Crystal lattices

- Classification of Bravais lattices and crystal structures
- The reciprocal lattice
- Experimental determination of crystal structure by X-ray diffraction

crystal ≠ a clear, transparent mineral or glass resembling ice

Most solids have crystal structure, even though they are lustreless and not transparent. For example, almost all metals are polycrystals (alloy of monocrystals 1-10^3μm).

A **crystal** is a solid material whose constituents, such as atoms, molecules or ions, are arranged with high order (periodically). The word *crystal* is derived from the Ancient Greek word κρύσταλλος (*krustallos*), meaning both "ice" and "rock crystal", from κρύος (*kruos*), "icy cold, frost".

Some History

Ancient studies – many thousands years.

Hauy R.J. – periodic array of identical elementary blocks (1784, 1801, 1822)

Lattices and their symmetries – Frankenheim, 1835

The 32 crystals classes – Frankenheim and Hessel

The 14 lattice classes – Frankenheim, 1856

Derivation of the Bravais classes from purely geometrical reasoning – Auguste Bravais (1848-1851); summarized in 1866

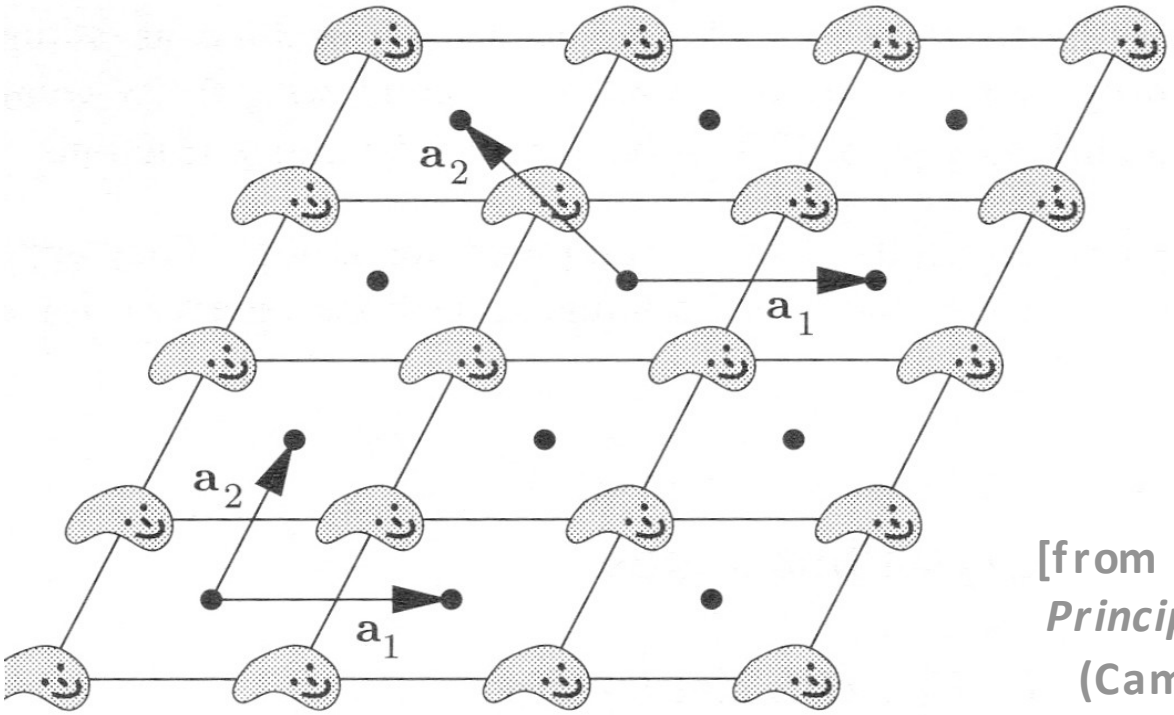
230 space groups – the full Euclidean symmetry of periodic patterns in three dimensions – Fedorov, Schoenflies, 1890

Microscopic symmetry – macroscopic consequences: morphology (the law of rational indices)

Ideal crystals – microscopic structure has the space group symmetry – von Laue, 1912 (from x-ray study)

Subsequent developments: Structure determination based on the results of Braggs (x-ray reflection).

Periodic crystal structure



A two-dimensional crystal consisting of identical unit cells periodically repeated to fill space. Two sets of primitive translation vectors are shown.

[from P. M. Chaikin and T. C. Lubensky, *Principles of Condensed Matter Physics* (Cambridge University Press, 2000)]

The atomic arrangement looks the same when viewed from any point r as when viewed from the point $\mathbf{r}' = \mathbf{r} + n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}$, where n_1, n_2, n_3 are arbitrary integers.

Basic (primitive) translation vectors are denoted a_1, a_2, a_3.

The operation of displacing a crystal parallel to itself by $n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}$ is called a translation operation. The totality of such operations, for all values of the integers n_1, n_2, n_3, is known as the translation group of the crystal.

Translational + point-group symmetry operations (example)

a

Fig. a. Portion of a crystal of an imaginary protein molecule (having no special symmetry of its own), in a 2D (two-dimensional) world. The vectors a_1 and a_2 are primitive translation vectors of the 2D lattice.

b

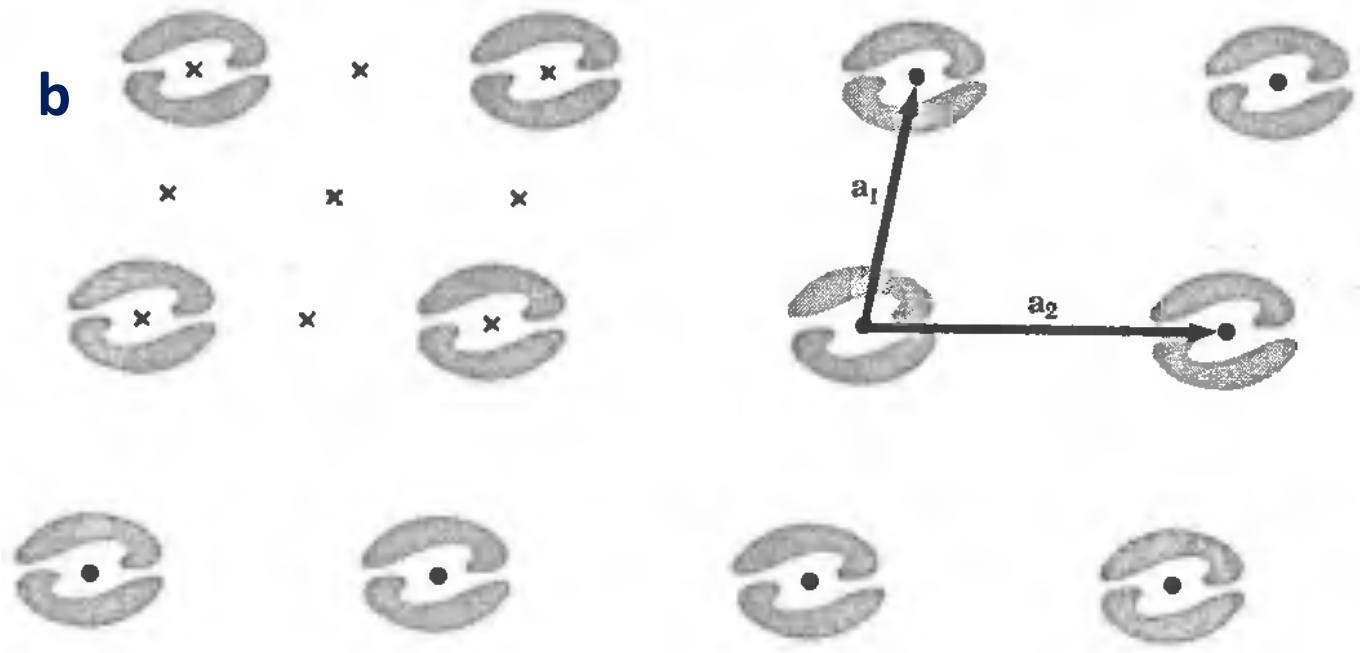
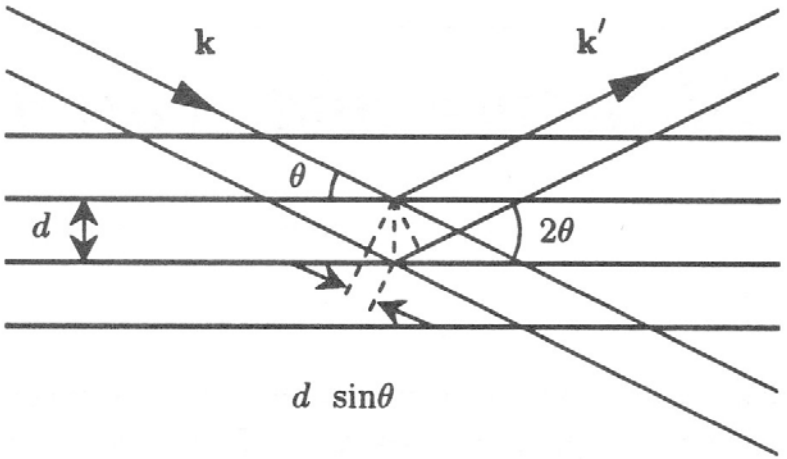


Fig. b. Similar to Fig. a, but with protein molecules associated in pairs. The crystal translation vectors are a_1 and a_2. A rotation of π radians about any point marked x will carry the crystal into itself.

Scattering from parallel planes showing the origin of Bragg's law. The planes are separated by a distance *d*.

The incident wave vector is **k** and the scattered wave vector is **k'**. The magnitude of both **k** and **k'** is $2\pi/\lambda$, and the path difference between waves partially reflected from successive planes is $2d\sin\theta$.



[from P. M. Chaikin and T. C. Lubensky, *Principles of Condensed Matter Physics* (Cambridge University Press, 2000)]

Primitive Lattice Cell

The parallelepiped defined by translation vectors a_1, a_2, a_3 is called a primitive cell (Fig. 1). A primitive cell is a type of unit cell. A unit cell will fill all space by the repetition of suitable crystal translation operations. A primitive cell is a minimum-volume cell.

There are many ways of choosing the primitive axes and primitive cell for a given lattice (Fig. 2). However, the number of atoms in a primitive cell is always the same for a given crystal structure.

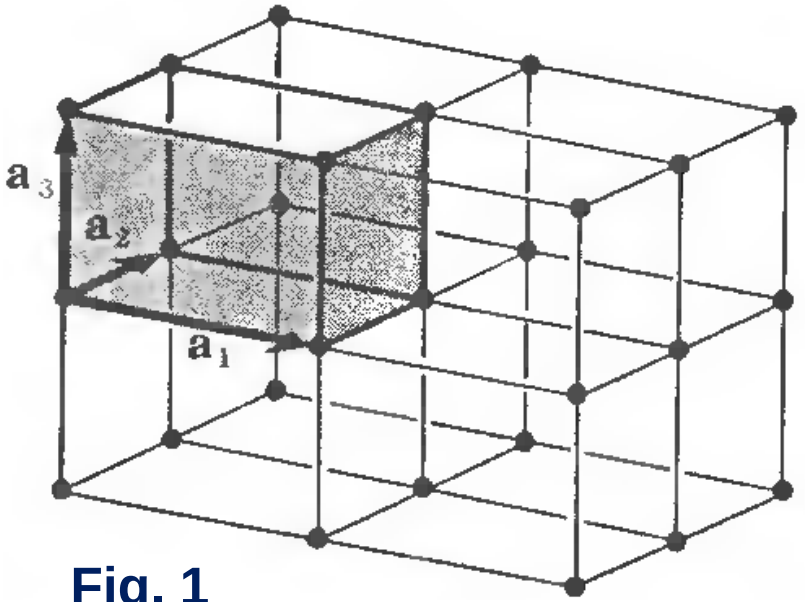


Fig. 1

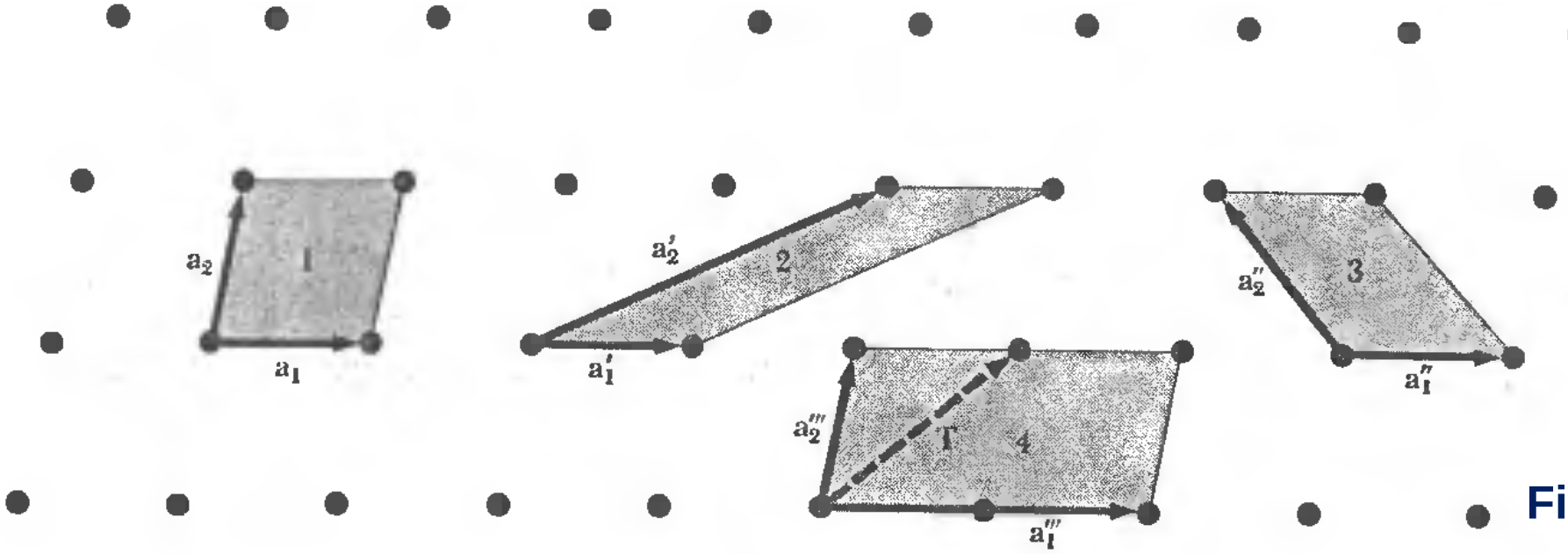


Fig. 2

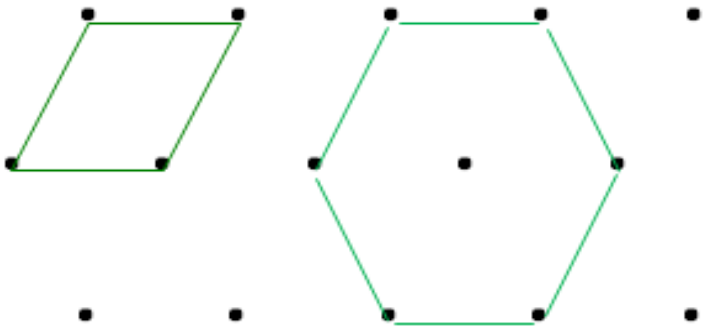
The volume of a parallelepiped with axes $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ is $V_c = |\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3|$

Unit Cell (**элементарная ячейка)**

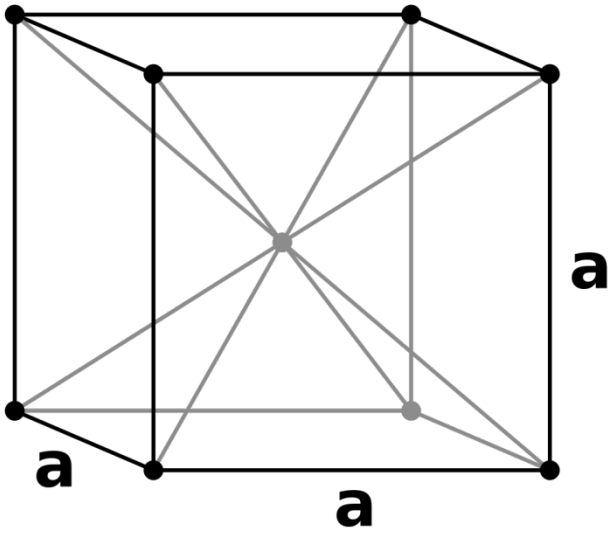
Crystal structure is described in terms of the geometry of arrangement of particles in the unit cell ≠ primitive cell.

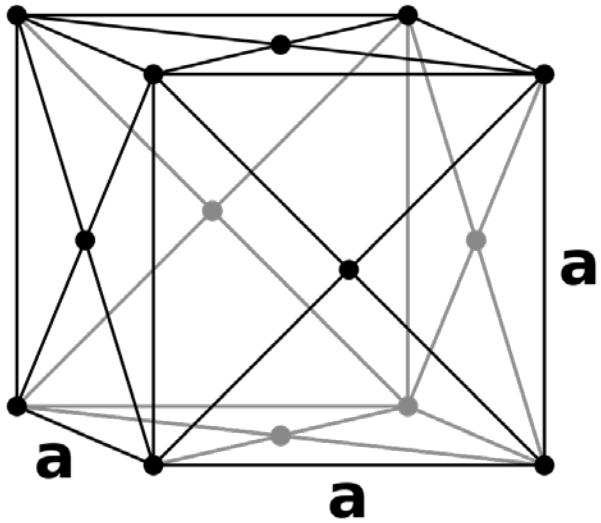
The unit cell is defined as the smallest repeating unit having the full symmetry of the crystal structure.

The geometry of the unit cell is defined as a parallelepiped, providing six lattice parameters taken as the lengths of the cell edges (*a*, *b*, *c*) and the angles between them (α, β, γ).



2D



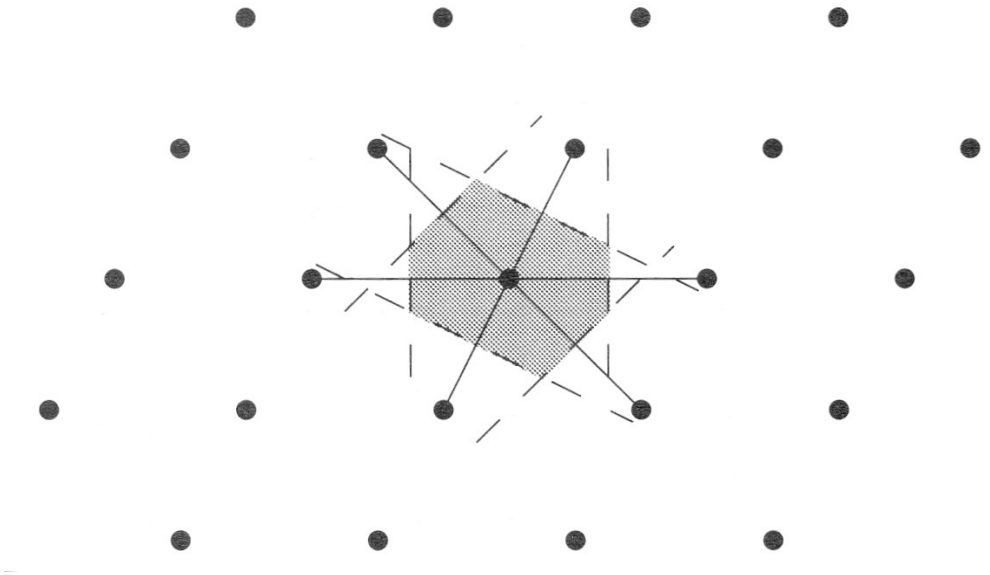


3D

Wigner-Seitz unit cell

The two-dimensional Bravais lattices – construction of the Wigner-Seitz unit cell for a low symmetry lattice.

Lattice sites – black dots. Solid lines connect the central lattice site to other sites; dashed lines are perpendicular bisectors of the solid lines.

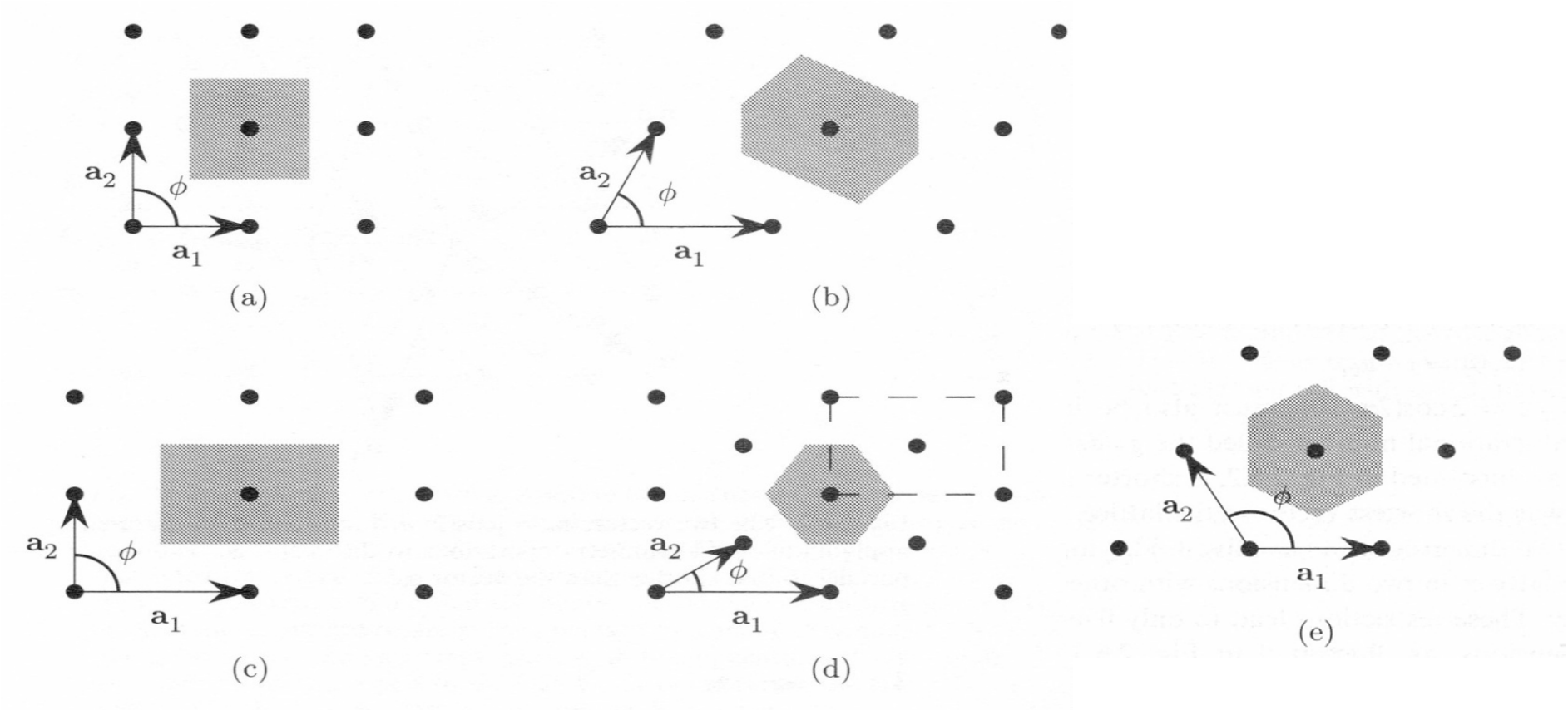


[from P. M. Chaikin and T. C. Lubensky, *Principles of Condensed Matter Physics* (Cambridge University Press, 2000)]

The Wigner-Seitz cell is shaded. All Wigner-Seitz cells, except those of the square and rectangular lattices, are hexagonal.

Construction of Wigner-Seitz unit cell

The five two-dimensional Bravais lattices: (a) square, (b) oblique, (c) rectangular, (d) centered rectangular, and (e) hexagonal lattice; $\mathbf{a}_1$ and $\mathbf{a}_2$ are primitive translation vectors and ϕ is the angle between $\mathbf{a}_1$ and $\mathbf{a}_2$.



[from P. M. Chaikin and T. C. Lubensky, *Principles of Condensed Matter Physics* (Cambridge University Press, 2000)]

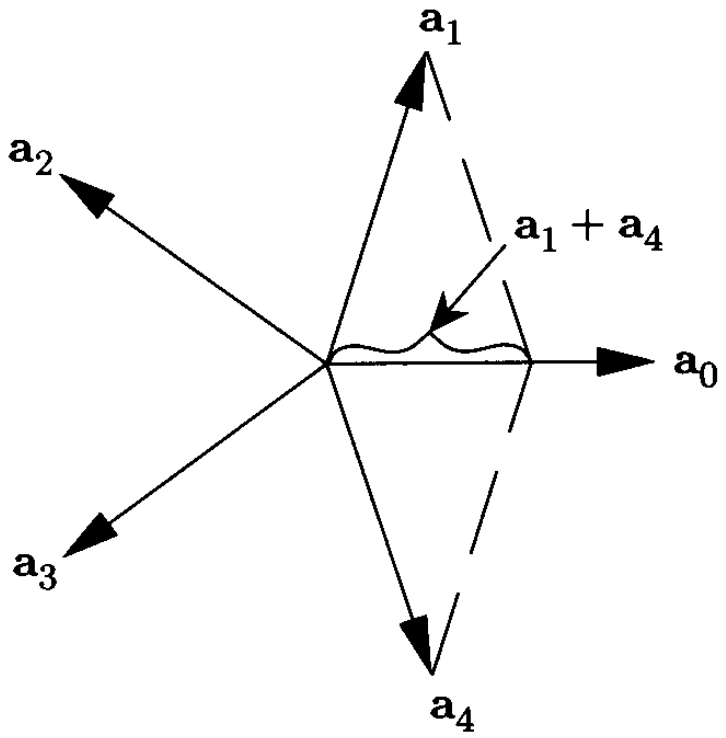
Point group crystal symmetries

In addition to translations, crystals are also invariant under point group operations consisting of rotations, reflections, and inversions about special symmetry points.

Molecules and finite size objects can have symmetry axes of arbitrary order. The requirement that a crystal be invariant under translations through any vector in its direct lattice, which, as we have seen, contains no vector shorter than some minimum length vector, places severe restrictions on possible rotational symmetries. For example, the symmetry axes can only be 1,2,3,4,6-th order.

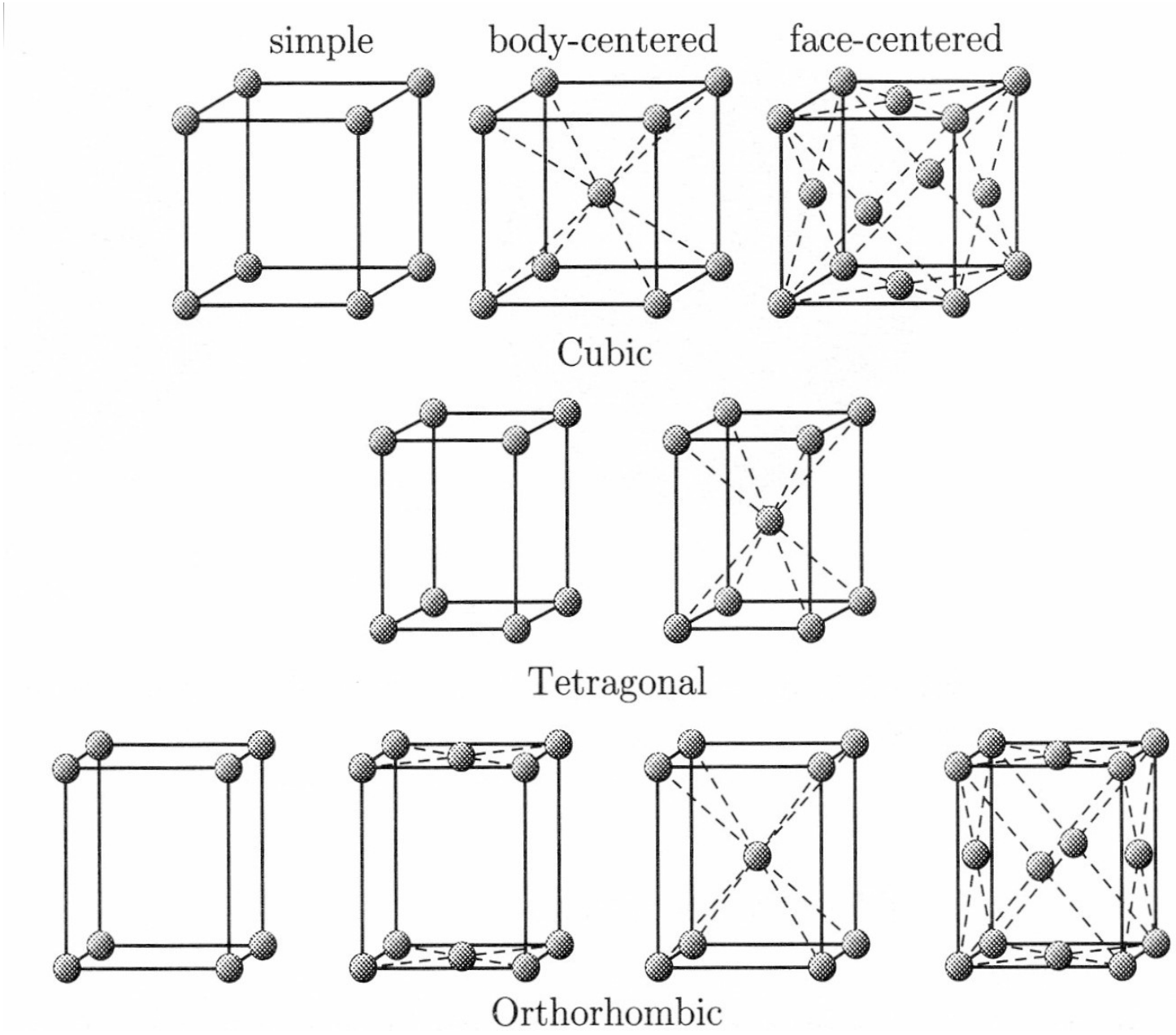
For example, 5-th or 7-th order rotation symmetry is incompatible with periodic crystal structure:

The set of all crystal symmetries determines the class of crystal lattice.



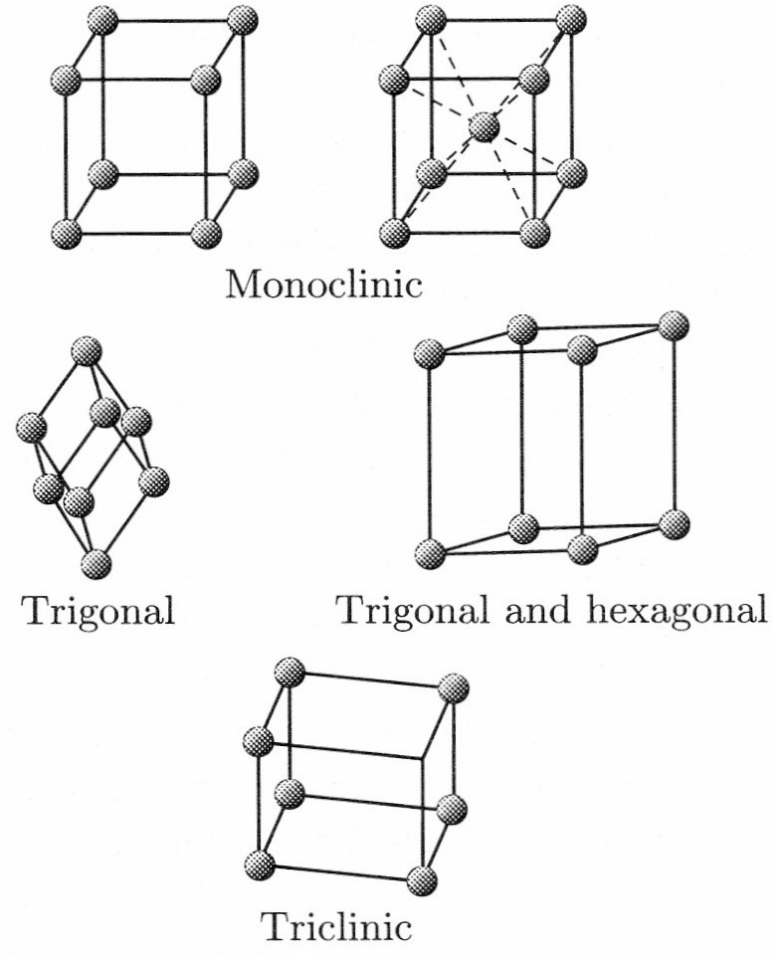
In 2D there are 5 different classes of crystal lattice, while in 3D there are 14 different symmetry classes.

9 of the 14 Bravais lattices in three dimensions

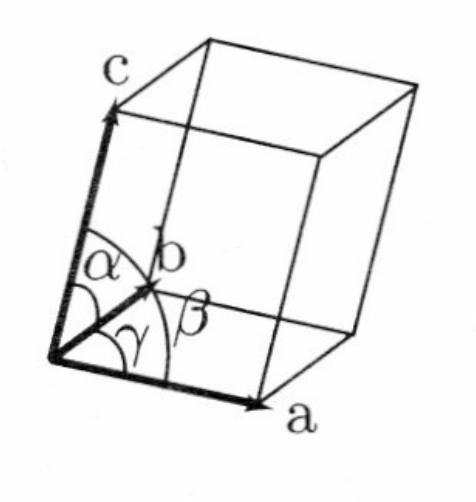


[from P. M. Chaikin and T. C. Lubensky, *Principles of Condensed Matter Physics* (Cambridge University Press, 2000)]

The remaining 5 of the 14 Bravais lattices



The lengths *a*, *b* and *c* and angles α, β and γ define the unit cell.



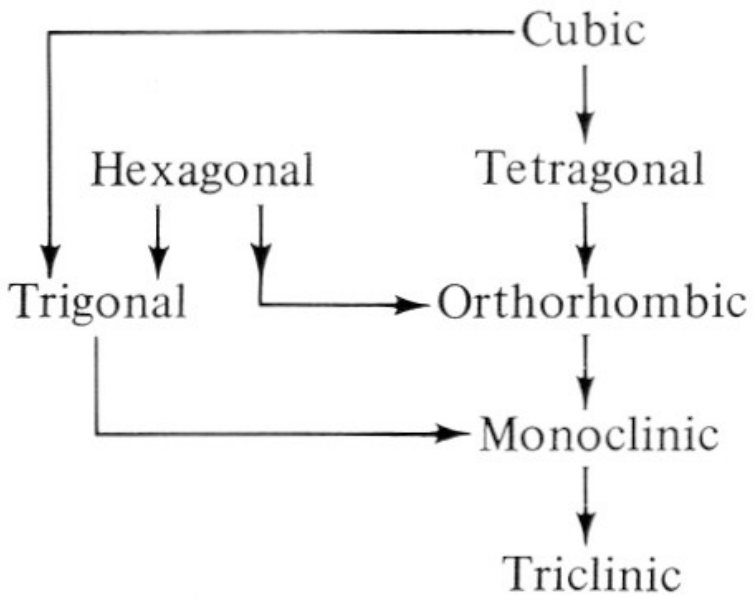
[from P. M. Chaikin and T. C. Lubensky, *Principles of Condensed Matter Physics* (Cambridge University Press, 2000)]

The 14 Bravais lattices in three dimensions

System	Number of lattices in system	Lattice symbols	Restrictions on conventional cell axes and angles
Triclinic	1	P	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$
Monoclinic	2	P,C	$a \neq b \neq c$ $\alpha = \gamma = 90^\circ \neq \beta$
Orthorhombic	4	P,C,I,F	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$
Tetragonal	2	P,I	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$
Cubic	3	P or SC I or BCC F of FCC	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$
Trigonal	1	R	$a = b = c$ $\alpha = \beta = \gamma < 120^\circ, \neq 90^\circ$
Hexagonal	1	P	$a = b \neq c$ $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$

[from P. M. Chaikin and T. C. Lubensky, *Principles of Condensed Matter Physics* (Cambridge University Press, 2000)]

The hierarchy of symmetries among the seven crystal systems. Each Bravais lattice point group contains all those that can be reached from it by moving in the direction of the arrows.



[from N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Sounders College Publishing, Fort Worth, 1976)]

Space group —the group of all translations and rotations that leave a crystal invariant.

Often the space group consists only of point group operations about symmetry points and translations by vectors in the direct lattice.

In this, the *symmorphic* case, the space group is a direct product of the point group and the translation group.

Glide planes and screw axes.

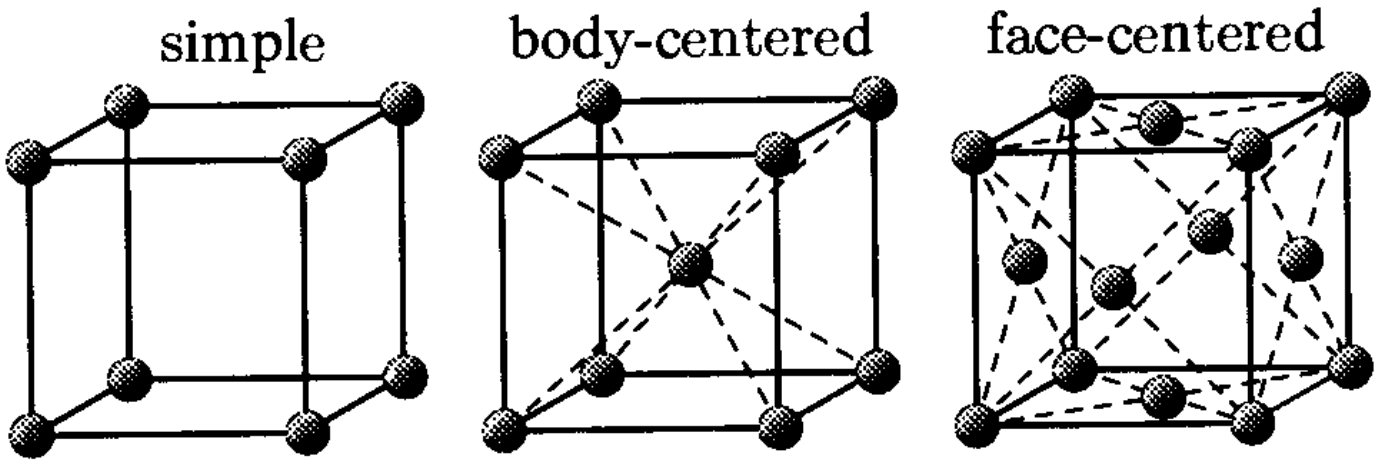
Nonsymmorphic space groups – *s*pace groups with glide planes or screw axes.

Point and space groups of Bravais lattices and crystal structures

	Bravais lattice (basis of spherical symmetry)	Crystal structure (basis of arbitrary symmetry)
Number of point groups:	7 ("the 7 crystal systems")	32 ("the 32 crystallographic point groups")
Number of space groups:	14 ("the 14 Bravais lattices")	230 ("the 230 space groups")

Table 2 Characteristics of cubic lattices[a]

	Simple	Body-centered	Face-centered
Volume, conventional cell	a^3	a^3	a^3
Lattice points per cell	1	2	4
Volume, primitive cell	a^3	$\frac{1}{2}a^3$	$\frac{1}{4}a^3$
Lattice points per unit volume	$1/a^3$	$2/a^3$	$4/a^3$
Number of nearest neighbors[a]	6	8	12
Nearest-neighbor distance	a	$3^{1/2}a/2 = 0.866a$	$a/2^{1/2} = 0.707a$
Number of second neighbors	12	6	6
Second neighbor distance	$2^{1/2}a$	a	a
Packing fraction[b]	$\frac{1}{6}\pi$ $= 0.524$	$\frac{1}{8}\pi\sqrt{3}$ $= 0.680$	$\frac{1}{6}\pi\sqrt{2}$ $= 0.740$



Point groups (Schoenflies notations)

In three dimensions, there are an infinite number of point groups, but all of them can be classified by several families.

- C_n (for cyclic) has an n-fold rotation axis.
  - C_{nh} is C_n with the addition of a mirror (reflection) plane perpendicular to the axis of rotation (*horizontal plane*).
  - C_{nv} is C_n with the addition of n mirror planes containing the axis of rotation (*vertical planes*).

S_{2n} (for *Spiegel*, German for mirror) contains only a $2n$-fold rotation-reflection axis. The index should be even because when n is odd an n-fold rotation-reflection axis is equivalent to a combination of an n-fold rotation axis and a perpendicular plane, hence $S_n = C_{nh}$ for odd n.

- D_n (for dihedral, or two-sided) has an n-fold rotation axis plus n twofold axes perpendicular to that axis.
  - D_{nh} has, in addition, a horizontal mirror plane and, as a consequence, also n vertical mirror planes each containing the n-fold axis and one of the twofold axes.
  - D_{nd} has, in addition to the elements of D_n, n vertical mirror planes which pass between twofold axes (*diagonal planes*).

Point groups (continuation)

- *T* (the chiral tetrahedral group) has the rotation axes of a tetrahedron (three 2-fold axes and four 3-fold axes).
  - T_d includes diagonal mirror planes (each diagonal plane contains only one twofold axis and passes between two other twofold axes, as in D_{2d}). This addition of diagonal planes results in three improper rotation operations $\mathbf{S_4}$.
  - T_h includes three horizontal mirror planes. Each plane contains two twofold axes and is perpendicular to the third twofold axis, which results in inversion center **i**.
- *O* (the chiral octahedral group) has the rotation axes of an octahedron or cube (three 4-fold axes, four 3-fold axes, and 6 diagonal 2-fold axes).
  - O_h includes horizontal mirror planes and, as a consequence, vertical mirror planes. It contains also inversion center and improper rotation operations.
- *I* (the chiral icosahedral group) indicates that the group has the rotation axes of an icosahedron or dodecahedron (six 5-fold axes, ten 3-fold axes, and 15 2-fold axes).
  - I_h includes horizontal mirror planes and contains also inversion center and improper rotation operations.

Hermann–Mauguin notations (**international notation**)

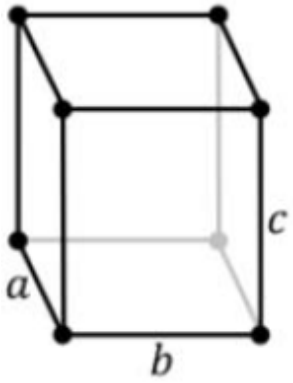
Schoenflies	**H–M symbol**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**...**	**∞**
C_n	n	3	4	5	6	7	8	9	10	11	12	...	∞
C_{nv}	nm	3m		5m		7m		9m		11m			∞m
	nmm		4mm		6mm		8mm		10mm		12mm		
S_{2n}	$\bar{n}$	3		5		7		9		11			$\frac{\infty}{m}$
S_n			4				8				12		
C^n_{2h}					$\bar{6}$				$\bar{10}$				
C_{nh}	$\frac{n}{m}$		$\frac{4}{m}$		$\frac{6}{m}$		$\frac{8}{m}$		$\frac{10}{m}$		$\frac{12}{m}$		
D_n	$n2$	32		52		72		92		(11)2			∞2
	$n22$		422		622		822		(10)22		(12)22		
D_{nd}	n^2_m	3^2_m		5^2_m		7^2_m		9^2_m		$\frac{(\bar{1}\bar{1})}{\frac{2}{m}}$			$\frac{\bar{\infty}}{m}m$
D^n_{2d}	$\bar{n}2m$ = $\bar{n}m2$		$\bar{4}2m$				$\bar{8}2m$				$(\bar{1}\bar{2})2m$		
D^n_{2h}					$\bar{6}m2$				$(\bar{1}\bar{0})m2$				
D_{nh}	$\frac{n\ 2\ 2}{m\ m\ m}$		$\frac{4\ 2}{m\ m}$ $\frac{2}{m}$		$\frac{6\ 2}{m\ m}$ $\frac{2}{m}$		$\frac{8\ 2}{m\ m}$ $\frac{2}{m}$		$\frac{10\ 2\ 2}{m\ m\ m}$		$\frac{12\ 2\ 2}{m\ m\ m}$		

Hermann–Mauguin (HM) notation (**international notation**)

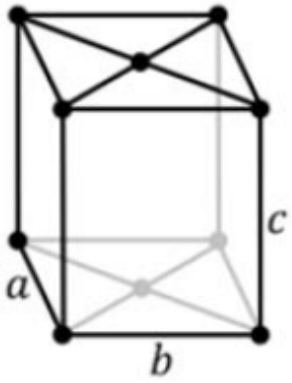
The Hermann–Mauguin notation, compared with the Schoenflies notation, is preferred in crystallography because it can easily be used to include translational symmetry elements, and it specifies the directions of the symmetry axes. Rotation axes are denoted by a number *n* — 1, 2, 3, 4, 5, 6, 7, 8 ... (angle of rotation $\varphi = 360°/n$). The rotoinversion axes are represented by the corresponding number with a macron, $\bar{n}$. If the symbol contains three positions, then they denote symmetry elements in the *x*, *y*, *z* direction, respectively. The direction of a symmetry element corresponds to its position in the Hermann–Mauguin symbol. If a rotation axis *n* and a mirror plane *m* have the same direction (i.e. the plane is perpendicular to axis *n*), then they are denoted as a fraction *n*/*m*. 1 and $\bar{1}$ (triclinic crystal system), 2, *m*, and 2/*m* (monoclinic), and 222, (2/*m* 2/*m* 2/*m*) and *mm*2 (orthorhombic). The short form of (2/*m* 2/*m* 2/*m*) is *mmm*. Plane groups can be depicted using the HM system. The first letter is lowercase **p** or **c** to represent primitive or centered unit cells. The next number is the rotational symmetry, as given above. The glide reflections are denoted **g**.

The symbol of a space group is defined by combining the uppercase letter describing the lattice type with symbols specifying the symmetry elements.

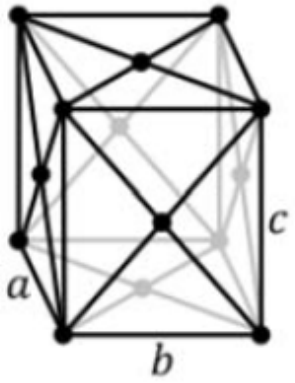
These are the Bravais lattice types in three dimensions:
P — Primitive
I — Body centered (from the German "Innenzentriert")
F — Face centered (from the German "Flächenzentriert")
A — Base centered on A faces only
B — Base centered on B faces only
C — Base centered on C faces only
R — Rhombohedral



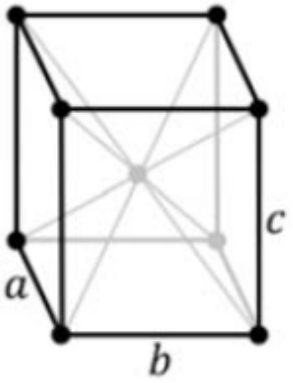
Primitive, ***P***



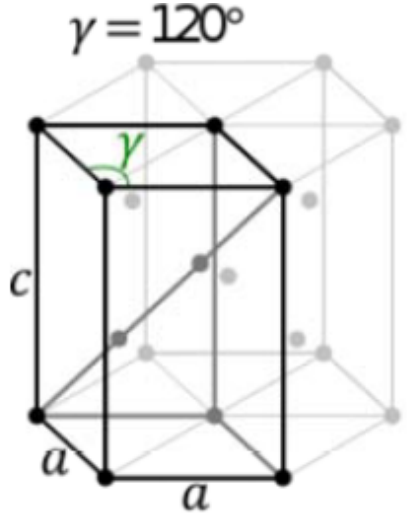
Base centered, ***C***



Face centered, ***F***

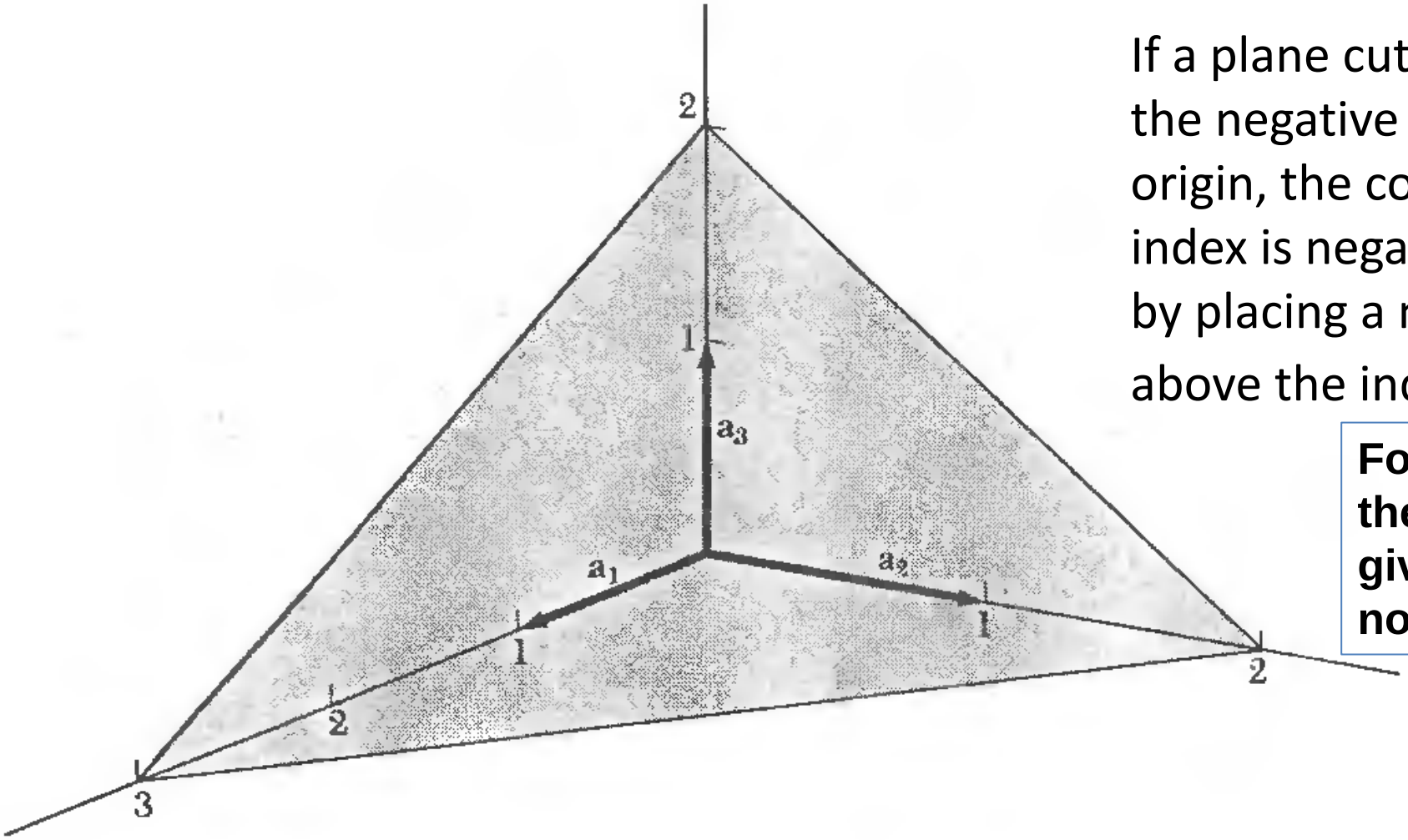


Body centered, ***I***



Rhombohedral in hexagonal setting, ***R***

Miller indices (to determine crystal planes)



If a plane cuts an axis on the negative side of the origin, the corresponding index is negative, indicated by placing a minus sign above the index: $(\bar{h}kl)$.

For cubic lattice the Miller indices give the vector, normal to plane.

Figure 13 This plane intercepts the a_1, a_2, a_3 axes at $3a_1$, $2a_2$, $2a_3$. The reciprocals of these numbers are $\frac{1}{3}$, $\frac{1}{2}$, $\frac{1}{2}$. The smallest three integers having the same ratio are 2, 3, 3, and thus the indices of the plane are (233).

Пример гранецентрированной кристаллической решетки

и представители кристаллов, имеющих структуру типа NaCl:

Кристалл	a, Å	Кристалл	a, Å
LiH	4,08	AgBr	5,77
NaCl	5,63	MgO	4,20
KCl	6,29	MnO	4,43
PbS	5,92	KBr	6,59

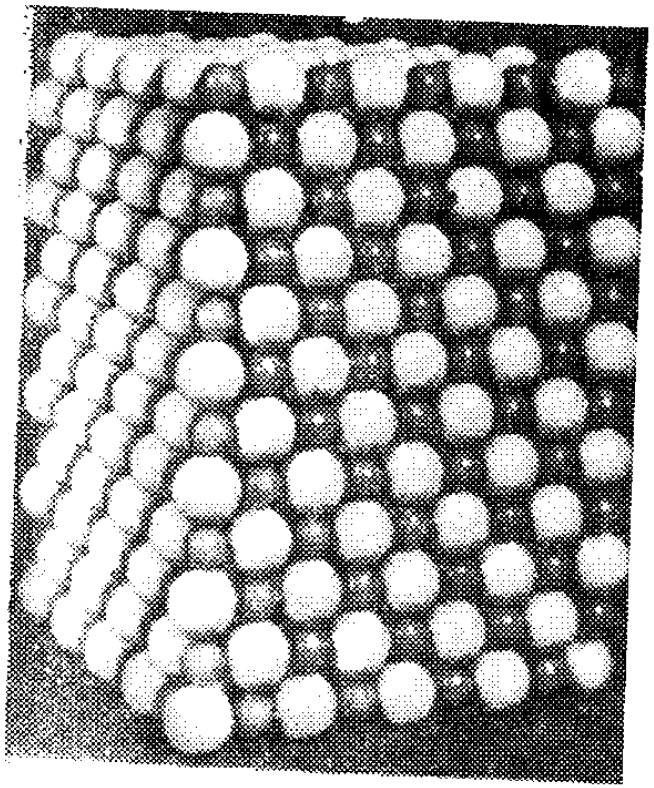


Рис. 1.23. Модель структуры хлористого натрия [20]. Ионы натрия имеют меньшие размеры, чем ионы хлора.

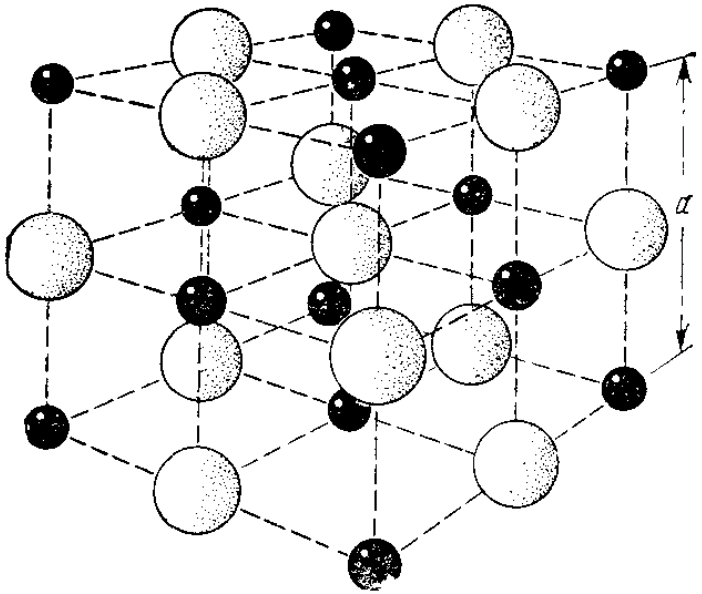


Рис. 1.24. Кристаллическая структура хлористого натрия. Пространственной решеткой является гранецентрированная кубическая решетка, а базис состоит из иона Na^+ с координатами 000 и иона Cl^- с координатами $\frac{1}{2}\frac{1}{2}\frac{1}{2}$.

Структура алмаза.

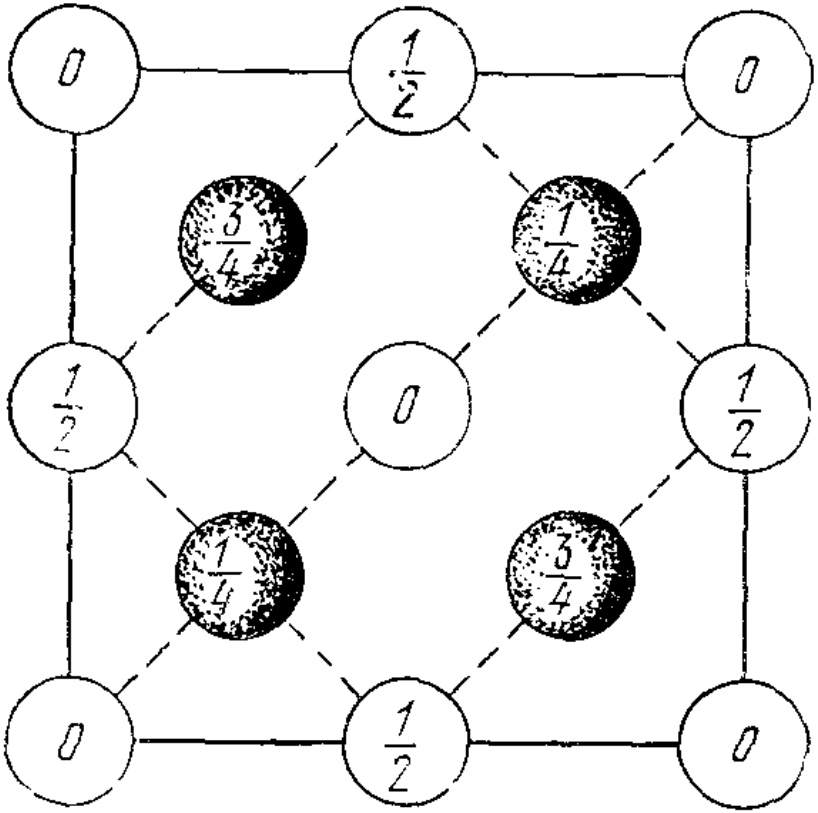
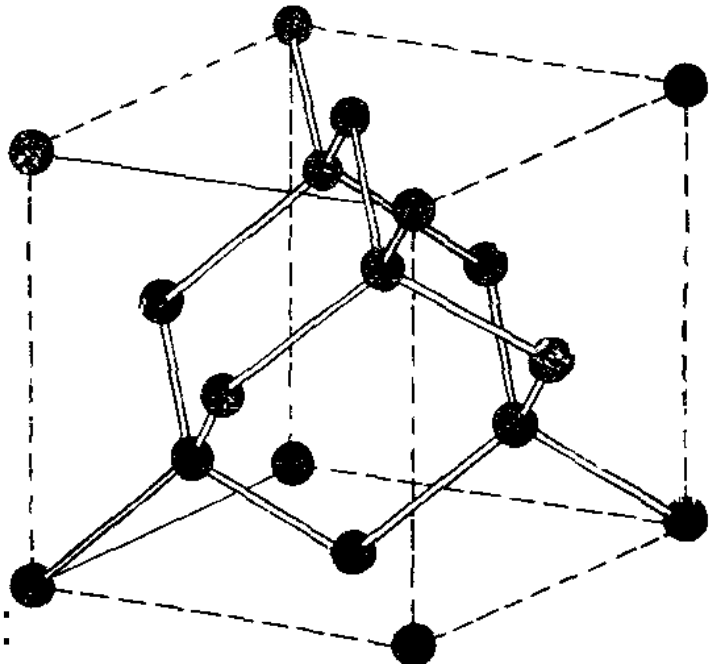


Рис 1.28 Расположение атомов в элементарной кубической ячейке алмаза (проекция на грань куба) Значения дробей указывают высоту атомов над базисной плоскостью (за единицу длины принято ребро куба) Точки с высотой 0 и $^1/_2$ составляют гранецентрированную кубическую решетку; точки с высотой $^1/_4$ и $^3/_4$ образуют такую же решетку, смещенную вдоль пространственной диагонали куба на четверть ее длины Базис состоит из двух одинаковых атомов, имеющих координаты 000 и $\frac{1}{4}\frac{1}{4}\frac{1}{4}$.

Пространственная решетка алмаза является кубической гранецентрированной. С каждым узлом решетки связан примитивный базис, состоящий из двух одинаковых атомов с координатами (000) **и (1/4, 1/4, 1/4)**



Изображение кристаллической структуры алмаза, показывающее тетраэдрическое расположение связей:

Пример объёмоцентрированной кристаллической решетки

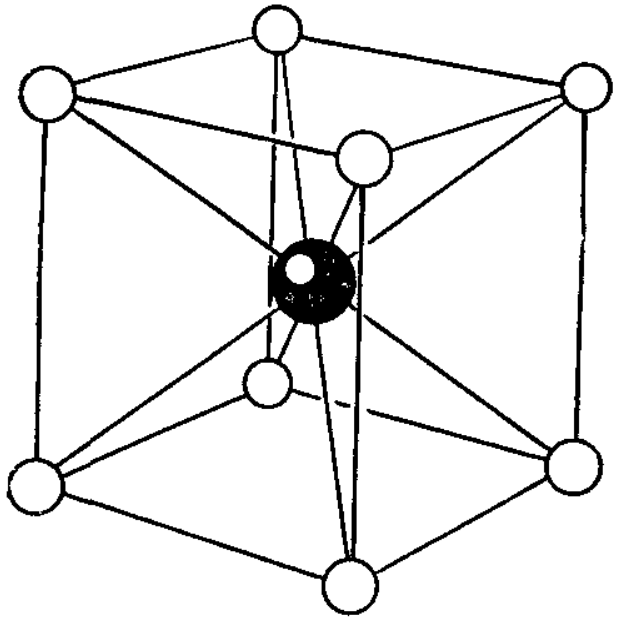


Рис. 1.26. Кристаллическая структура хлористого цезия. Пространственной решеткой является простая кубическая решетка, а базис состоит из иона Cs^+ с координатами 000 и иона Cl^- с координатами $\frac{1}{2}\frac{1}{2}\frac{1}{2}$.

и представители кристаллов, имеющих структуру типа CsCl:

Кристалл	a, Å	Кристалл	a, Å
CsCl	4,11	CuZn (β-латунь)	2,91
TlBr	3,97	AgMg	3,28
TlI	4,20	LiHg	3,29
NH_4Cl	3,87	AlNi	2,88
CuPd	2,99	BeCu	2,70

Hexagonal structures 1.

1. Tight-packed hexagonal structure

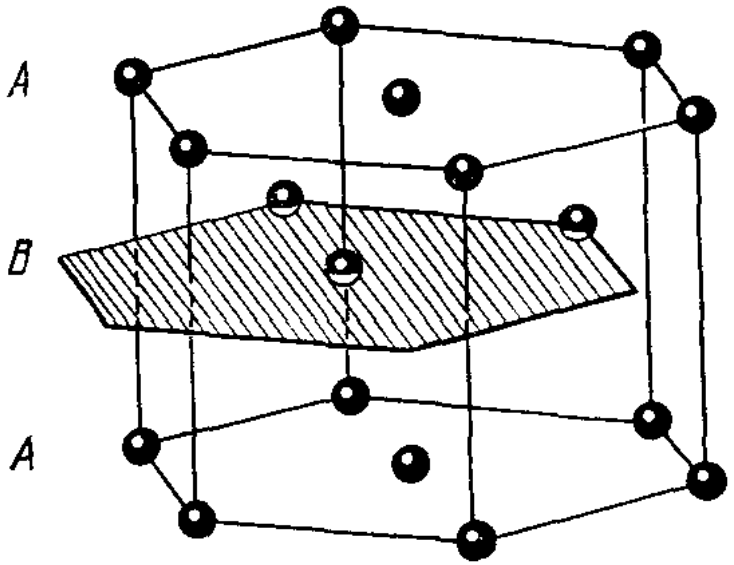
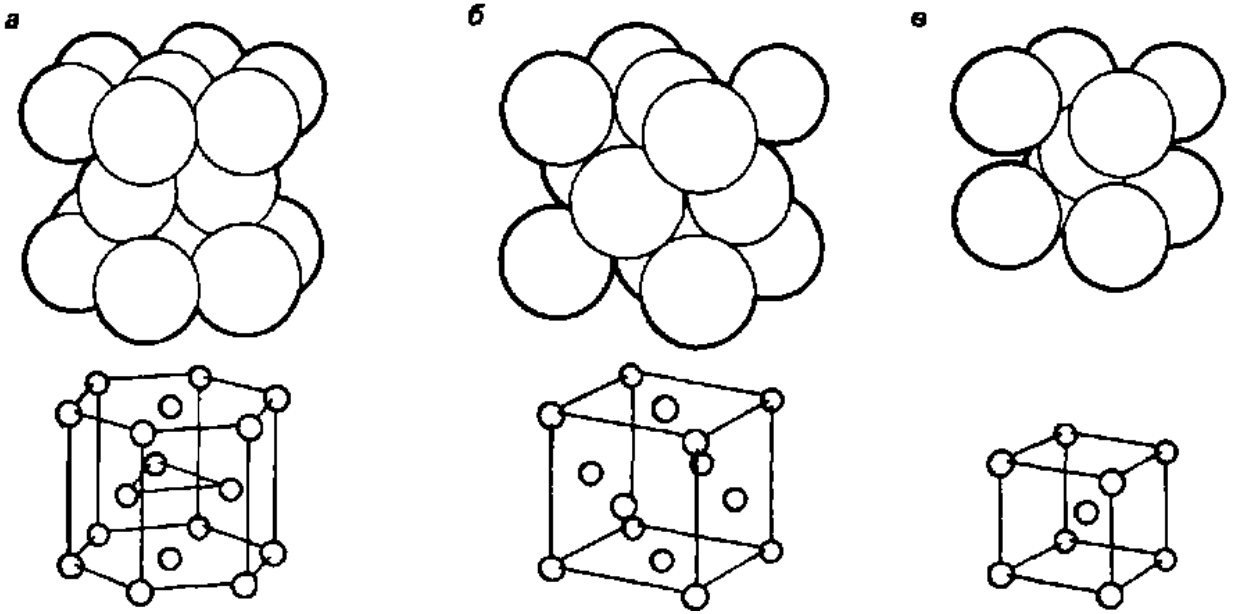


Рис. 1.27в. Гексагональная структура с плотной упаковкой. Расположение атомов в этой структуре не отвечает пространственной решетке. Пространственной решеткой является простая гексагональная решетка, базис которой состоит из двух одинаковых атомов, связанных с каждой точкой решетки.

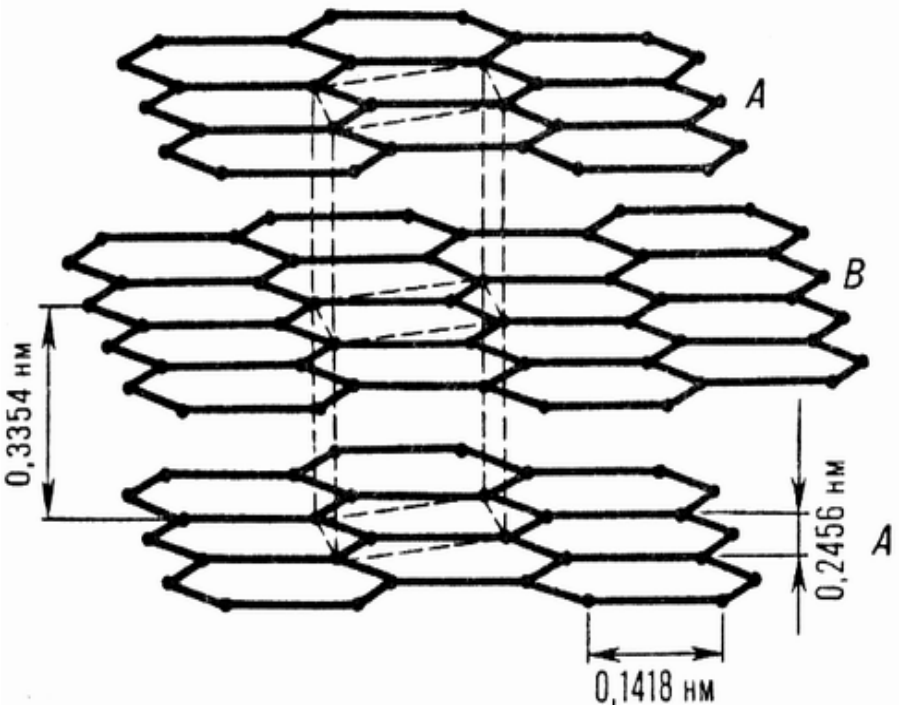
Examples of crystals with tight-packed hexagonal structure:

Кристалл	*c/a*	Кристалл	*c/a*	Кристалл	*c/a*
He	1,633	Zn	1,861	Zr	1,594
Be	1,581	Cd	1,886	Gd	1,592
Mg	1,623	Co	1,622	Lu	1,586
Ti	1,586	Y	1,570		

Packages of spheres:



Гексагональные структуры 2: кристаллическая решетка графита



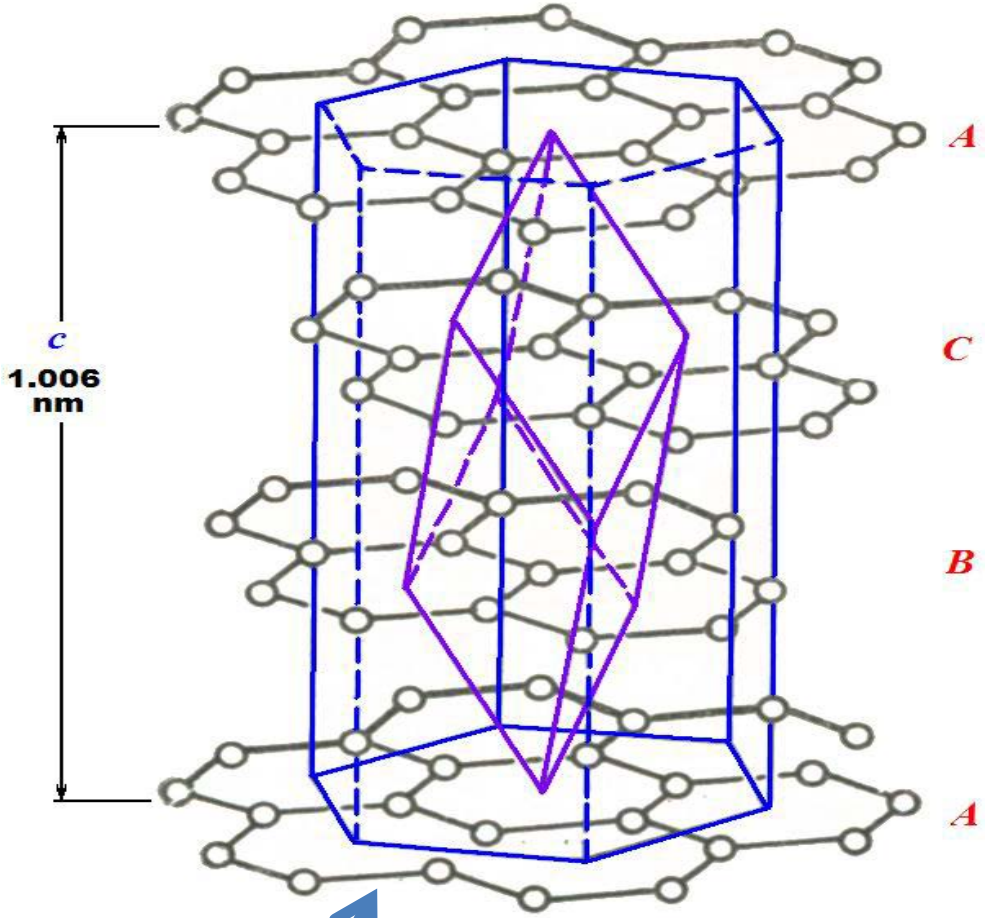


Рис. 1: кристаллическая решетка α-графита. **A, B-углеродные слои; пунктирными линиями показана элементарная кристаллическая ячейка**

Кристаллическая решетка графита бывает гексагональная и ромбоэдрическая. Гексагональная состоит из параллельных слоев (базисных плоскостей), образованных правильными шестиугольниками из атомов С. Углеродные атомы каждого слоя расположены против центров шестиугольников, находящихся в соседних слоях (нижнем и верхнем); положение слоев повторяется через один, а каждый слой сдвинут относительно другого в горизонтальном направлении на 0,1418 нм.