



Mineralogija

Sveučilišni prijediplomski studij Znanosti o okolišu – 1. godina (253566)

Doc. dr. sc. Petra Schneider

akad. god.: 2024./25.

Sadržaj

- Simetrija molekula
- Kristalna struktura
- Elementi simetrije fine strukture
- Jedinične ćelije
- Bravaisove rešetke
- Prostorne grupe
- *International tables for crystallography*



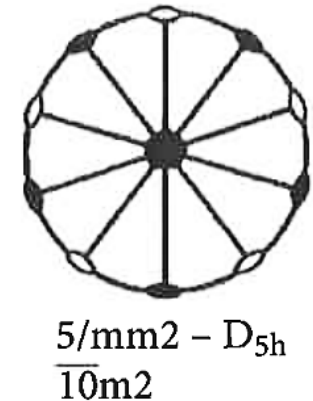
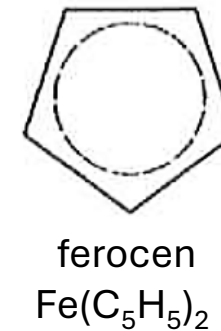
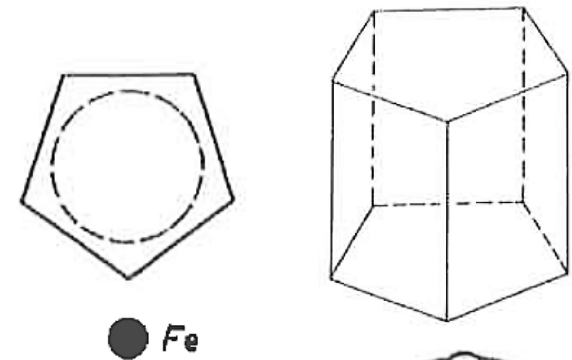
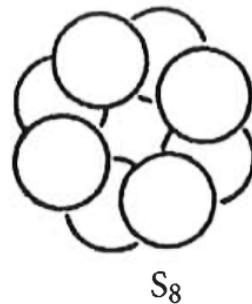
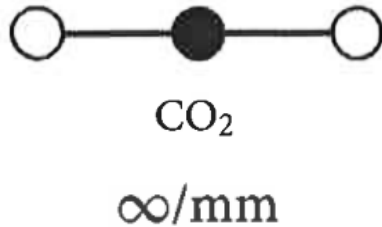
Simetrija molekula

Osim simetrije kristalnih poliedara može se proučavati i **simetrija molekula**.

! Simetrija molekula nije ograničena na simetriju 32 točkine grupe → **nekristalografske točkine grupe**

→ mogući su i elementi simetrije koji nisu u skladu s trodimenzionalnim periodičnim rasporedom materije

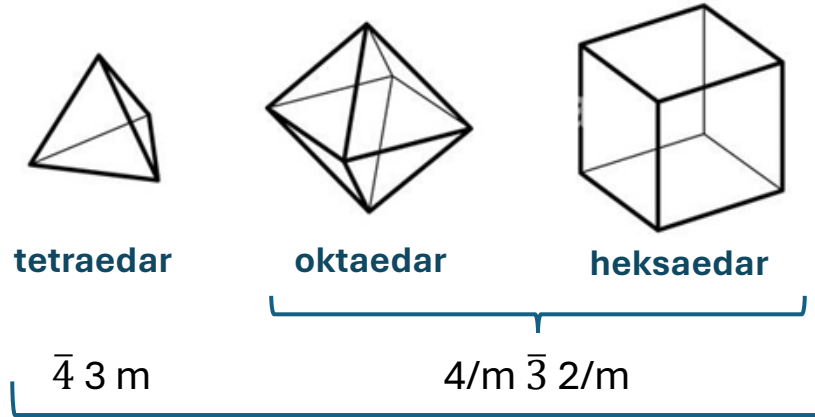
→ osi simetrije (gire) 5.-, 7.-, 8.- ∞ -reda



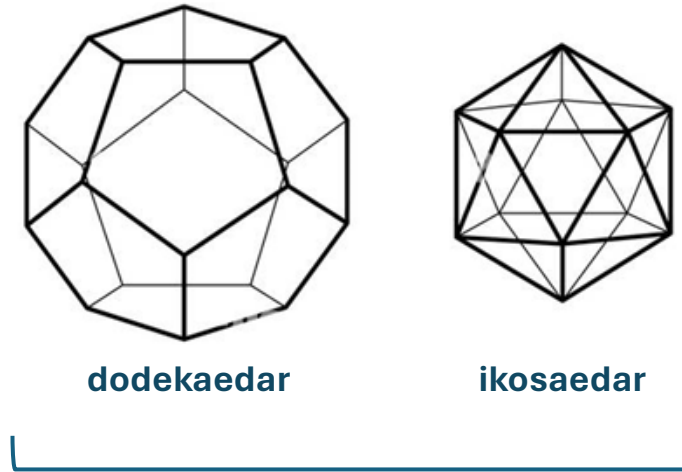
! Prizme i (di)piramide reda većeg od 6 nisu kristalne forme, tj. ne mogu činiti prirodne granice ploha na kristalima.

Simetrija molekula

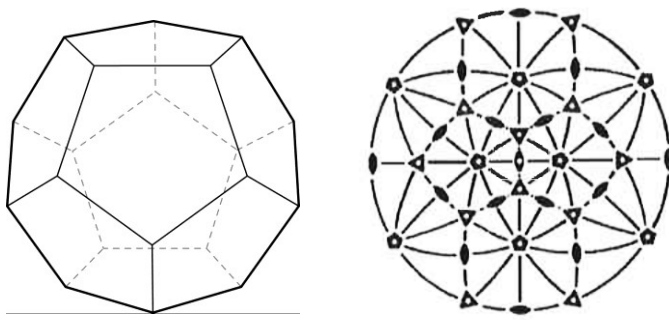
Platonova tijela (pravilni poliedri)



simetrija: kristalografska

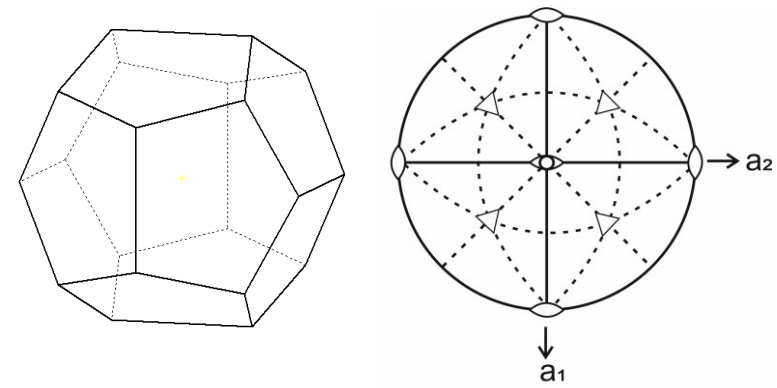


simetrija: nekristalografska
točkina grupa: $2/m \bar{3} 5$



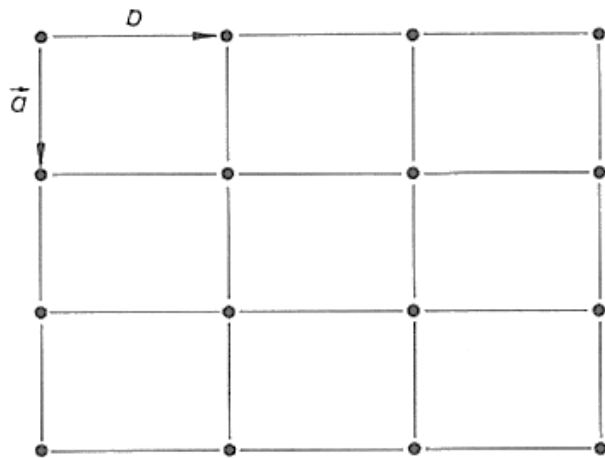
platonov (pravilni, nekristalografski)
pentagonski dodekaedar

vs.

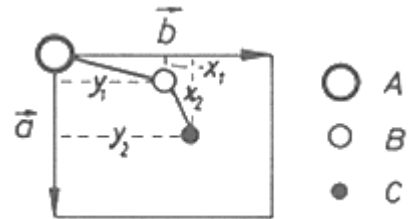


kristalografski kubični
pentagonski dodekaedar

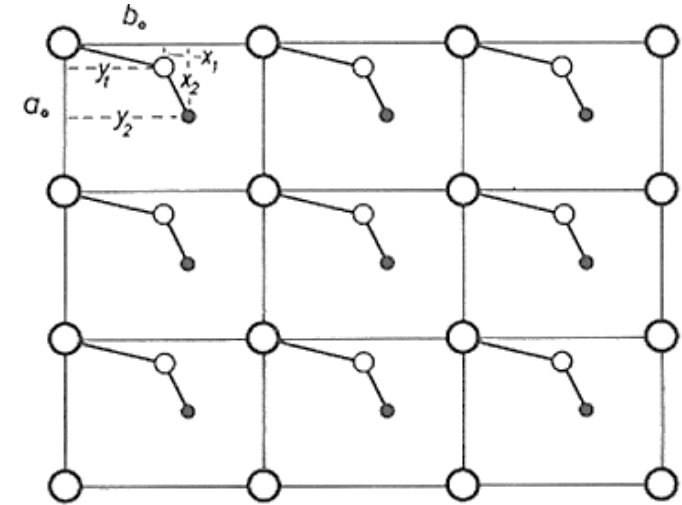
Kristalna struktura



ćelija



sadržaj
(čvor = motiv)



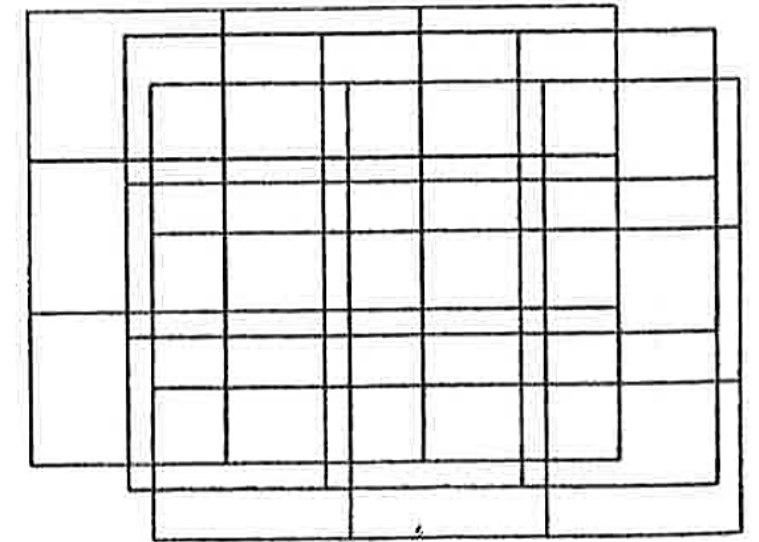
struktura

Definiranje kristalne strukture nekog materijala:

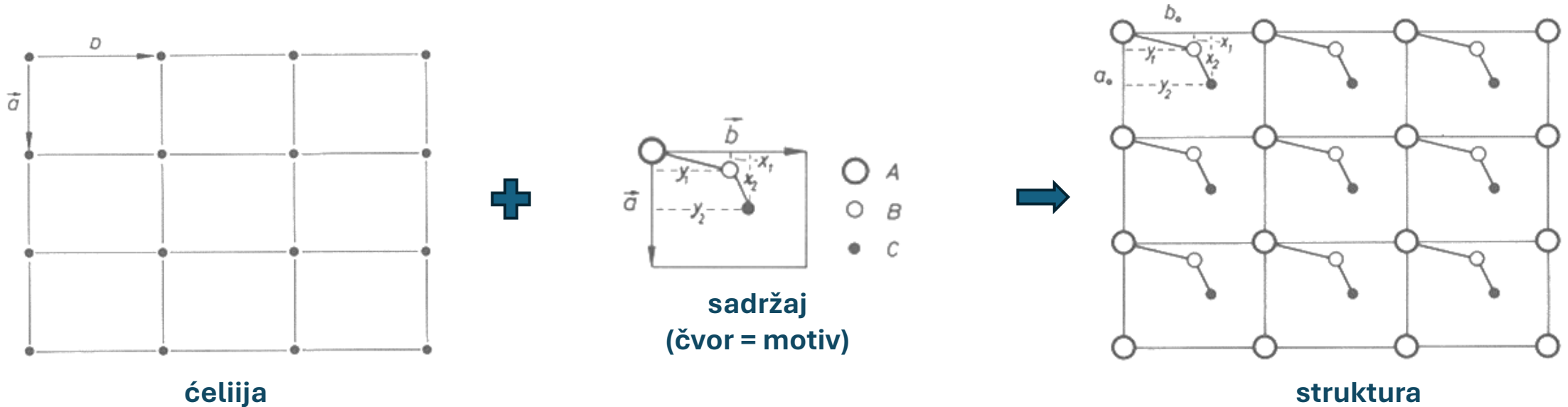
(a) **dimenzije** jedinične ćelije

&

(b) **sadržaj** jedinične ćelije (vrsta i položaj atoma)



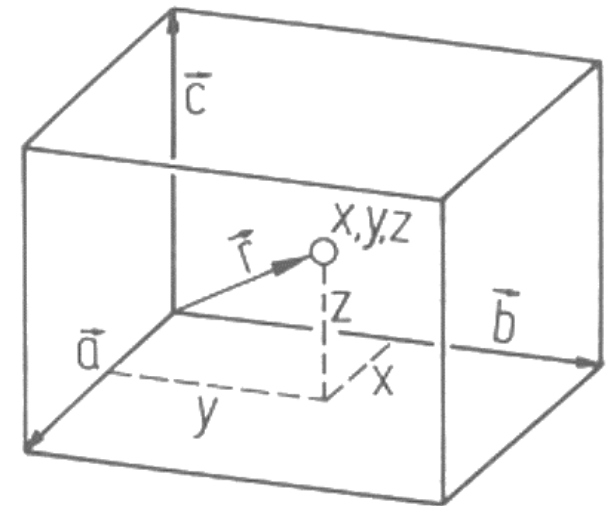
Kristalna struktura



- Ishodište je u gornjem lijevom kutu.
- Orijentacija kao i kristalografske osi.
- Koordinate atoma: x, y, z (izražene u dijelovima perioda identičnosti duž kristalografskih osi a, b, c)

$$0 \leq x, y, z \leq 1$$

- Z = broj formulačkih jedinica u jediničnoj ćeliji

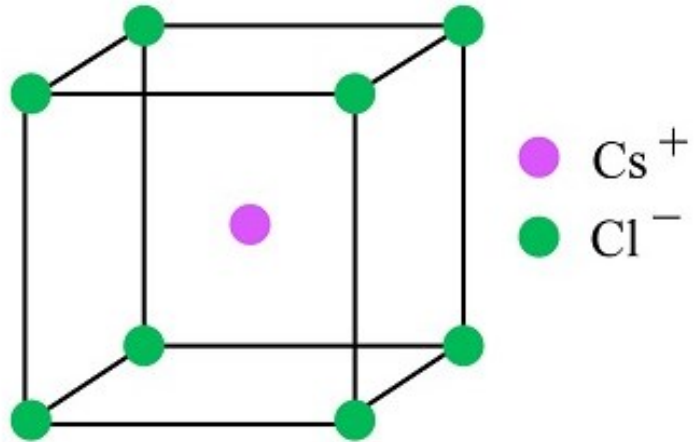


Kristalna struktura

Z = broj formula jedinica u jediničnoj ćeliji

Primjer:

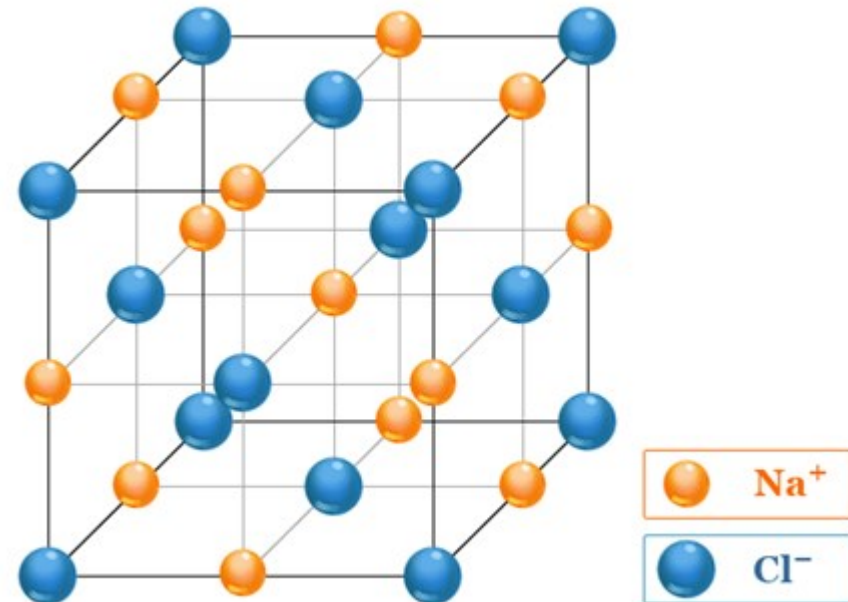
struktura CsCl



$Z = 1$

vs.

struktura NaCl



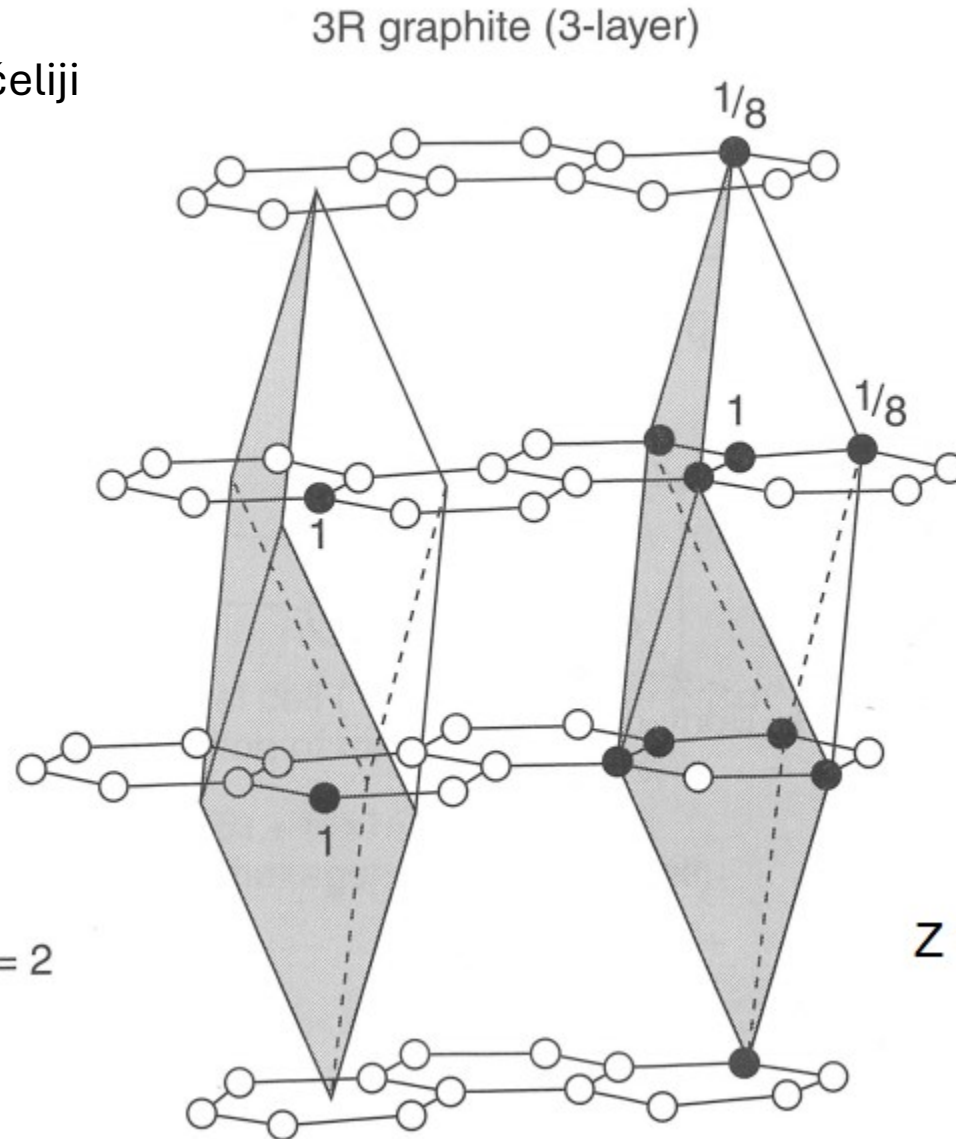
$Z = 4$

Kristalna struktura

Z = broj formulskih jedinki u jediničnoj ćeliji

! Z je konstantan neovisno o poziciji jedinične ćelije u strukturi.

$$Z = (2 \times 1) = 2$$



$$Z = (8 \times 1/8) + (1 \times 1) = 2$$

Kristalna struktura

Simetrija na razini strukture:

→ atomi u kristalnim strukturama su pravilno tj. simetrično raspoređeni

! Mogući elementi simetrije koji nisu u skladu s trodimenzionalnim periodičnim rasporedom materije → elementi simetrije koji uključuju translaciju

(1) Osnovni elementi simetrije: ravnina simetrije, osi simetrije (gire), centar simetrije

(2) Elementi simetrije fine strukture: klizne ravnine, vijčane (helikoidalne) osi

Elementi simetrije fine strukture

(1) Vijčane (helikoidalne) osi simetrije (gire)

rotacija za određeni kut (180° , 120° , 90° ili 30°)

+

pomak (translacija) duž osi za određeni dio periode

→ duž smjerova paralelnih s onima duž kojih na kristalima idu obične osi simetrije

Oznake: 2_1 – pomak za $\frac{1}{2}$ periode

$3_1 - \frac{1}{3}$

$3_2 - \frac{2}{3}$

$4_1 - \frac{1}{4}$

$4_2 - \frac{1}{2}$

$4_3 - \frac{3}{4}$

$6_1 - \frac{1}{6}$

$6_2 - \frac{1}{3}$

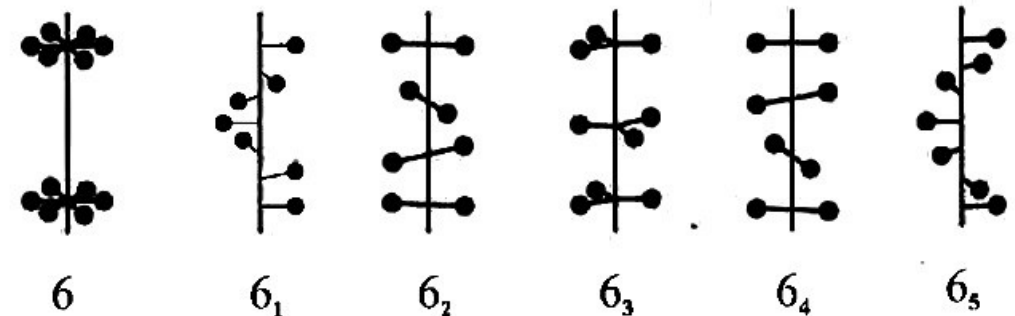
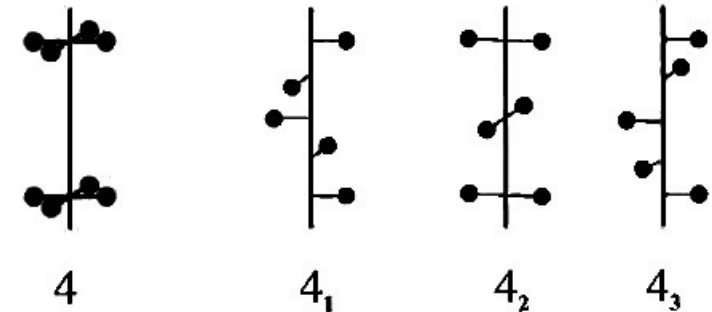
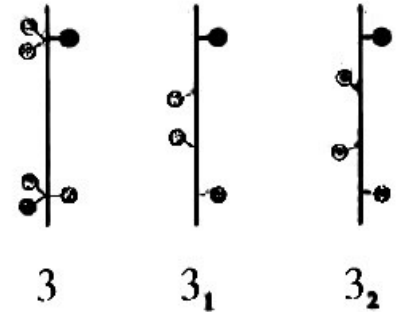
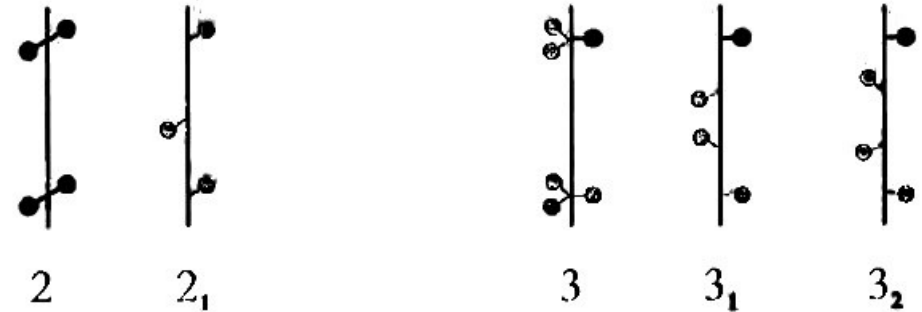
$6_3 - \frac{1}{2}$

$6_4 - \frac{2}{3}$

$6_5 - \frac{5}{6}$



pravilo desne ruke



Elementi simetrije fine strukture

(1) Vijčane (helikoidalne) osi simetrije (gire)

rotacija za određeni kut (180° , 120° , 90° ili 30°)

+

pomak (translacija) duž osi za određeni dio periode

→ duž smjerova paralelnih s onima duž kojih na kristalima idu obične osi simetrije

Oznake: 2_1 – pomak za $\frac{1}{2}$ periode

$3_1 - \frac{1}{3}$

$3_2 - \frac{2}{3}$

$4_1 - \frac{1}{4}$

$4_2 - \frac{1}{2}$

$4_3 - \frac{3}{4}$

$6_1 - \frac{1}{6}$

$6_2 - \frac{1}{3}$

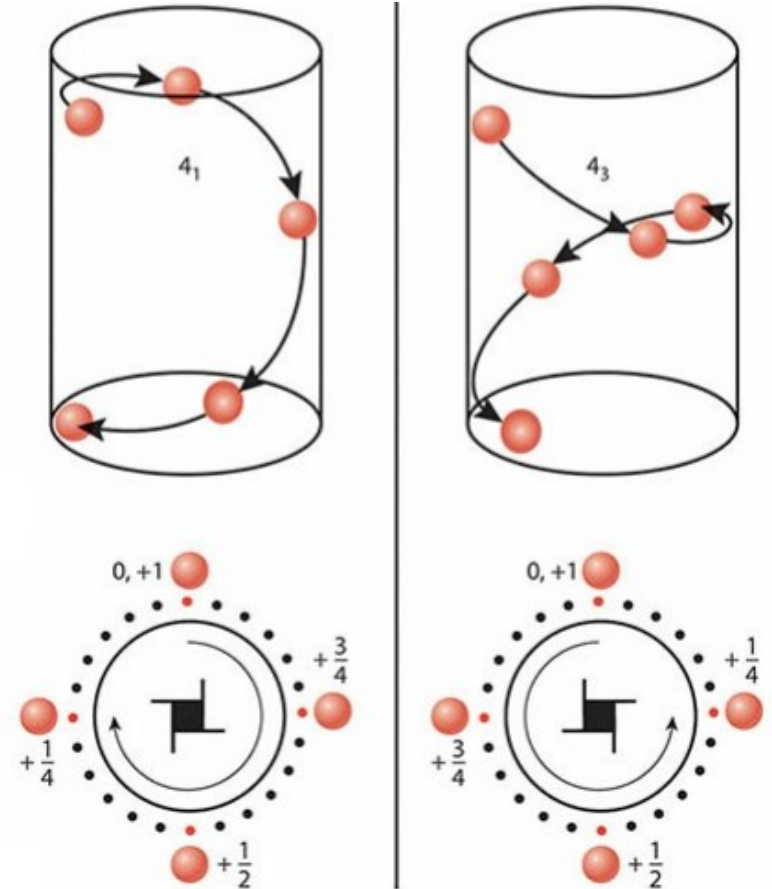
$6_3 - \frac{1}{2}$

$6_4 - \frac{2}{3}$

$6_5 - \frac{5}{6}$



pravilo desne ruke



Preuzeto iz Klein & Philpotts (2013).

Elementi simetrije fine strukture

(2) Klizne ravnine

zrcaljenje

+

pomak (translacija) smjerom paralelnim s ravninom simetrije

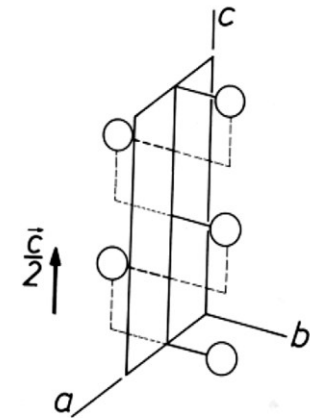
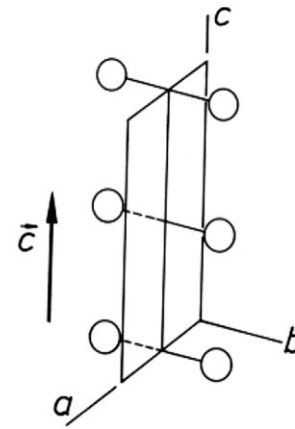
Oznake: $\mathbf{a} - \frac{1}{2}\vec{a}$

$\mathbf{b} - \frac{1}{2}\vec{b}$

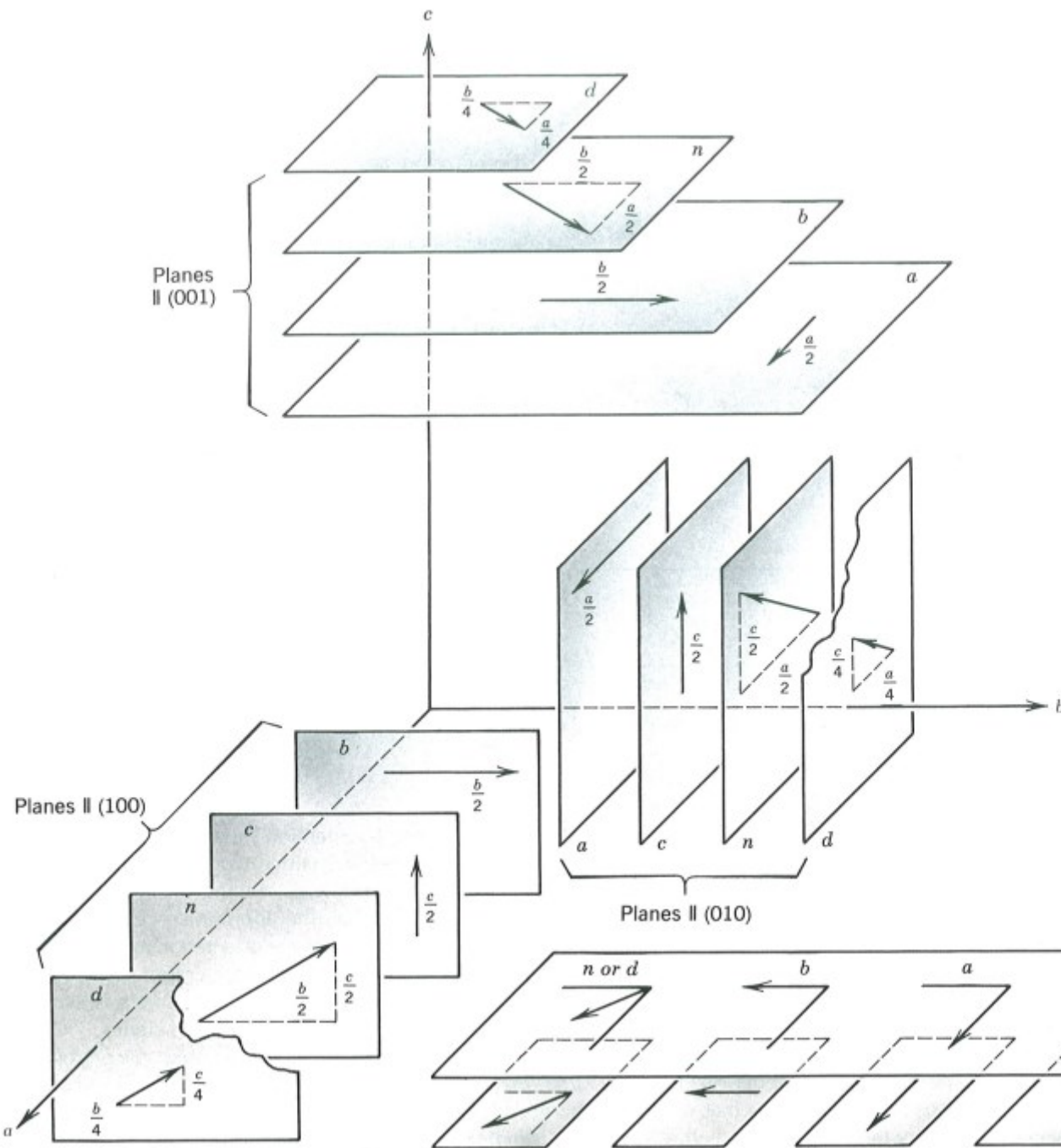
$\mathbf{c} - \frac{1}{2}\vec{c}$

$\mathbf{n} - \frac{1}{2}\vec{a} + \frac{1}{2}\vec{b}; \frac{1}{2}\vec{b} + \frac{1}{2}\vec{c}; \frac{1}{2}\vec{a} + \frac{1}{2}\vec{c}$

$\mathbf{d} - \frac{1}{4}\vec{a} + \frac{1}{4}\vec{b}; \frac{1}{4}\vec{b} + \frac{1}{4}\vec{c}; \frac{1}{4}\vec{a} + \frac{1}{4}\vec{c}$



Preuzeto iz Slovenec (2011).



$$\mathbf{a} - \frac{1}{2}\vec{a}$$

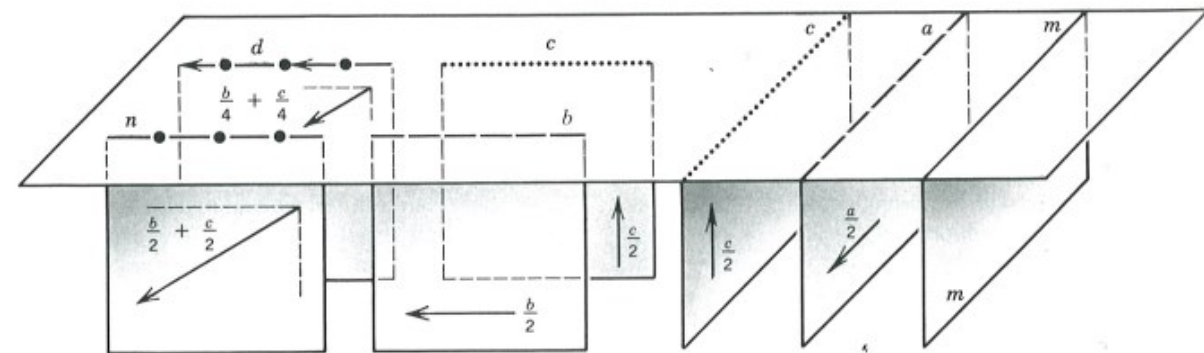
$$\mathbf{b} - \frac{1}{2}\vec{b}$$

$$\mathbf{c} - \frac{1}{2}\vec{c}$$

$$\mathbf{n} - \frac{1}{2}\vec{a} + \frac{1}{2}\vec{b}; \frac{1}{2}\vec{b} + \frac{1}{2}\vec{c}; \frac{1}{2}\vec{a} + \frac{1}{2}\vec{c}$$

$$\mathbf{d} - \frac{1}{4}\vec{a} + \frac{1}{4}\vec{b}; \frac{1}{4}\vec{b} + \frac{1}{4}\vec{c}; \frac{1}{4}\vec{a} + \frac{1}{4}\vec{c}; \frac{1}{4}\vec{a} + \frac{1}{4}\vec{b} + \frac{1}{4}\vec{c}$$

(2) Klizne ravnine



Elementi simetrije fine strukture

TABLE 6.3 Symbols for Symmetry Axes (All Graphic Symbols Are for Axes Normal to the Page, Unless Otherwise Noted)

Symbol	Symmetry Axis	Graphic Symbol	Type of Translation (If Present)	Symbol	Symmetry Axis	Graphic Symbol	Type of Translation (If Present)
1	onfold rotation	None	None	4	fourfold rotation		None
$\bar{1}$	onfold rotoinversion		None	4_1	fourfold screw (right-handed)		$\frac{1}{4}c$
2	twofold rotation		None	4_2	fourfold screw (neutral)		$\frac{2}{4}c = \frac{1}{2}$
		→ (parallel to paper)		4_3	fourfold screw (left-handed)		$\frac{3}{4}c$
2_1	twofold screw		$\frac{1}{2}c$ $\frac{1}{2}a$ or $\frac{1}{2}b$	$\bar{4}$	fourfold rotoinversion		None
3	threefold rotation		None	6	sixfold rotation		None
3_1	threefold screw (right-handed)		$\frac{1}{3}c$	6_1	sixfold screw (right-handed)		$\frac{1}{6}c$
3_2	threefold screw (left-handed)		$\frac{2}{3}c$	6_2	sixfold screw (right-handed)		$\frac{2}{6}c$
$\bar{3}$	threefold rotoinversion		None	6_3	sixfold screw (neutral)		$\frac{3}{6}c = \frac{1}{2}$
				6_4	sixfold screw (left-handed)		$\frac{4}{6}c$
				6_5	sixfold screw (left-handed)		$\frac{5}{6}c$
				$\bar{6}$	sixfold rotoinversion		None

Elementi simetrije fine strukture

TABLE 6.4 Symbols for Mirror and Glide Planes*

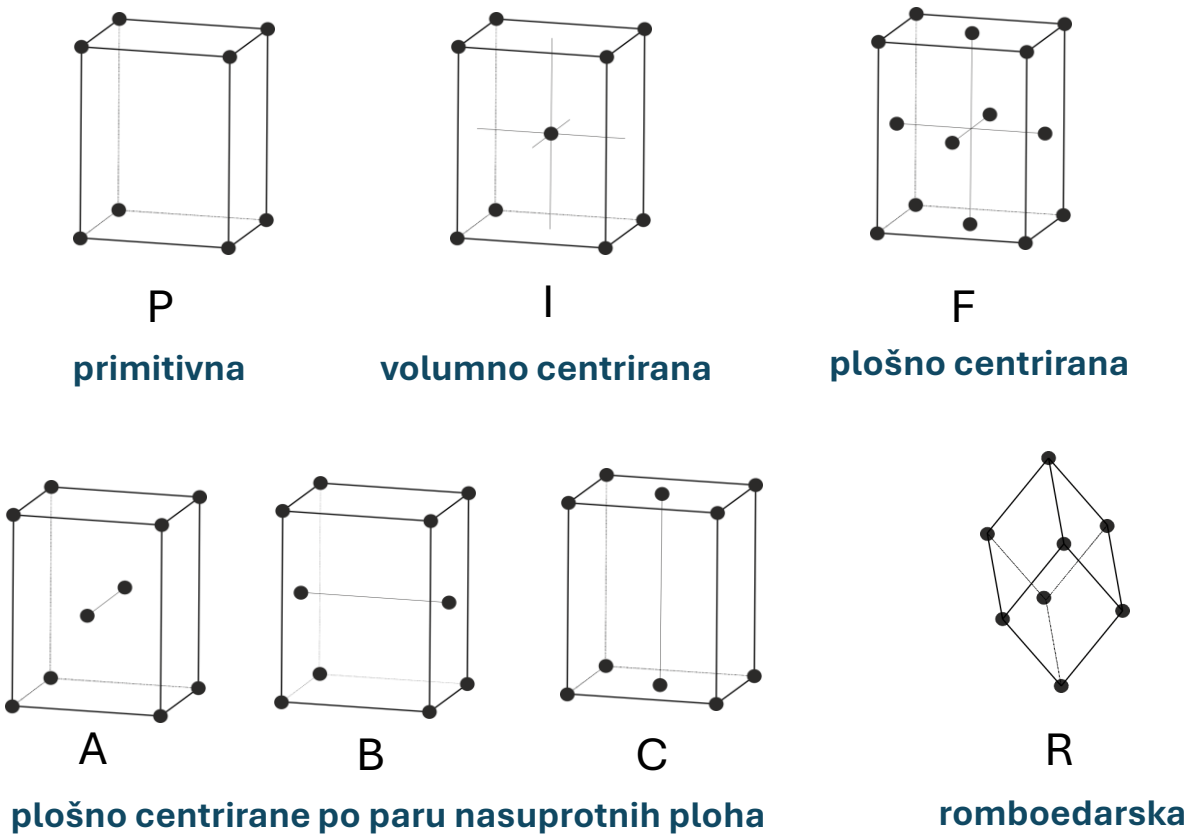
Symbol	Symmetry Plane	Graphic Symbol		Nature of Glide Translation
		Normal to Plane of Projection	Parallel to Plane of Projection†	
m	Mirror			None
a, b	Axial glide plane			$a/2$ along $[100]$ or $b/2$ along $[010]$
c			None	$c/2$ along the c axis
n	Diagonal glide plane			$a/2 + b/2$; $a/2 + c/2$; $b/2 + c/2$; or $a/2 + b/2 + c/2$ (tetragonal and isometric)
d	Diamond glide plane			$a/4 + b/4$; $b/4 + c/4$; $a/4 + c/4$; or $a/4 + b/4 + c/4$ (tetragonal and isometric)

*From *International Tables for X-ray Crystallography*, 1969, v. 1, N. F. M. Henry and K. Lonsdale, eds.; Birmingham, England: Symmetry Groups. International Union of Crystallography, Kynoch Press.

†When planes are parallel to the paper, heights other than zero are indicated by writing the z coordinate next to the symbol (e.g., $\frac{1}{4}$ or $\frac{3}{8}$). The arrows indicate the direction of the glide component.

Jedinična ćelija

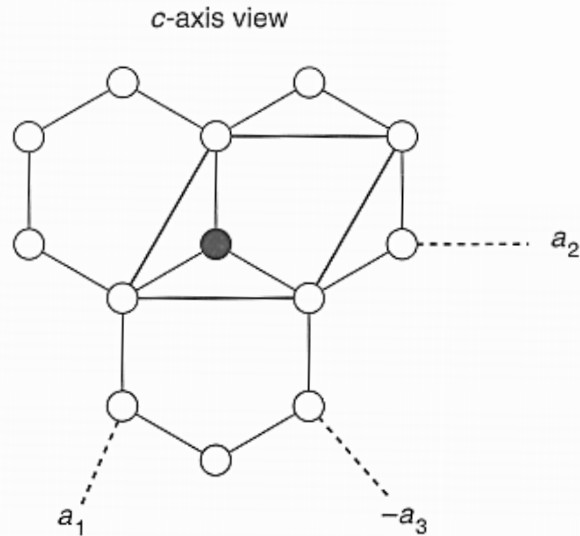
- najmanja strukturna jedinica kojom se može opisati cijela struktura (najmanji volumen čijim ponavljanjem se može dobiti čitava rešetka)
- različiti oblici ovisno o **parametrima jedinične ćelije**, tj. o sustavu u kojem je materijal kristalizirao
- različiti tipovi ovisno o **centriranosti**



Tip rešetke	Broj čvorova u ćeliji	Koordinate čvorova
P	1	0,0,0
A	2	0,0,0 0, 1/2, 1/2
B	2	0,0,0 1/2, 0, 1/2
C	2	0,0,0 1/2, 1/2, 0
I	2	0,0,0 1/2, 1/2, 1/2
F	4	0,0,0 0, 1/2, 1/2 1/2, 0, 1/2 1/2, 1/2, 0
R	1 ili 3*	0,0,0 ili 0,0,0 2/3, 1/3, 1/3 1/3, 2/3, 2/3

Kristalna struktura

* Primjer: odabir različitih jediničnih ćelija u grafitu



RHOMBOHEDRAL UNIT CELL

GRAPHITE C

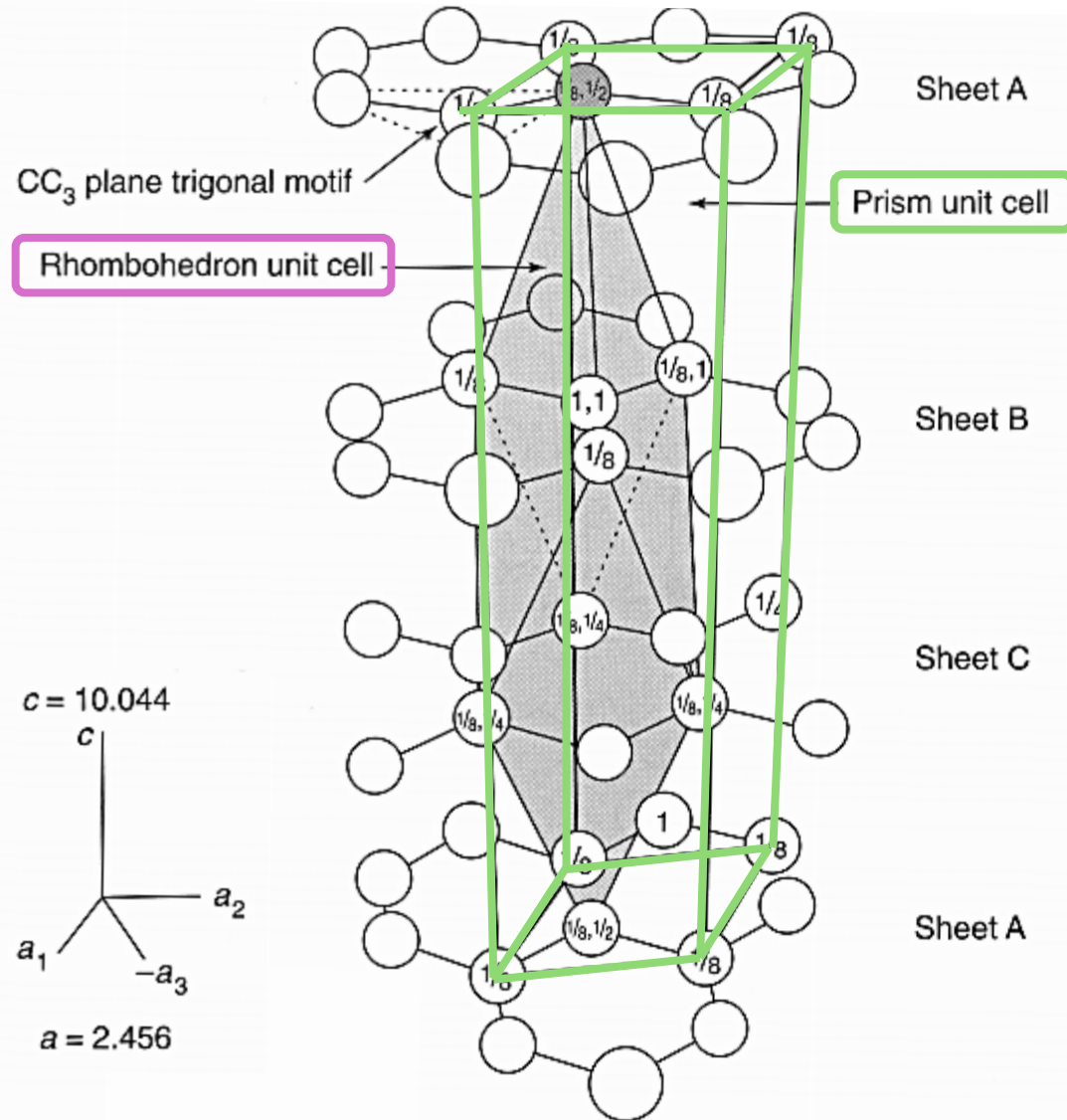
System: Rhombohedral

Point group: $\bar{3}2/m$

Space group: $R\bar{3}m$ (166)

Polytype: $3R$ (3 layer)

$Z = 6$ or 2



$$C: (8 \times 1/8) + (4 \times 1/4) + (2 \times 1/2) + (3 \times 1) = 6$$

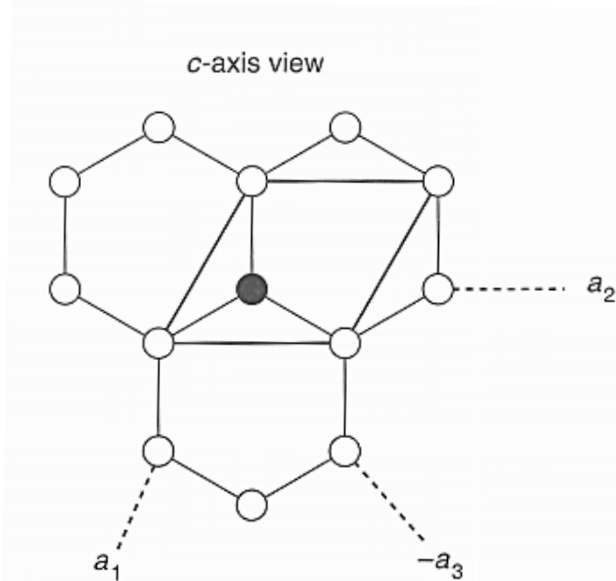
$$Z = 6 \text{ (prism unit cell)}$$

$$C: (8 \times 1/8) + (1 \times 1) = 2$$

$$Z = 2 \text{ (rhombohedral unit cell)}$$

Kristalna struktura

* Primjer: odabir različitih jediničnih ćelija u grafitu



RHOMBOHEDRAL UNIT CELL

GRAPHITE C

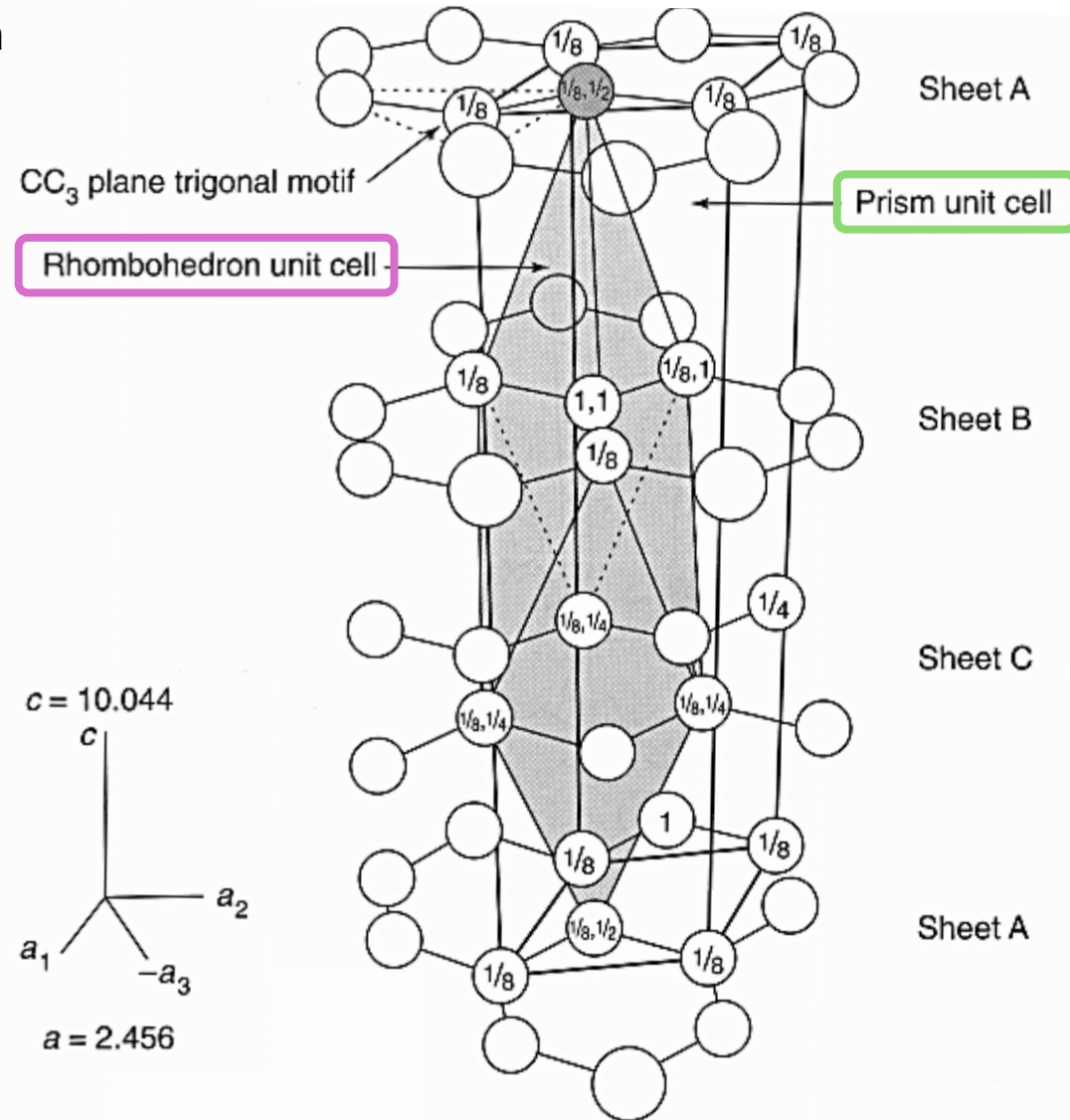
System: Rhombohedral

Point group: $\bar{3}2/m$

Space group: $R\bar{3}m$ (166)

Polytype: $3R$ (3 layer)

$Z = 6$ or 2



$$C: (8 \times 1/8) + (4 \times 1/4) + (2 \times 1/2) + (3 \times 1) = 6$$

$$Z = 6 \text{ (prism unit cell)}$$

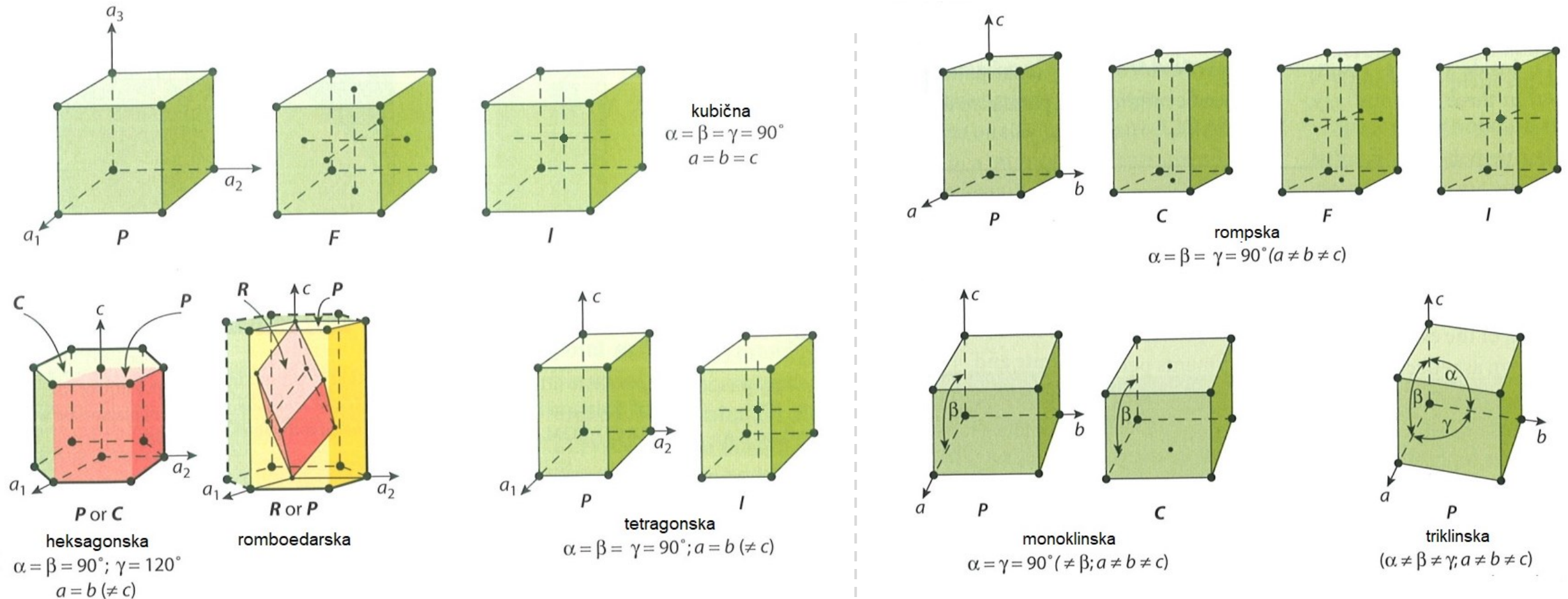
$$C: (8 \times 1/8) + (1 \times 1) = 2$$

$$Z = 2 \text{ (rhombohedral unit cell)}$$

Bravaisove rešetke

→ 14 različitih ćelija = 14 mogućih načina periodičnog ponavljanja točaka u prostoru

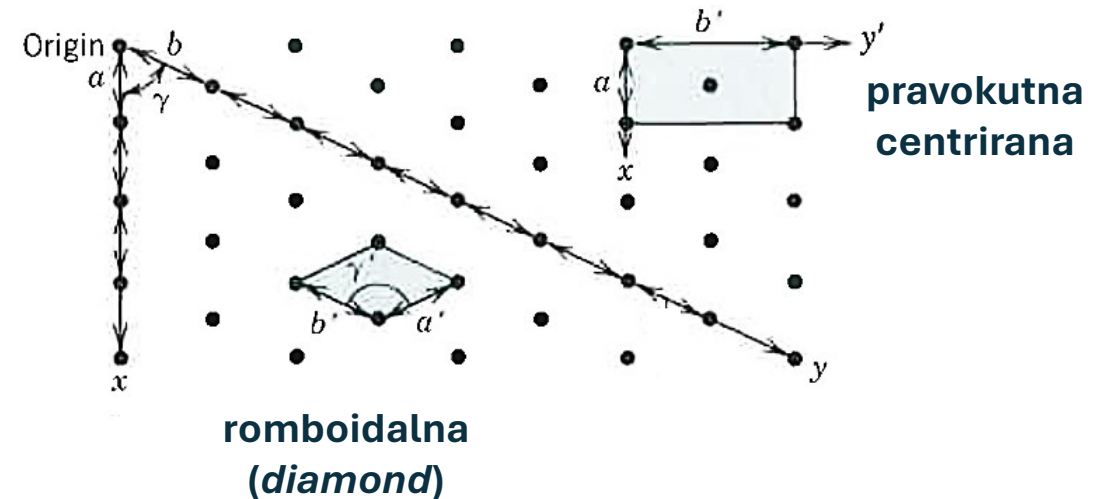
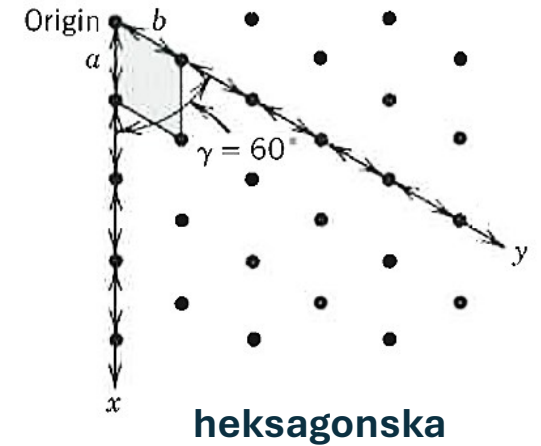
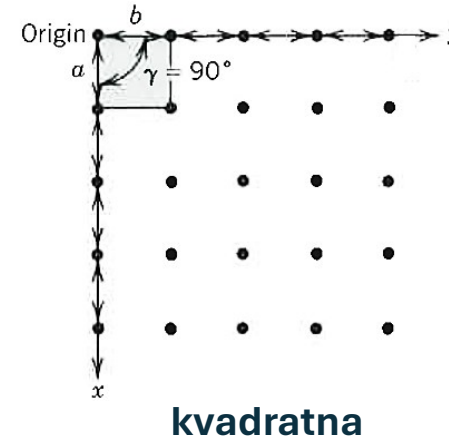
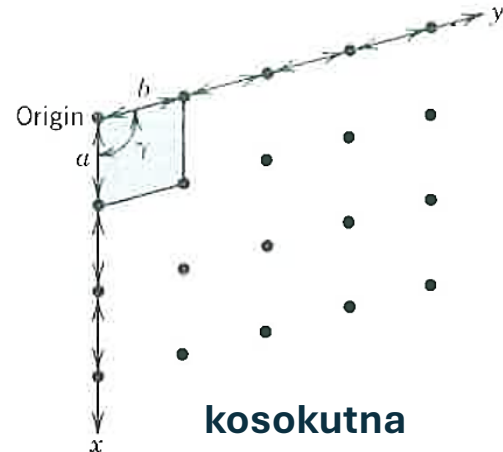
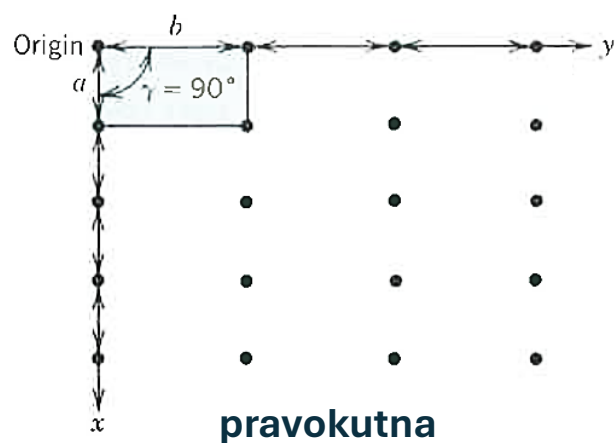
kombinacija: 7 (6) kristalnih sustava + 7 tipova jedinične ćelije po centiranosti



Prostorne rešetke

Pravila za mogućnost odabira:

1. simetrija paralelopipeda mora biti jednaka kao simetrija rešetke
2. broj pravih kutova između bridova paralelopipeda mora uz zadovoljenje 1. uvjeta biti maksimalan
3. uz zadovoljenje uvjeta 2. i 3., volumen paralelopipeda mora biti minimalan



romboidalna
(diamond)

Prostorne grupe

= 230 kombinacija za ponavljanje nekog **motiva u prostoru**

32 kristalne klase (točkine grupe) $\times$ 14 Bravaisovih rešetki
+
elementi simetrije s translacijom

Oznake: tip Bravaisove rešetke + elementi simetrije

Primjer:

(a) I mmm $\rightarrow$ volumno centrirana rešetka (2 čvora)
 $\rightarrow$ holodrija rompskog sustava (2/m 2/m 2/m)

(b) F mcm = C mmm*
 $\rightarrow$ plošno centrirana rešetka (4 čvora)
 $\rightarrow$ holodrija rompskog sustava (2/m 2/m 2/m)

* elemente s translacijom zamijeniti s „normalnim” elementima simetrije

! Morfološka kristalografija → određivanje **točkine grupe** (kristalne klase)

32 klase = simetrija oko točke (centra) u kristalu
= **vanjska simetrija**

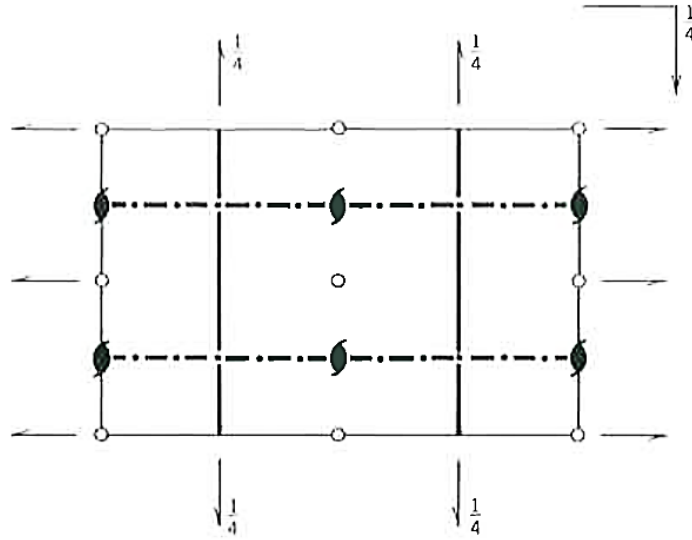
Kristalna struktura → određivanje **prostorne grupe**

230 prostornih grupa = kristalna klasa + jedinična ćelija + elementi simetrije s
translacijom
= **unutarnja simetrija**

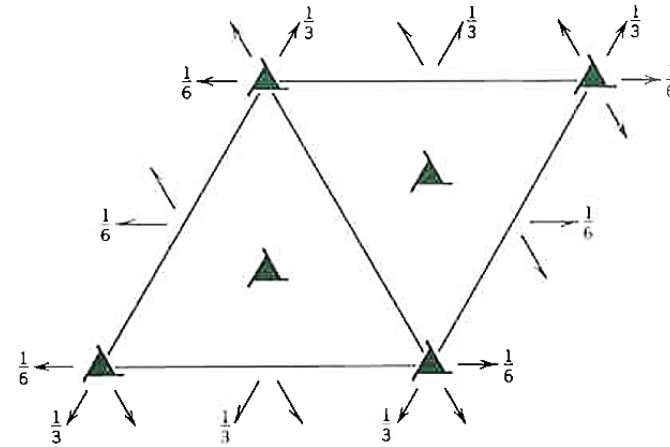
Prostorne grupe

Primjeri

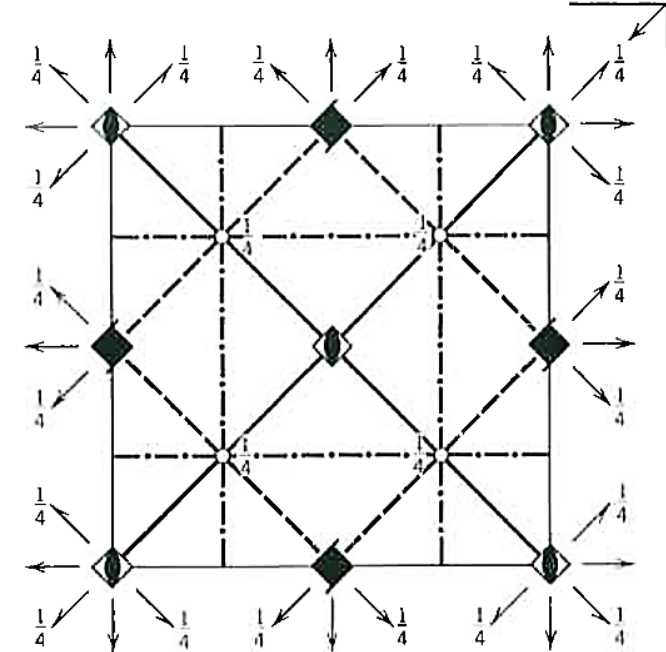
$P n m a$



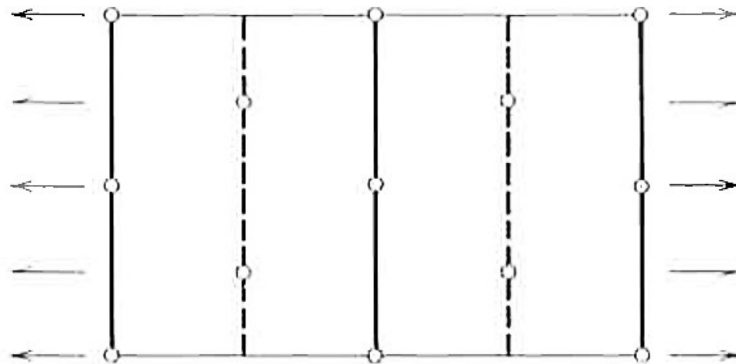
$P3_121$



$P 4_2/n n m$



$C2/m$



Kristalna struktura

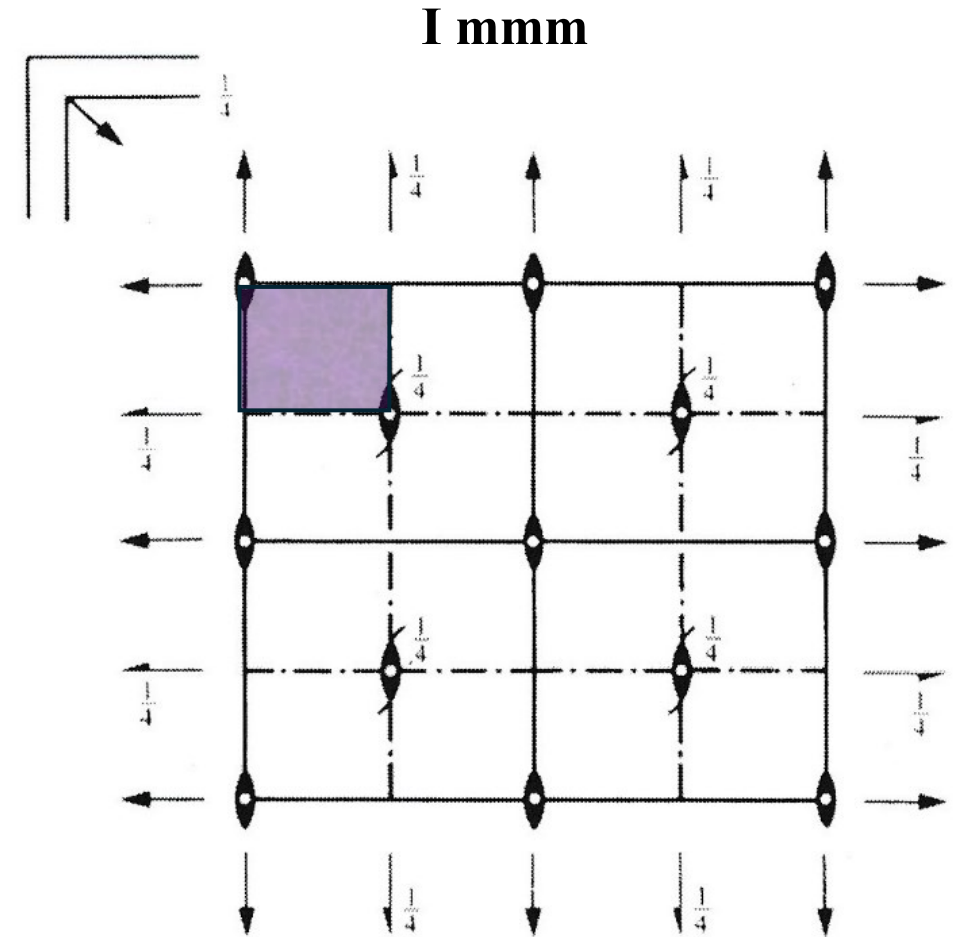
Kod opisa strukture treba:

(a) navesti sve atome u jediničnoj ćeliji

ili

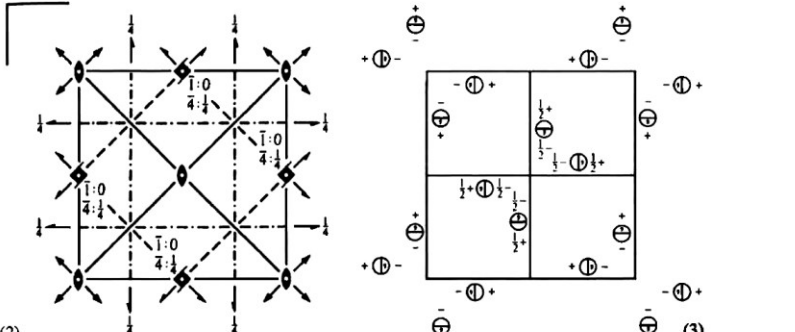
(b) reći o kojoj je prostornoj grupi riječ, tj. definirati simetriju
i dati podatke za sve atome u asimetričnoj jedinici

Asimetrična jedinica = najmanji dio jedinične ćelije koji će ponovljen putem elemenata simetrije dati čitavu ćeliju
→ ne postoji simetrijska veza među točkama unutar asimetrične jedinice



International tables for crystallography

(1) **P4₂/mnm** **D_{4h}¹⁴** 4/mmm Tetragonal
No. 136 P4₂/m 2₁/n 2/m

(2) 

(4) Origin at centre (m m m) at 2/m 1 2/m

(5) Asymmetric unit $0 \leq x \leq \frac{1}{2}; 0 \leq y \leq \frac{1}{2}; 0 \leq z \leq \frac{1}{2}; x \leq y$

(6) Symmetry operations

(1) 1	(2) $z \rightarrow 0, z$	(3) $4^+(0, 0, \frac{1}{2}) \rightarrow 0, \frac{1}{2}, z$	(4) $4^-(0, 0, \frac{1}{2}) \rightarrow \frac{1}{2}, 0, z$
(5) $2(0, \frac{1}{2}, 0) \rightarrow \frac{1}{2}, y, \frac{1}{2}$	(6) $2(\frac{1}{2}, 0, 0) \rightarrow x, \frac{1}{2}, \frac{1}{2}$	(7) $2x, x, 0$	(8) $2x, \bar{x}, 0$
(9) $\bar{1} \rightarrow 0, 0, 0$	(10) $m \rightarrow x, y, 0$	(11) $4^+(\frac{1}{2}, 0, z) \rightarrow \frac{1}{2}, 0, \frac{1}{2}$	(12) $4^-(0, \frac{1}{2}, z) \rightarrow 0, \frac{1}{2}, \frac{1}{2}$
(13) $n(\frac{1}{2}, 0, \frac{1}{2}) \rightarrow x, \frac{1}{2}, z$	(14) $n(0, \frac{1}{2}, \frac{1}{2}) \rightarrow \frac{1}{2}, y, z$	(15) $m \rightarrow x, \bar{x}, z$	(16) $m \rightarrow x, x, z$

(7) Positions

Multiplicity	Wyckoff letter	Site symmetry	Coordinates
16 k 1	(1) x, y, z	(2) $\bar{x}, \bar{y}, z$	(3) $\bar{y} + \frac{1}{2}, x + \frac{1}{2}, z + \frac{1}{2}$
	(5) $\bar{x} + \frac{1}{2}, y + \frac{1}{2}, \bar{z} + \frac{1}{2}$	(6) $x + \frac{1}{2}, \bar{y} + \frac{1}{2}, \bar{z} + \frac{1}{2}$	(7) $x, y, \bar{z}$
	(9) $\bar{x}, \bar{y}, \bar{z}$	(10) $x, y, \bar{z}$	(11) $y + \frac{1}{2}, \bar{x} + \frac{1}{2}, \bar{z} + \frac{1}{2}$
	(13) $x + \frac{1}{2}, \bar{y} + \frac{1}{2}, z + \frac{1}{2}$	(14) $\bar{x} + \frac{1}{2}, y + \frac{1}{2}, z + \frac{1}{2}$	(15) $\bar{y}, \bar{x}, z$
8 j .m	x, x, z	$\bar{x}, \bar{x}, z$	$\bar{x} + \frac{1}{2}, x + \frac{1}{2}, z + \frac{1}{2}$
	$\bar{x} + \frac{1}{2}, x + \frac{1}{2}, \bar{z} + \frac{1}{2}$	$x, x, \bar{z}$	$\bar{x}, \bar{x}, \bar{z}$
8 i m..	$x, y, 0$	$\bar{x}, \bar{y}, 0$	$\bar{y} + \frac{1}{2}, x + \frac{1}{2}, \frac{1}{2}$
	$\bar{x} + \frac{1}{2}, y + \frac{1}{2}, \frac{1}{2}$	$x + \frac{1}{2}, \bar{y} + \frac{1}{2}, \frac{1}{2}$	$y, x, 0$
8 h 2..	$0, \frac{1}{2}, z$	$0, \frac{1}{2}, \bar{z}$	$\frac{1}{2}, 0, \bar{z}$
	$0, \frac{1}{2}, z$	$0, \frac{1}{2}, \bar{z}$	$\frac{1}{2}, 0, z$
4 g m.2m	$x, \bar{x}, 0$	$\bar{x}, x, 0$	$\bar{x} + \frac{1}{2}, \bar{x} + \frac{1}{2}, \frac{1}{2}$
4 f m.2m	$x, x, 0$	$\bar{x}, \bar{x}, 0$	$\bar{x} + \frac{1}{2}, x + \frac{1}{2}, \frac{1}{2}$
4 e 2.mm	$0, 0, z$	$0, 0, \bar{z}$	$0, 0, \bar{z}$
4 d 4..	$0, \frac{1}{2}, \frac{1}{4}$	$0, \frac{1}{2}, \frac{3}{4}$	$\frac{1}{2}, 0, \frac{1}{4}$
4 c 2/m..	$0, \frac{1}{2}, 0$	$0, \frac{1}{2}, \frac{1}{2}$	$\frac{1}{2}, 0, 0$
2 b m.mm	$0, 0, \frac{1}{2}$	$0, 0, \frac{1}{2}$	
2 a m.mm	$0, 0, 0$	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	

Fig. 10.17 Space group P4₂/mnm, from *International Tables for Crystallography*, Vol. A. [16]

• opći podaci: skraćeni simbol prostorne grupe, Schönfliesov simbol, kristalna klasa (točkina grupa), kristalni sustav, broj prostorne grupe, puni simbol prostorne grupe

• desno: projekcija elemenata simetrije na ravninu xy
• lijevo: projekcija točka u općem položaju

• podaci o simetriji i prisutnim simetrijskim operacijama

• popis koordinata ekvivalentnih točaka na općem i svim specijalnim položajima

