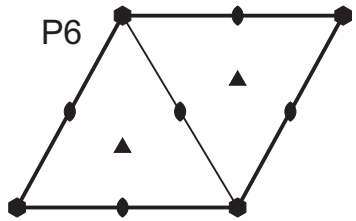


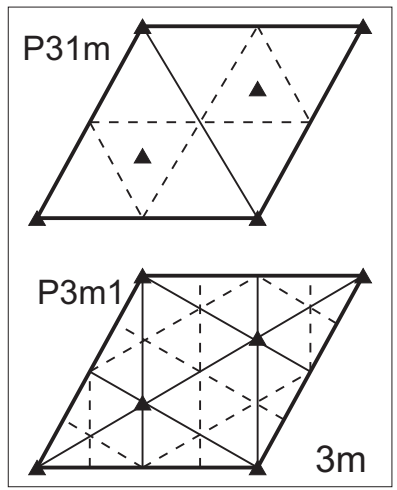


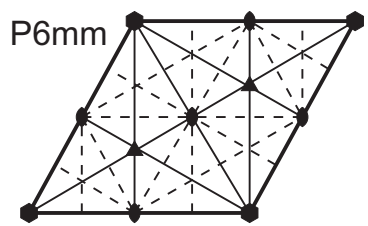












Bravais lattices:

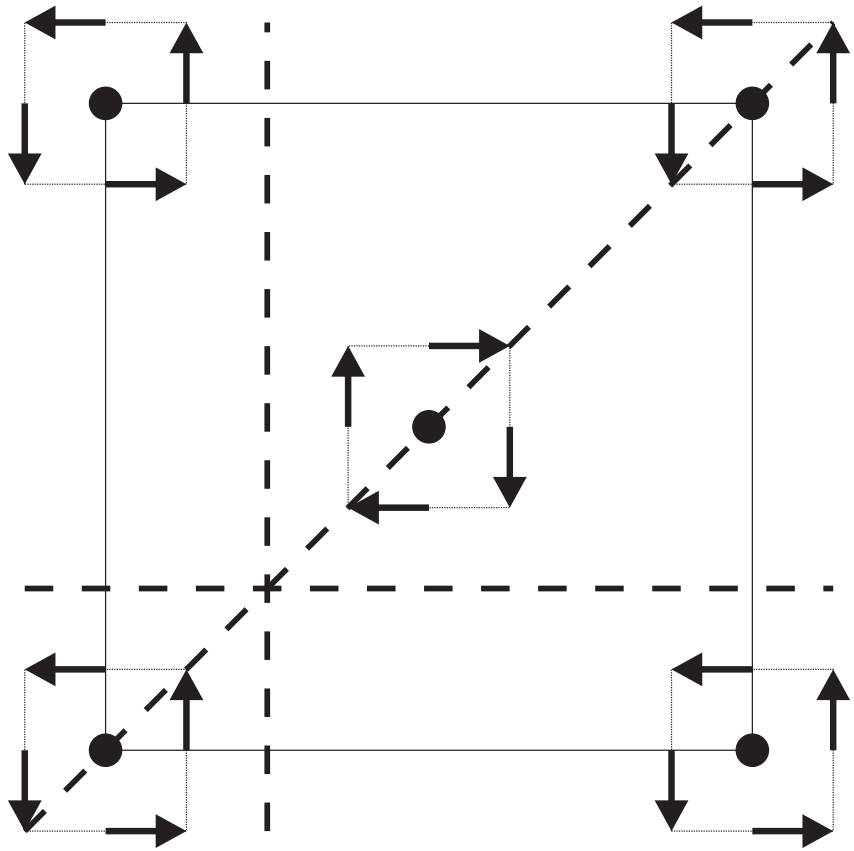
P2	oblique
Pmm2	rectangular
Cmm2	rhombic
P4mm	square
P6mm	hexagonal

Point groups:

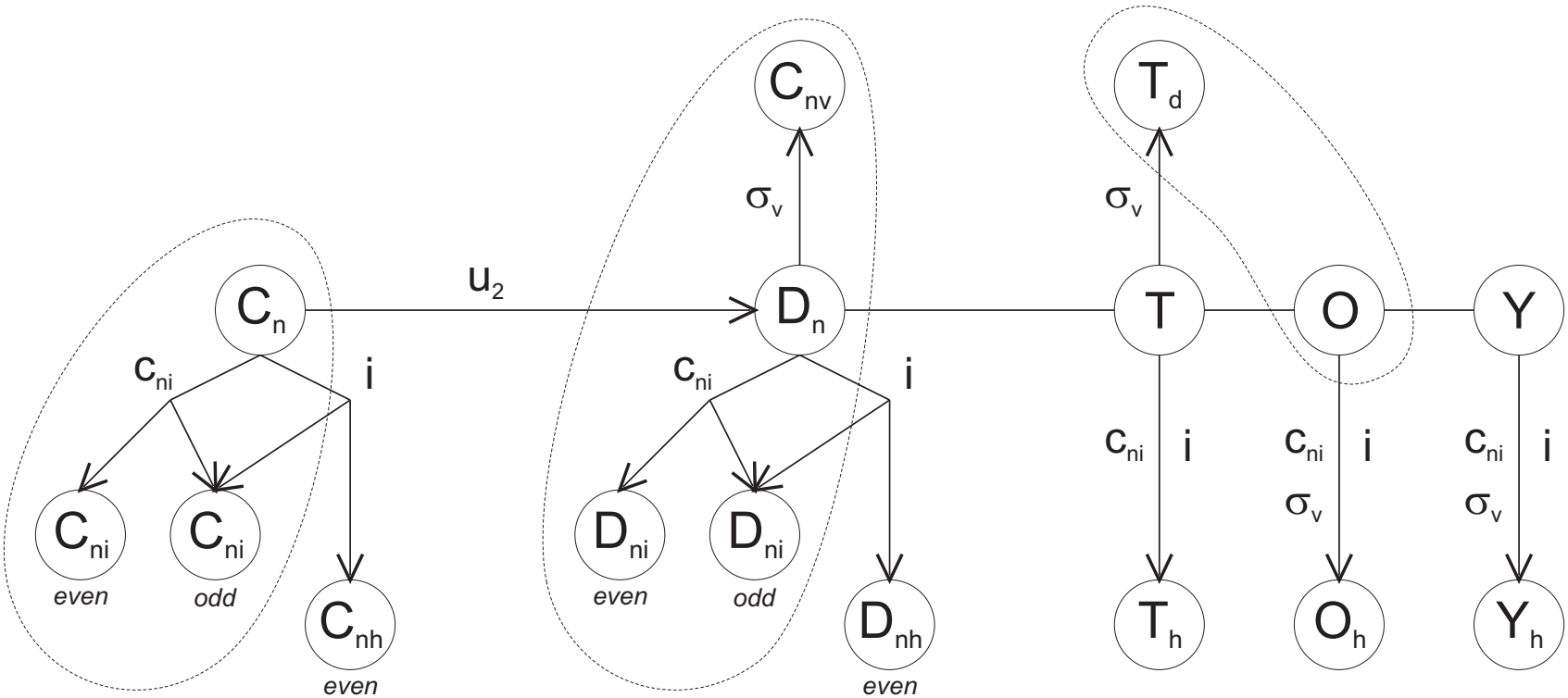
1-6	$C_{1\text{-}6}$
m	D_1
mm2	D_2
3m	D_3
4mm	D_4
6mm	D_6

Symmetries:

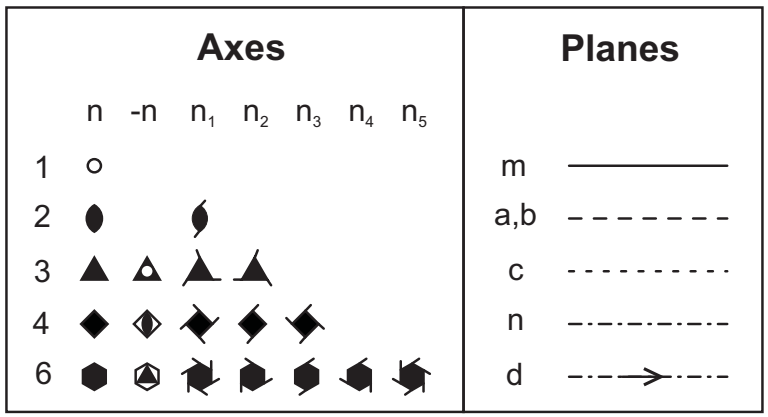
2D glide plane

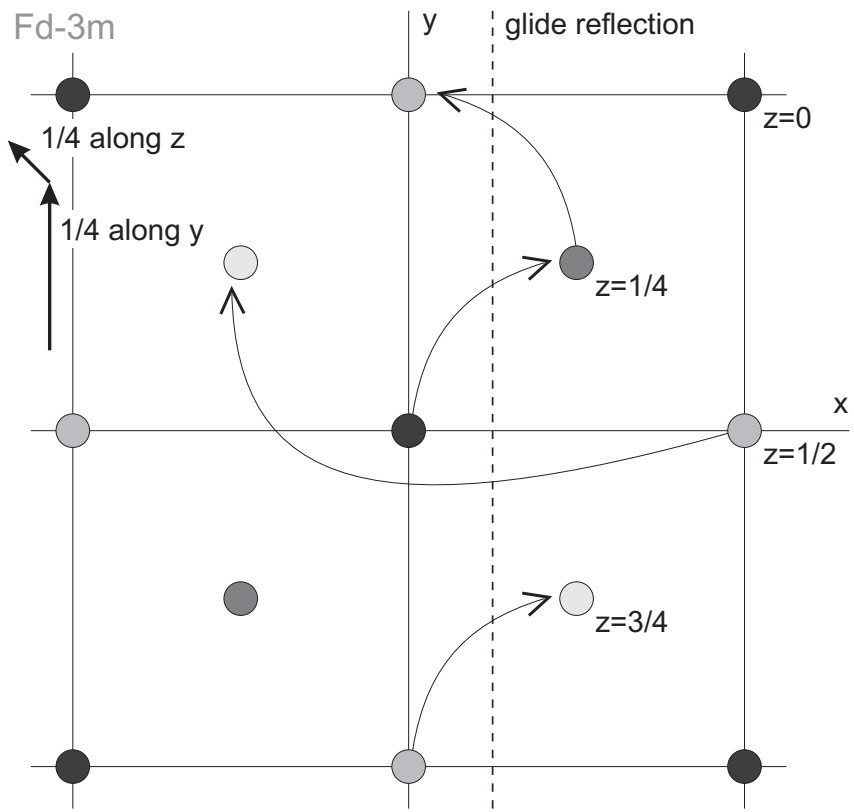


3D point groups



3D symmetry elements





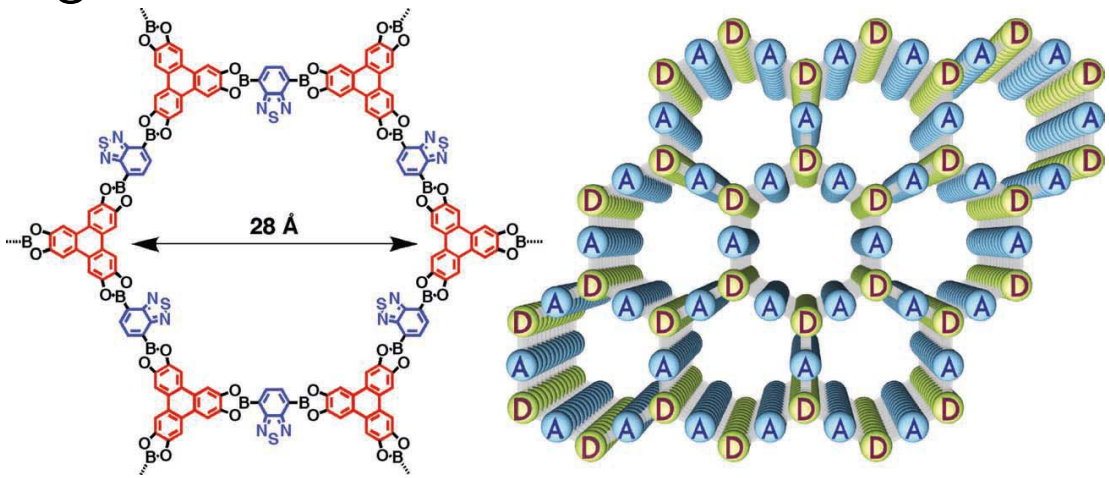
Group Fd-3m, $G_{124} = \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1/4 \\ 0 & 0 & 1 & 1/4 \end{pmatrix} = d(0, 1/4, 1/4)\ 0, y, z$

3D crystallography

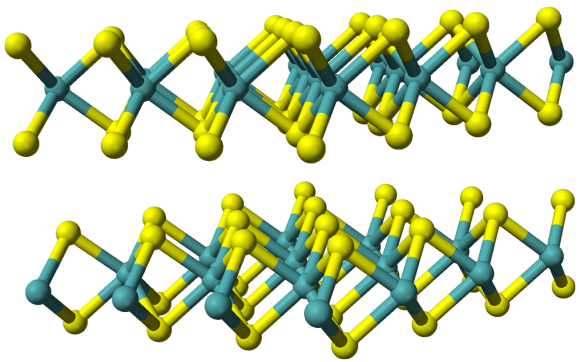
Lecture of Artem Abakumov or any textbook

2D materials in 3D space – layer groups

- graphene, BN
- organic networks

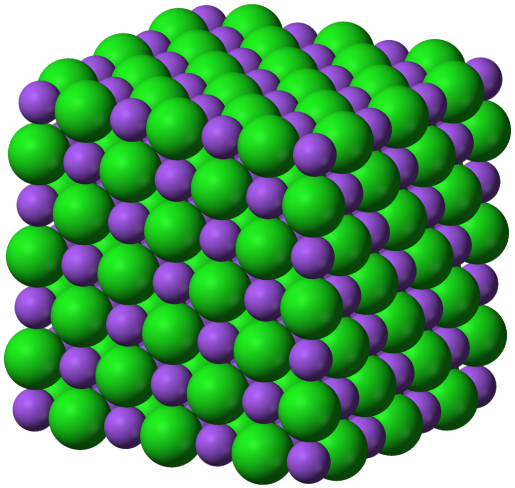


- MoS_2

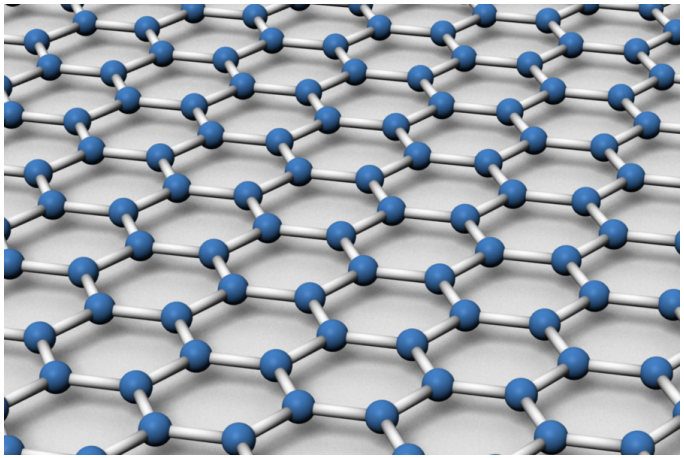


- P, As

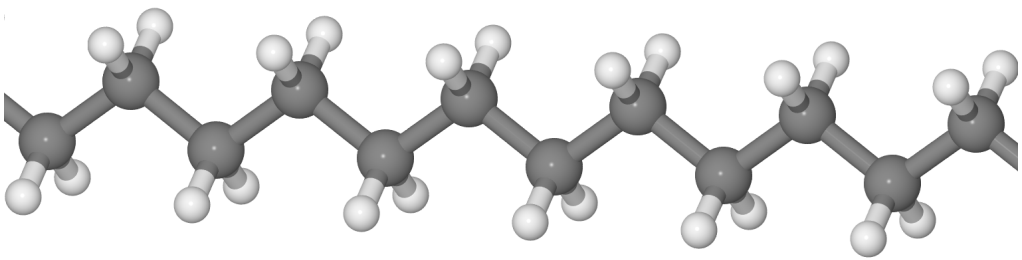
All groups in 3D space



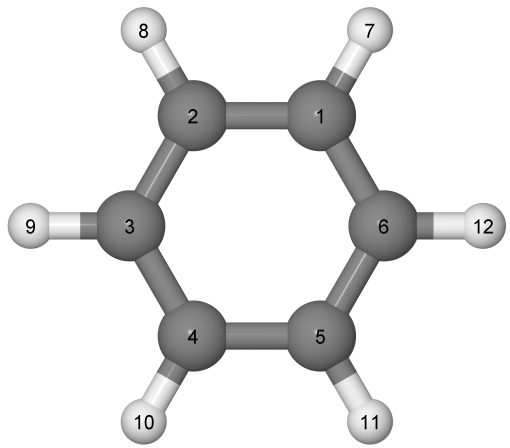
space groups



layer groups



rod groups



point groups

Subperiodic groups

Table 1.2.1.1. *Classification of layer groups*

Bold or bold underlined symbols indicate Laue groups. Bold underlined point groups are also lattice point symmetries (holohedries).

Two-dimensional Bravais system	Symbol	Three-dimensional crystal system	Crystallographic point groups	No. of layer-group types	Restrictions on conventional coordinate system	Cell parameters to be determined	Bravais lattice
Oblique	*m*	Triclinic	1, $\bar{\mathbf{1}}$	2	None	*a*, *b*, γ†	*mp*
		Monoclinic	2, *m*, **2/*m***	5	$\alpha = \beta = 90°$		
Rectangular	*o*			11	$\beta = \gamma = 90°$	*a*, *b*	*op*
		Orthorhombic	222, 2*mm*, ***mmm***	30	$\alpha = \beta = \gamma = 90°$		*oc*
Square	*t*	Tetragonal	4, $\bar{4}$, **4/*m***	16	$a = b$	*a*	*tp*
			422, 4*mm*, $\bar{4}$2*m*, **4/*mmm***		$\alpha = \beta = \gamma = 90°$		
Hexagonal	*h*	Trigonal	3, $\bar{\mathbf{3}}$	8	$a = b$	*a*	*hp*
			32, 3*m*, $\bar{\mathbf{3}}$***m***				
		Hexagonal	6, $\bar{6}$, **6/*m***	8	$\gamma = 120°$		
			622, 6*mm*, $\bar{6}$*m*2, **6/*mmm***		$\alpha = \beta = 90°$		

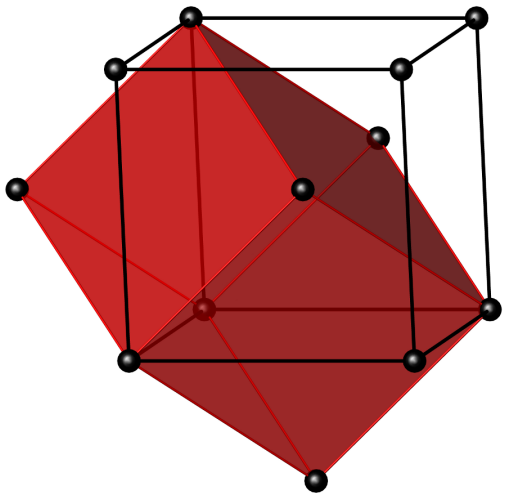
† This angle is conventionally taken to be non-acute, *i.e.* $\geq 90°$.

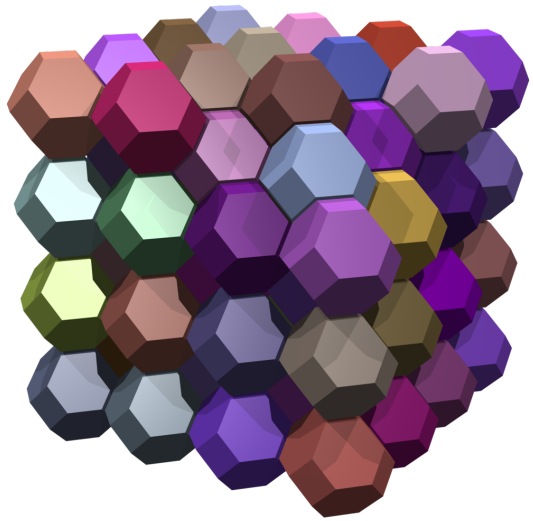
Table 1.2.1.2. *Classification of rod groups*

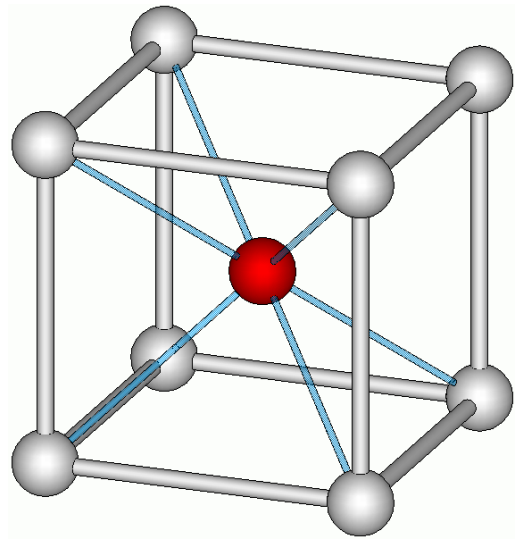
Bold symbols indicate Laue groups.

Three-dimensional crystal system	Crystallographic point groups	No. of rod-group types	Restrictions on conventional coordinate system
Triclinic	1, $\bar{\mathbf{1}}$	2	None
Monoclinic (inclined)	2, *m*, **2/*m***	5	$\beta = \gamma = 90°$
Monoclinic (orthogonal)		5	$\alpha = \beta = 90°$
Orthorhombic	222, 2*mm*, ***mmm***	10	$\alpha = \beta = \gamma = 90°$
Tetragonal	4, $\bar{4}$, **4/*m***	19	
	422, 4*mm*, $\bar{4}$2*m*, **4/*mmm***		
Trigonal	3, $\bar{\mathbf{3}}$	11	$\alpha = \beta = 90$, $\gamma = 120°$
	32, 3*m*, $\bar{\mathbf{3}}$***m***		

Unit cell







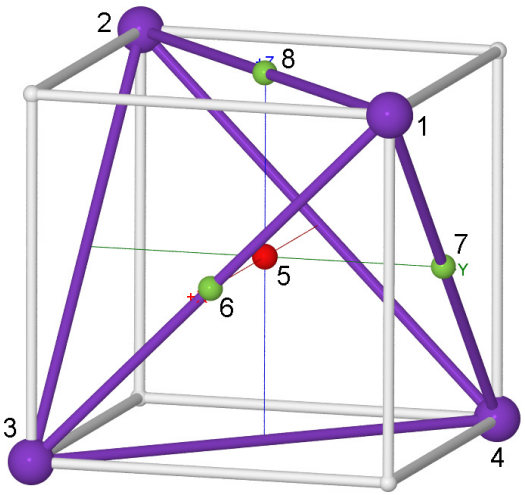
	min.size	parallelepiped	symmetric
primitive	+	+	−
Wigner–Seitz	+	−	+
Bravais	−	+	+

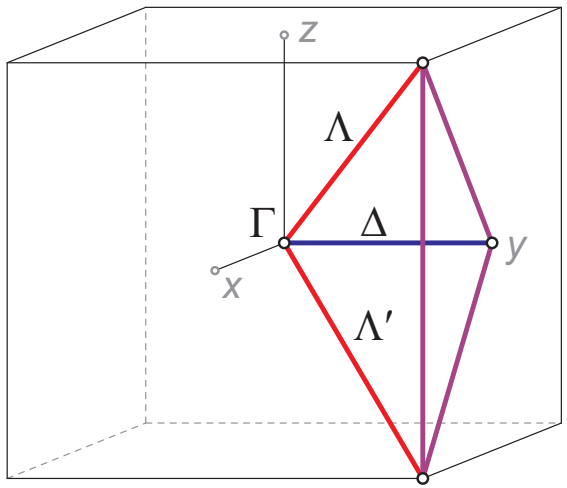
Generators, fundamental domain, asymmetric unit

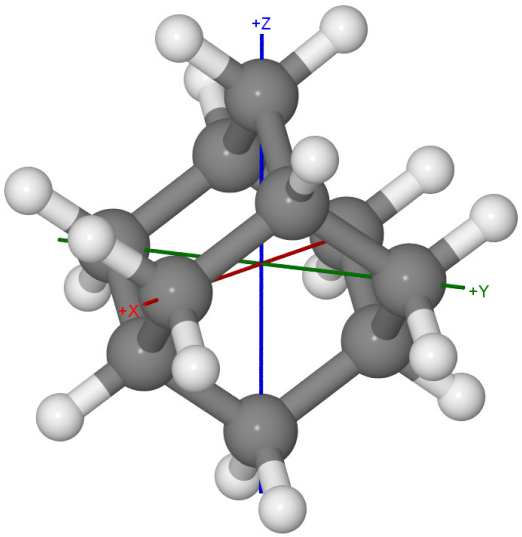
also orbits (Wyckoff positions), stabilizators, independent geometrical parameters etc.

-43m $\equiv T_d = \{1, 8c_3, 3c_2, 6c_{4i}, 6\sigma_v\} \sim O$

Generators: $c_3(1)$ and $\sigma_v(34)$, e.g. $c_3(1)\sigma_v(34) = c_{4i}^{-1}(7)$, $c_{4i}^2 = c_2$







	orbit	WP	stab.	atoms
000	Γ	1a	-43m	
xxx	Λ	4e	3m	CH
x00	Δ	6f	2mm	C
xxz	ΛΔ	12i	m	H
xyz		24j	1	

Fundamental domain is $\Lambda\Delta\Lambda'$-pyramid ($V = 1/24$)

See XYZ and CIF of adamantane

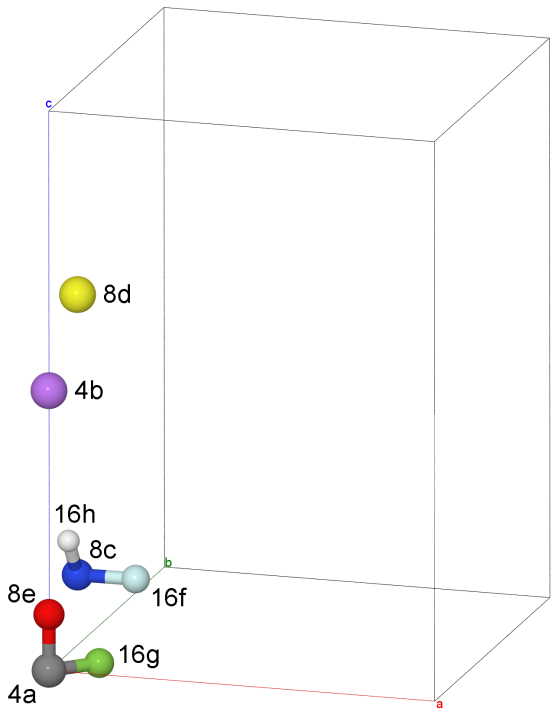
Asymmetric unit is HCCH

Geometrical parameters are CC, 2×CH, CCC, HCH or $x(C_1), x(H_1), x(C_2), x(H_2), z(H_2)$

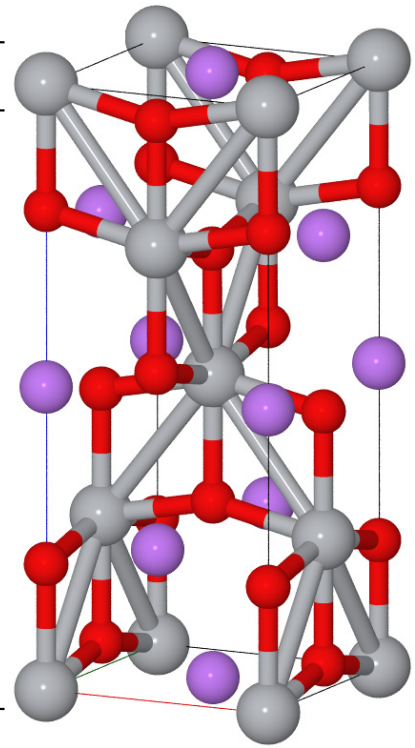
The same for crystal

I41/amd:1 $\equiv D_{4h}^{19}$ (see CIF file for Wyckoff positions)

Generators: -4_{001}, 2_{110}, $\left(\frac{1}{2}\frac{1}{2}\frac{1}{2}\right)$, $\left\{-1\,\middle|\,0\frac{1}{2}\frac{1}{4}\right\}$, (100), (010), (001)



	WP	stab.	atom
000	4a	-4m2	Ti
$00\frac{1}{2}$	4b	-4m2	Li
$0\frac{1}{4}\frac{1}{8}$	8c	.2/m.	
$0\frac{1}{4}\frac{5}{8}$	8d	.2/m.	
$00z$	8e	2mm.	O
$x\frac{1}{4}\frac{1}{8}$	16f	.2.	
$xx0$	16g	..2	
$0yz$	16h	.m.	
xyz	32i	1	



Fundamental domain is the box $(1/2, 1/2, 1/8)$ with $V = 1/32$

See CIF file for $LiTiO_2$. Asymmetric unit is TiOLi

Geometrical parameters are a, c, ζ or $2\times$TiO and OTiO

Classification of space groups

Let consider group Fd-3m, element

$$G_{124} = \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1/4 \\ 0 & 0 & 1 & 1/4 \end{pmatrix} + \text{translations}^1$$

- (geometric) crystal class – $\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$, no translations
- Bravais lattice class – only translations
- arithmetic crystal class – $\begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ + translations

[1] Centering is included in translations

Lattice system vs crystal system, crystal family

(lattice and crystal class classifications are mutually inconsistent)

space groups			lattice system	crystal family	crystal system
P1	...	P-1	anorthic*	a	anorthic
P2	...	C2/c	monoclinic	m	monoclinic
P222	...	Imma	orthorhombic	o	orthorhombic
P4	...	$I4_1/acd$	tetragonal	t	tetragonal
R3	...	R-3c	rhombohedral	**h**	trigonal
P3	...	P-3c1	**hexagonal**	**h**	**trigonal**
P6	...	$P6_3/mmc$	hexagonal	**h**	hexagonal
P23	...	Ia-3d	cubic	c	cubic

* anorthic is also called triclinic

Classification of space groups: example

structural type	A4 (dia)	A3 (hcp)	A7 (α-As)
space group	Fd-3m	P63/mmc	R-3m
arithmetic crystal class	Fm-3m	P6/mmm	R-3m
Bravais lattice	cF	hP	hR
lattice centering	F	P	R
crystal class	m-3m	6/mmm	-3m
crystal family	c	h	h*

* Lattice system is rhombohedral, crystal system is trigonal

Settings

Take diamond lattice and compare its symmetry in two settings

- Fd-3m:1 – origin is at the carbon atom
- Fd-3m:2 (ITA[1] default) – origin is at the inversion point, carbon is at $(1/8, 1/8, 1/8)$

Other examples:

- R-3m:r vs R-3m:h≡R-3m
- C2/c≡C12/c1 vs C2/c11
- Pnma vs Pmnb vs Pbnm vs Pcmn vs ...

[1] International Tables for Crystallography

Bilbao Crystallographic Server

http://www.cryst.ehu.es

- Generators and elements of space and subperiodic groups
- Wyckoff positions
- Identification of a space group from a set of generators
- The k-vector types and Brillouin zones
- Space groups representations
- Subgroups and supergroups
- Many more tools

CIF – Crystallographic Information File

Part 1: preamble and publication data, see template

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# CIF template
data_nolabel
loop_
_publ_author_name
'B L Ellis'
'T N Ramesh'
'L J M Davis'
'G R Goward'
'L F Nazar'
_publ_section_title
;
 Structure and Electrochemistry of Two-Electron Redox Couples
 in Lithium Metal Fluorophosphates Based on the Tavorite Structure
;
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_journal_volume                    23
_journal_page_first                5138
_journal_year                      2011
_journal_paper_doi                 10.1021/cm201773n
```

CIF – Crystallographic Information File

Part 2: chemical formula and name, unit cell, symmetry, experimental conditions

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_cell_length_b                       7.49936(2)
_cell_length_c                       5.16888(1)
_cell_angle_alpha                    112.933
_cell_angle_beta                     81.664
_cell_angle_gamma                    113.125
_cell_formula_units_Z                2      # useful but optional
_symmetry_space_group_name_H-M       'P-1'
_space_group_IT_number               2      # optional
_diffrn_ambient_temperature          300    # K
_diffrn_ambient_pressure             100    # kPa
loop_
_symmetry_equiv_pos_as_xyz    # needed only for nonstandard settings
x,y,z
-x,-y,-z
```

CIF – Crystallographic Information File

Part 3: atomic positions

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loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_Wyckoff_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
_atom_site_B_iso_or_equiv
_atom_site_description
Li1   Li   2i   .389(2)   .334(1)   .659(2)   .18   2.2   01
Li2   Li   2i   .373(2)   .236(1)   .517(2)   .82   2.2   02
V1    V    1a    0         0         0        1     1.2   03
V2    V    1b    0        .5        .5        1     1.2   04
P1    P    2i   .3524(2)  .7485(2)  .0719(2)  1     1.2   05
O1    O    2i   .2109(4)  .9064(3)  .1701(4)  1     1.2   06
O2    O    2i   .6580(4)  .8625(3)  .1705(4)  1     1.2   07
O3    O    2i   .2373(4)  .5900(3)  .2163(4)  1     1.2   08
O4    O    2i   .3305(4)  .6403(3)  .7497(4)  1     1.2   09
F1    F    2i   .0875(3)  .2450(2)  .3585(4)  1     1.2   10
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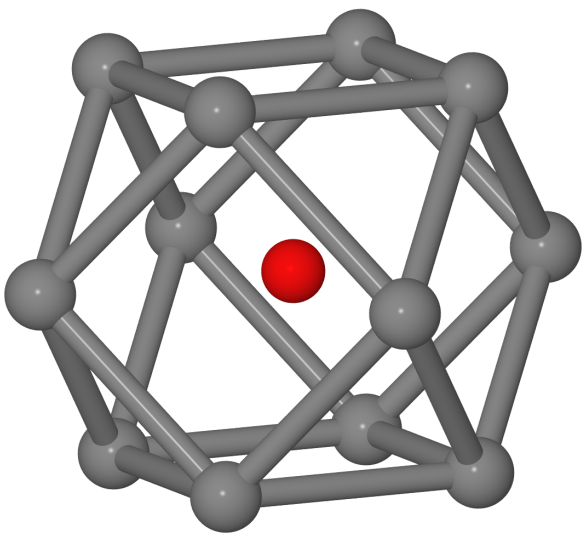
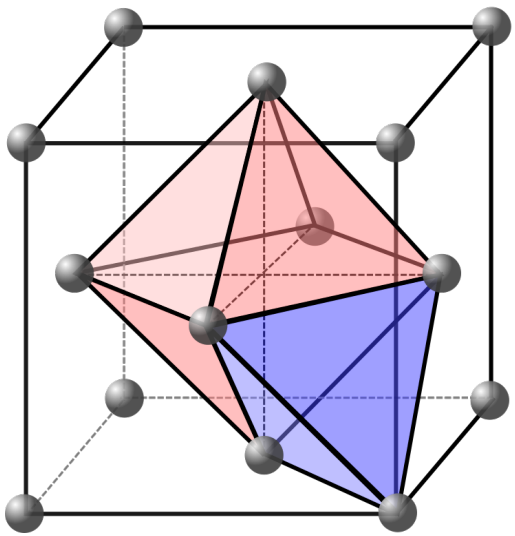
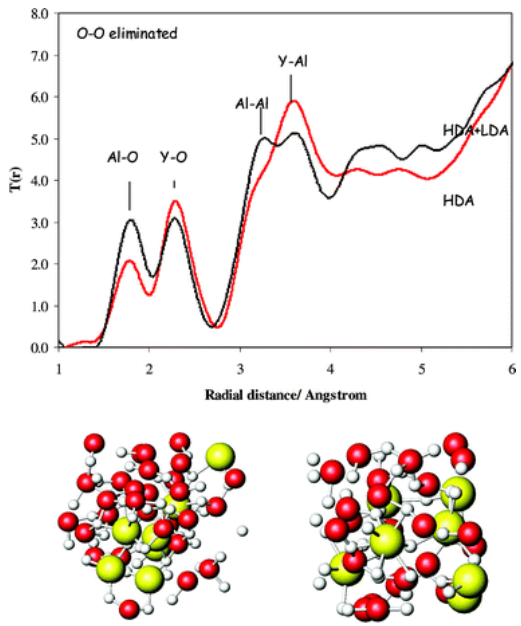
Coordination polyhedron/number and voids

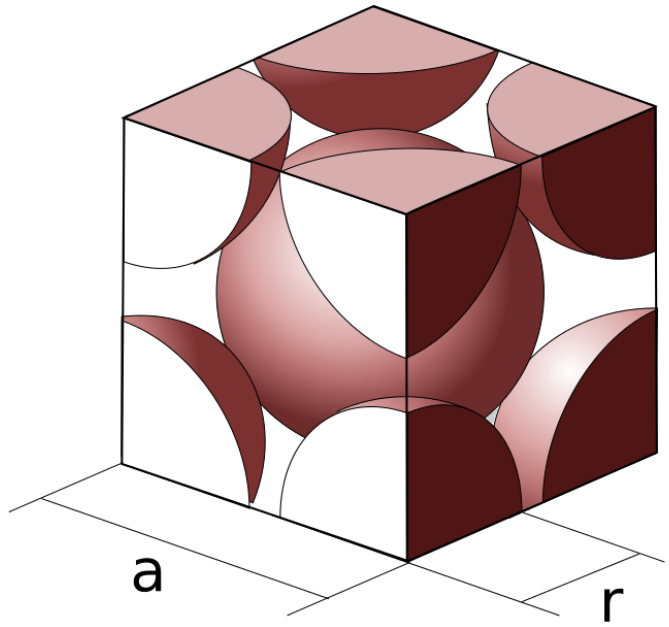






See here

Atomic packing factor

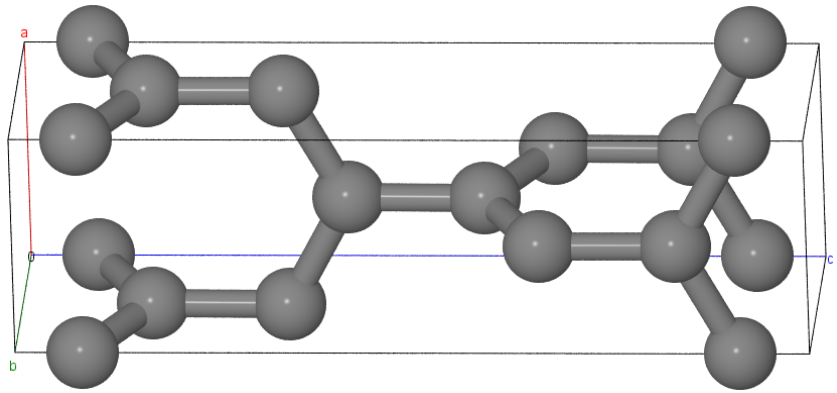


Atomic packing factor = "occupied volume" / "unit cell volume"

Relative packing factor $\delta = V_1^{\max}/V_1 = \frac{d_1^3}{\sqrt{2}V_1}$, where V_1 is volume per atom and d_1 is minimal distance between atoms (sometimes average distance to the nearest neighbors might be more relevant)

Relative packing factor: example

BCT-4 carbon, see CIF file



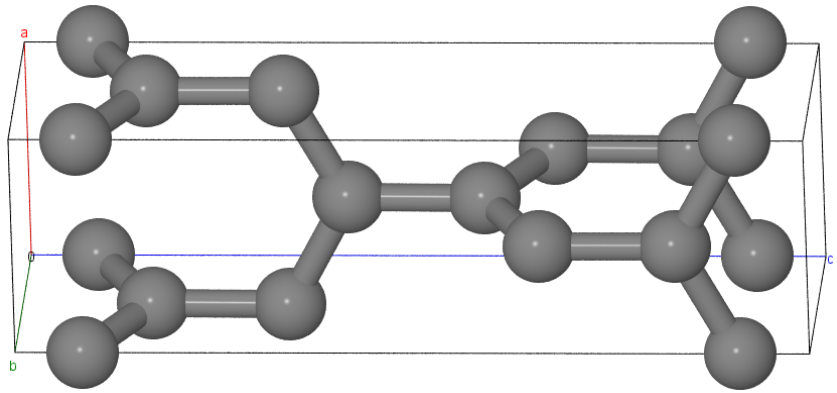
Space group I41/amd:1, carbon atoms occupy site (8e). Let's take the 1st atom at position $(0, 0, \zeta)$. Then it's two symmetry unique neighbors have coordinates $(0, 0, -\zeta)$ and $(0, 1/2, 1/4 - \zeta)$. Thus the relative packing factor

$$\delta = \frac{\min\left(4q\zeta, \sqrt{1 + q^2(1/2 - 4\zeta)^2}\right)^3}{\sqrt{2}q}, \text{ where } q = c/a.$$

Using data [Phys Rev B 78, 125415 (2008)], we get $\delta = 0.301$.

Relative packing factor: example continuation

BCT-4 carbon – trying to guess structure, see CIF file



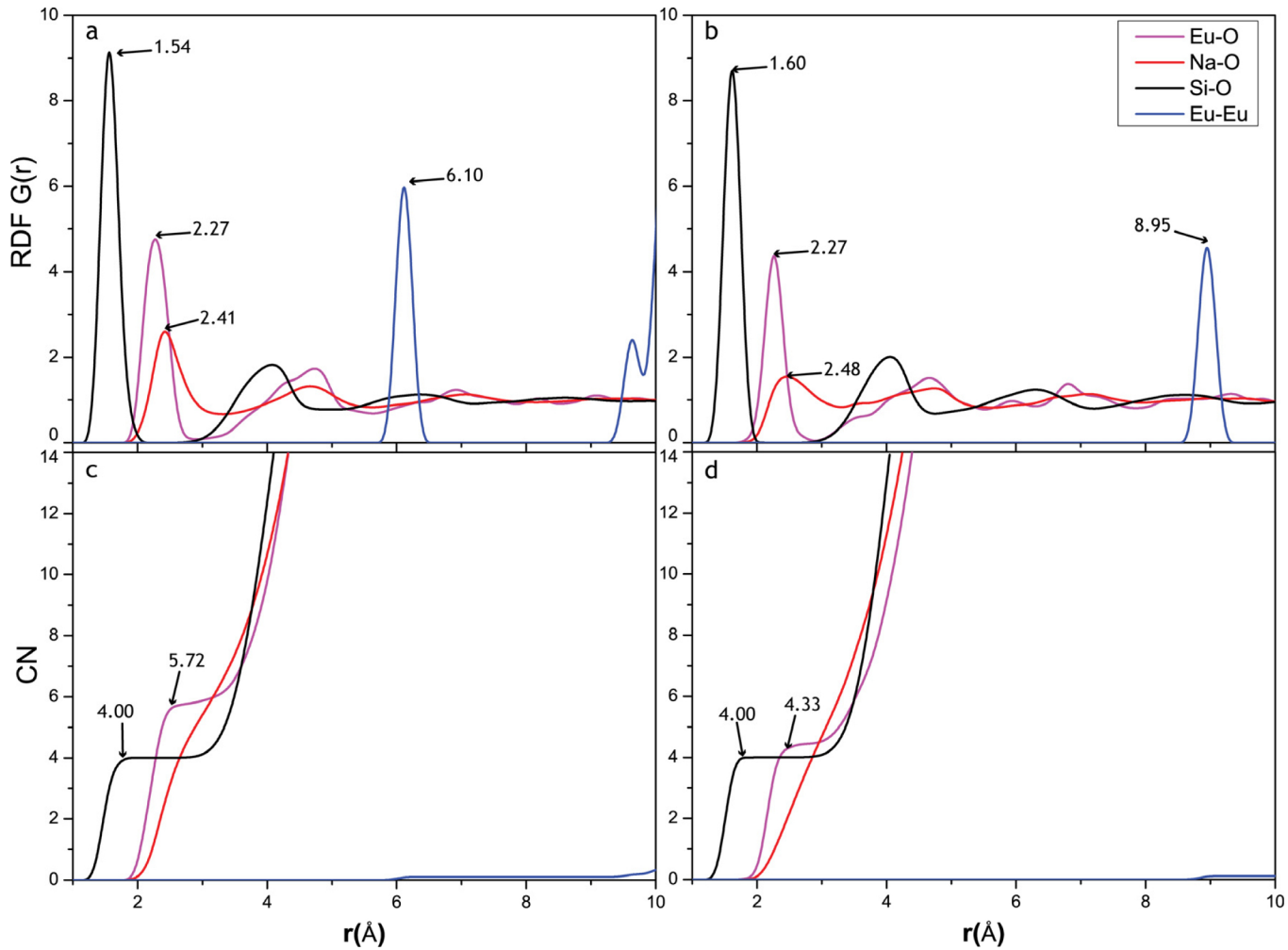
The independent geometrical parameters are either (a, c, ζ) or (d_1, d_2, α_{22}), where d_1 and d_2 are the distances to $(0, 0, -\zeta)$ and $(0, 1/2, 1/4 - \zeta)$ neighbors and α_{22} is the angle between d_2 bonds. The two sets are related by

$$a = 2d_2 \sin\frac{\alpha_{22}}{2}, \quad c = 4\left(d_1 + d_2 \cos\frac{\alpha_{22}}{2}\right), \quad \zeta = \frac{d_1}{2c}$$

The d_2 bond is in planar configuration, so we can take graphene's value, $d_2 = 1.42$ Å, $\alpha_{22} = 120°$. The d_1 bond resembles twisted ethylene, where bond is elongated by 0.05 Å, so $d_1 = 1.47$ Å. With these data we get $\delta = 0.307$, close to the above value 0.301.

Structure factor and radial distribution function

$$S(\boldsymbol{q}) = \frac{1}{N}\left|\sum_i \mathrm{e}^{-\mathrm{i}\boldsymbol{q}\boldsymbol{r}_i}\right| \equiv 1+\rho\int_V \mathrm{e}^{-\mathrm{i}\boldsymbol{q}\boldsymbol{r}} g(\boldsymbol{r})\,\mathrm{d}V,\ g(\boldsymbol{r}) = \sum_{i\neq 0}\delta\left(\boldsymbol{r}-\boldsymbol{r}_i\right)$$



Summary and Resources

See summary here

- Wikipedia
- Bilbao Crystallographic Server
- Crystal structures
- References: crystallography, symmetry
- Textbooks (sections General, Crystallography, Symmetry)

Visualization software:

- Jmol
- Mercury
- VESTA
- Surface explorer (online tool)