Crystal Structure

face-centered cubic
body-centered cubic
hexagonal close-packed
simple cubic
rhombohedral
diamond cubic
hexagonal
tetrahedral
complex

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H hcp																	He hcp
Li bcc	Be hcp											B rhom	C diamo	N cubic	O compl	F --	Ne fcc
Na bcc	Mg hcp											Al fcc	Si diamo	P compl	S compl	Cl compl	Ar fcc
K bcc	Ca fcc	Sc hcp	Ti hcp	V bcc	Cr bcc	Mn cubic	Fe bcc	Co hcp	Ni fcc	Cu fcc	Zn hcp	Ga compl	Ge diamo	As rhom	Se hexag	Br compl	Kr fcc
Rb bcc	Sr fcc	Y hcp	Zr hcp	Nb bcc	Mo bcc	Tc hcp	Ru hcp	Rh fcc	Pd fcc	Ag fcc	Cd hcp	In tetrah	Sn diamo	Sb rhom	Te hexag	I compl	Xe fcc
Cs bcc	Ba bcc	La hexag	Hf hcp	Ta bcc	W bcc	Re hcp	Os hcp	Ir fcc	Pt fcc	Au fcc	Hg rhom	Tl hcp	Pb fcc	Bi rhom	Po sc	At --	Rn --
Fr --	Ra --	Ac fcc	Rf --	Db --	Sg --	Bh --	Hs --	Mt --	Uun --	Uuu --	Uub --	113 --	Uuq --	115 --	116 --	117 --	118 --

Ce fcc	Pr hexag	Nd hexag	Pm --	Sm compl	Eu bcc	Gd hcp	Tb hcp	Dy hcp	Ho hcp	Er hcp	Tm hcp	Yb fcc	Lu hcp
Th fcc	Pa tetrah	U compl	Np compl	Pu compl	Am hexag	Cm --	Bk --	Cf --	Es --	Fm --	Md --	No --	Lr --

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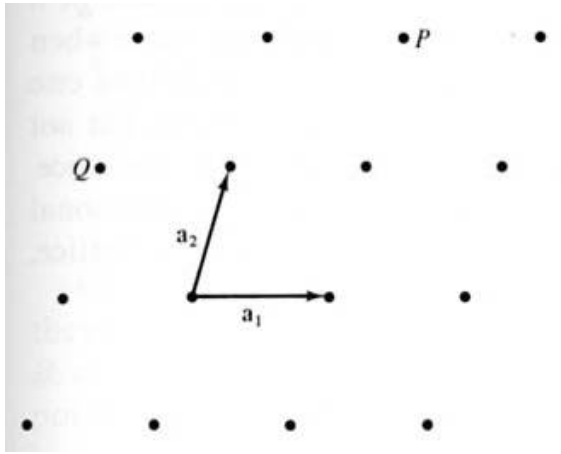
Bravais lattice

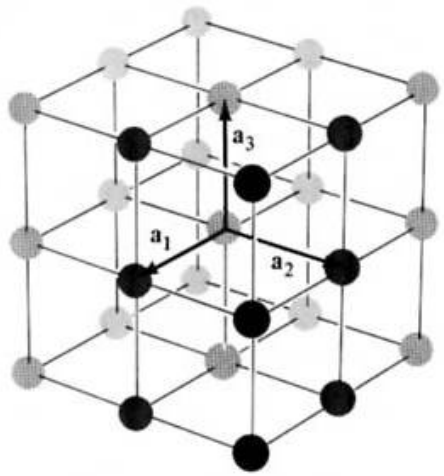
a lattice is a regular periodic array of points in space
a (3D) Bravais lattice consists of all points with position vectors **R** of the form
$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$ where $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ are any vectors not all in the same plane
and n_i range through all the integer values

$\mathbf{a}_i$ – primitive vectors
primitive vectors generate the lattice

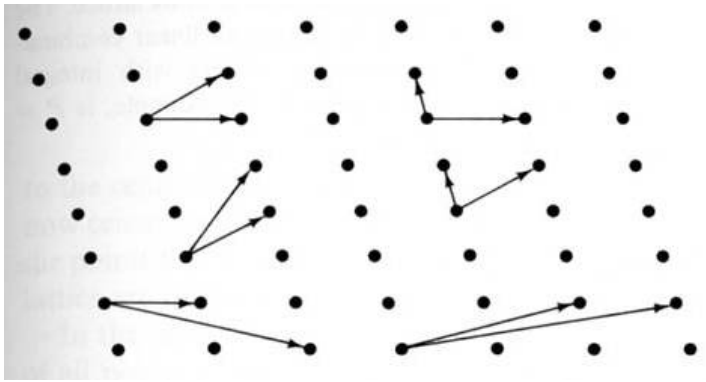
the Bravais lattice specifies the periodic array in which the repeated units of the crystal are arranged
the units themselves may be single atoms, groups of atoms, molecules, ions, etc.



2D Bravais lattice
$\mathbf{P} = \mathbf{a}_1 + 2\mathbf{a}_2$
$\mathbf{Q} = -\mathbf{a}_1 + \mathbf{a}_2$



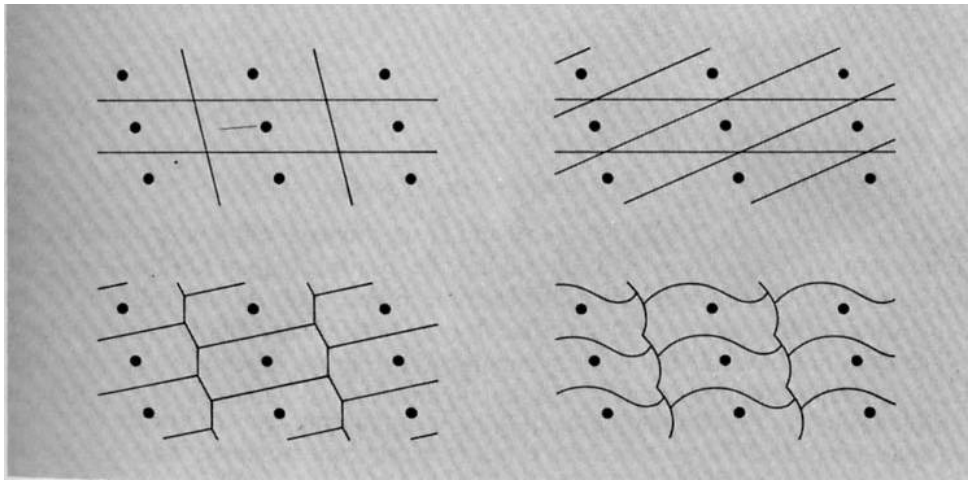
a simple cubic
3D Bravais lattice



the set of primitive vectors is not unique – there are infinitely many nonequivalent choices

primitive cell

a volume of space that, when translated through all the vectors in a Bravais lattice, just fills all the space without overlapping itself or leaving voids is called a primitive cell or primitive unit cell of the lattice



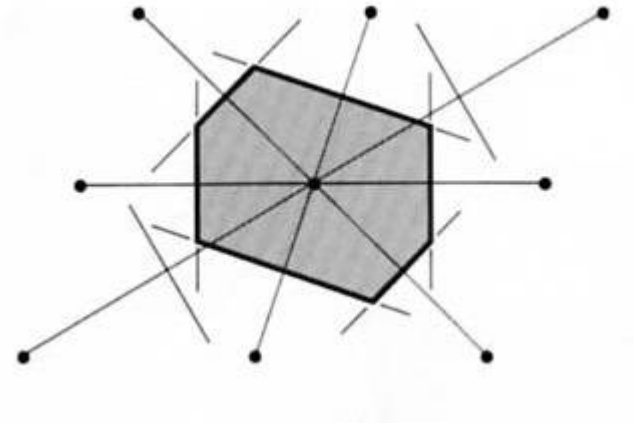
several possible choices of primitive cell
there is no unique way of choosing a primitive cell for a given Bravais lattice

a primitive cell must contain exactly one lattice point

the volume of the primitive cell $v = V/N = 1/n$, where n is the density of points in the lattice

the volume of the primitive cell is independent of the choice of cell

Wigner-Seitz cell
a primitive cell with the full symmetry of the Bravais lattice

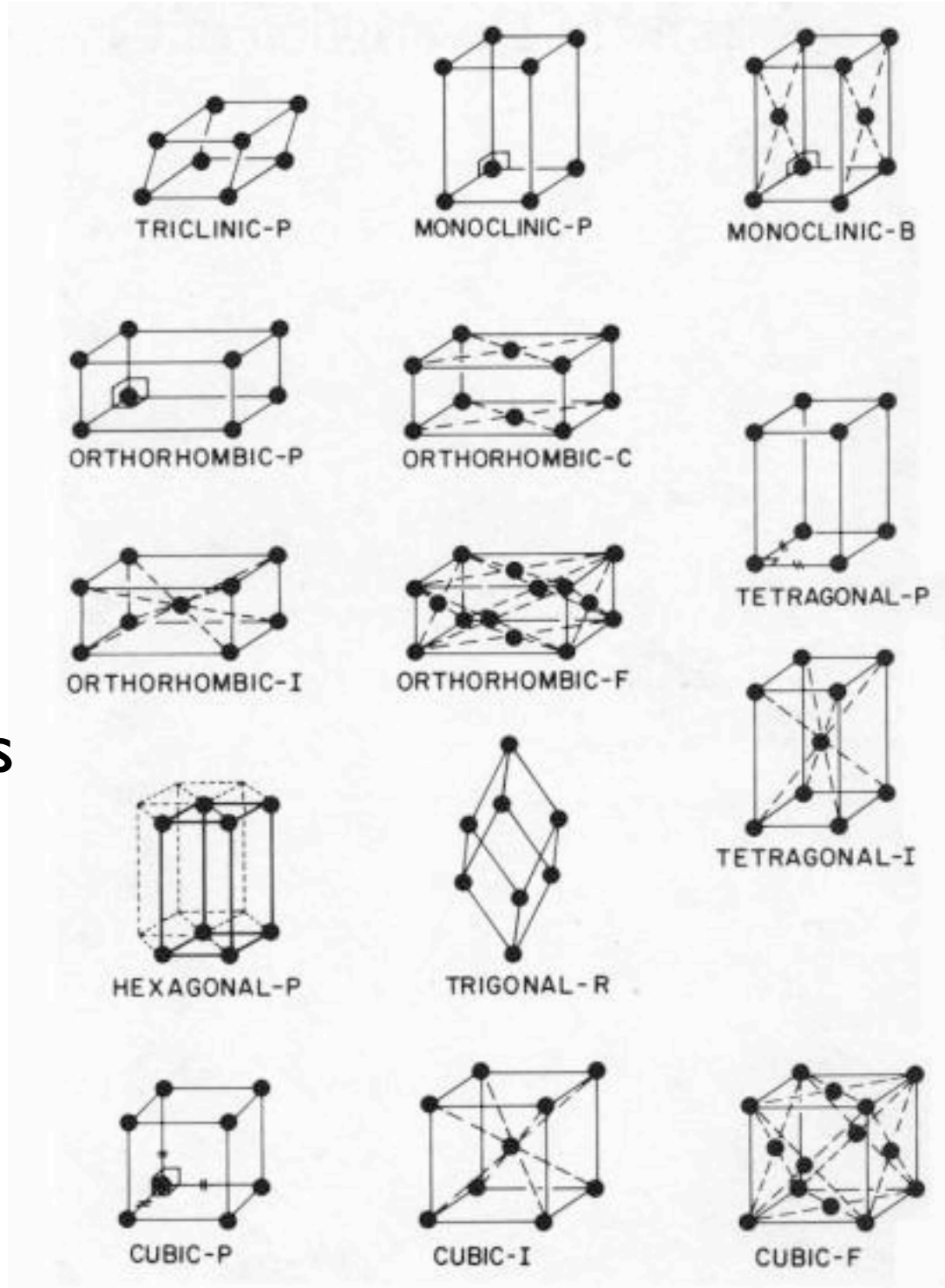


Bravais lattices

(few notes/
pictures
complementary to
the A&M book)

The 14 Bravais lattices in 3D

the dashed lines in this figure indicate
the nearest neighbour distances =>



M. Peressi
Cond Matt Phys 1, UniTS

see also this figure that specifies the cell parameters (distances and angles):

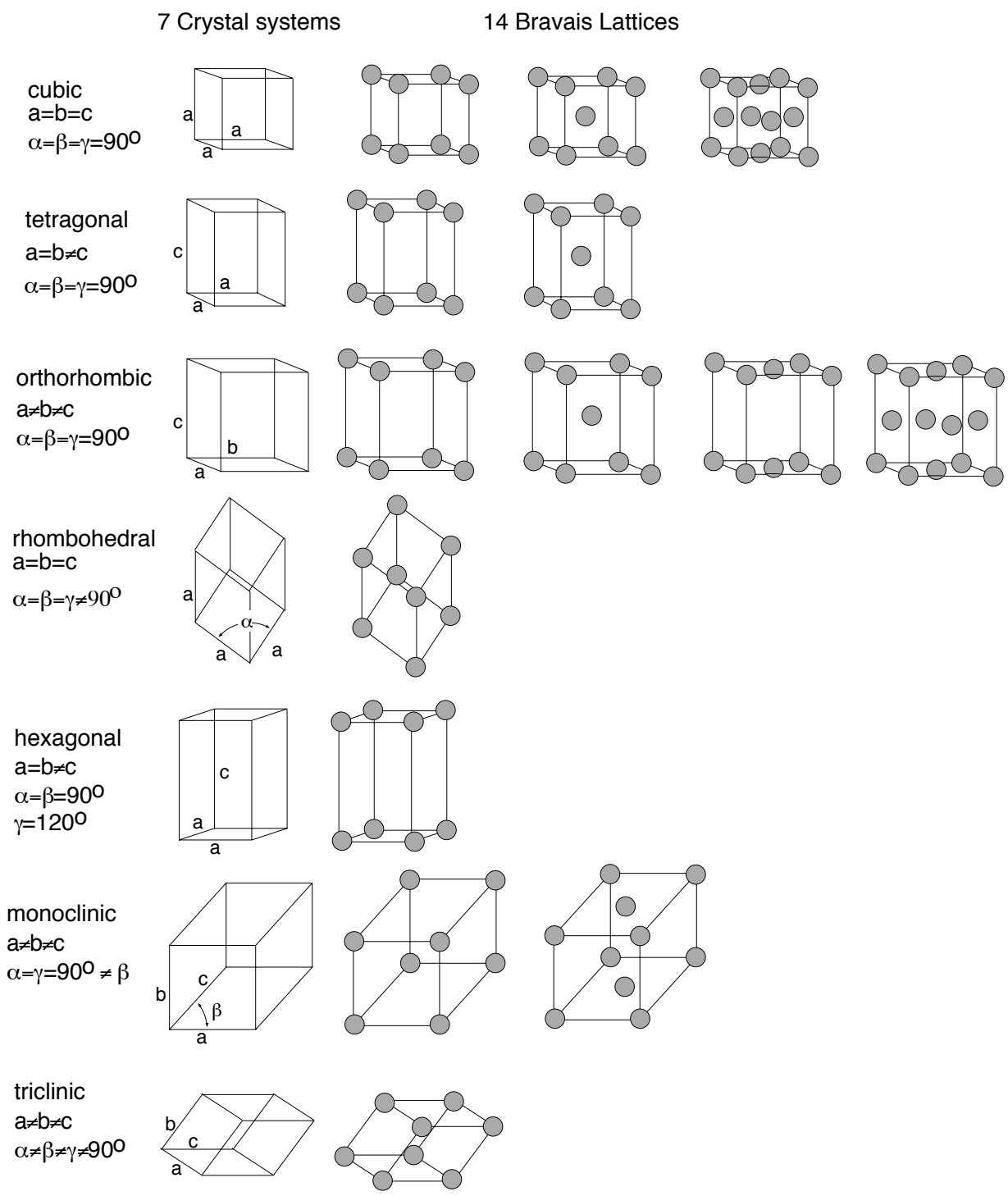
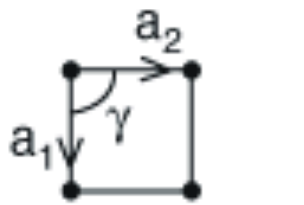


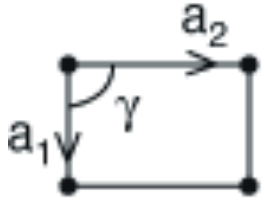
Figure 4 The 7 crystal systems and the 14 Bravais lattices

The 5 Bravais lattices in 2D

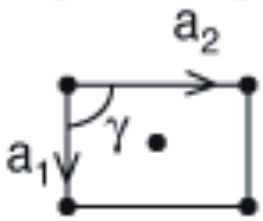


square $a_1 = a_2$ $\gamma = 90°$

hexagonal $a_1 = a_2$ $\gamma = 120°$



rectangular $a_1 \neq a_2$ $\gamma = 90°$



centered rectangular $a_1 \neq a_2$ $\gamma = 90°$

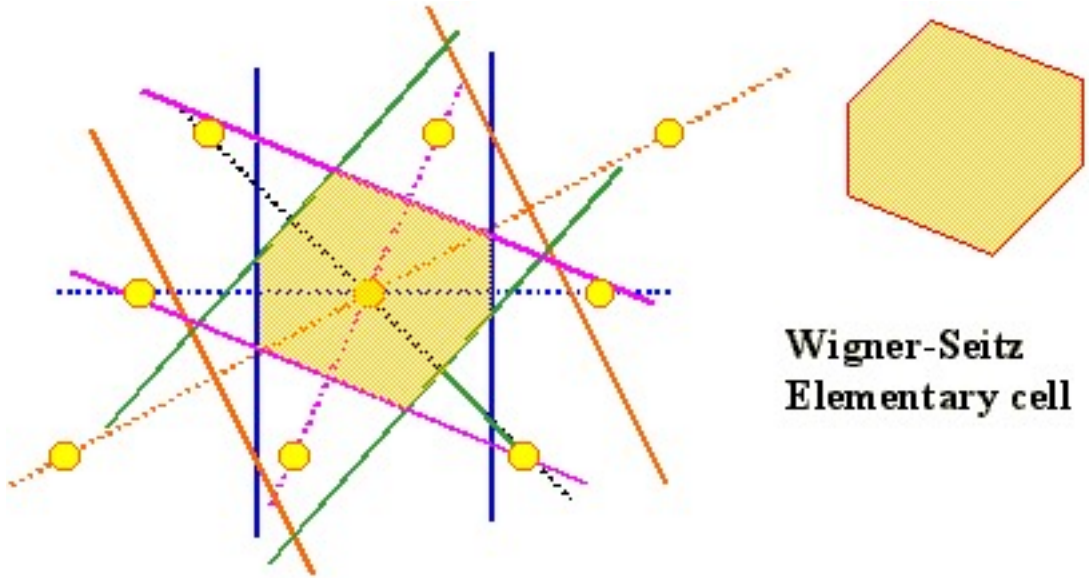
oblique $a_1 \neq a_2$ $\gamma \neq 90°, 120°$

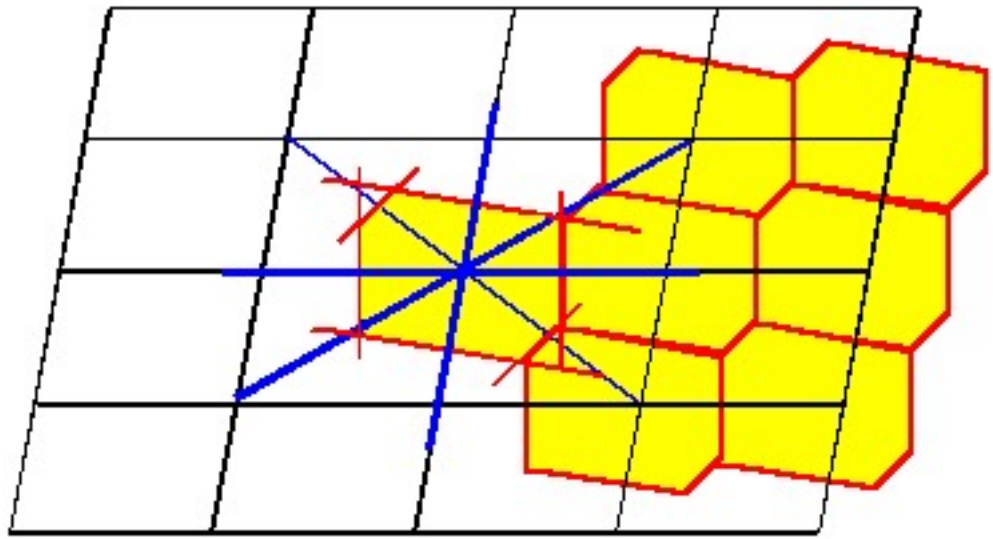
Wigner-Seitz cell

around a lattice point

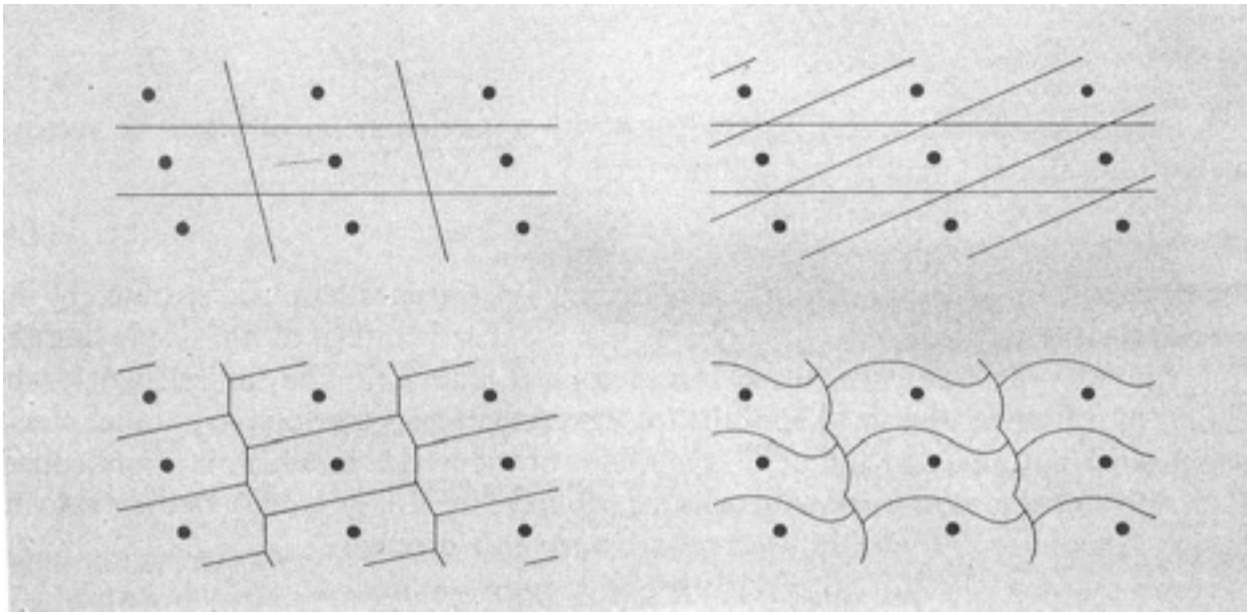
- region of space that is closer to that point than to any other lattice point (topological def.)
- each point pertains to 1 WS cell
- translation => covers the whole space
- no reference to a particular choice of the primitive vectors: same symmetry of the lattice!

a Wigner-Seitz cell: construction and properties

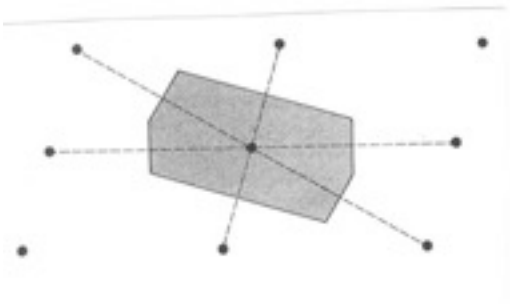




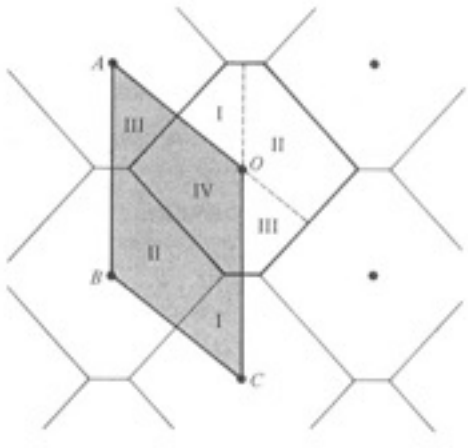
2D examples



some possible choices of **primitive unit cells** for oblique lattice

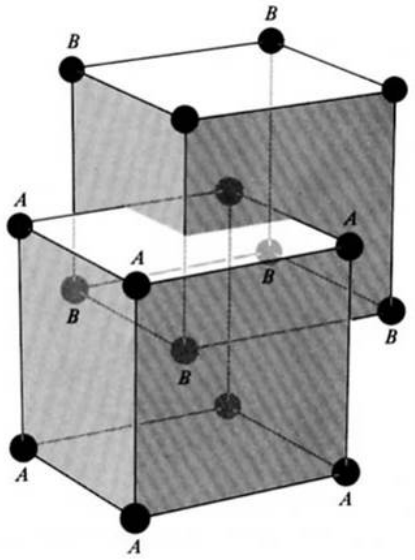


Wigner-Seitz cell for oblique lattice

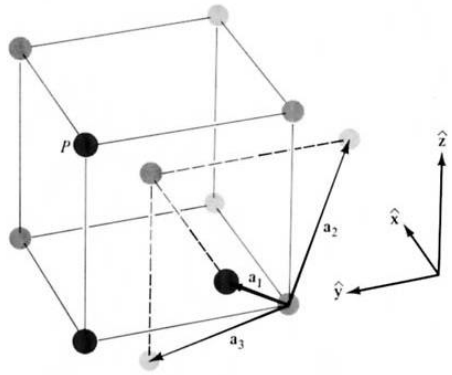


examples of crystal structures

body-centered-cubic (bcc) Bravais lattice



bcc = $sc_A + sc_B$

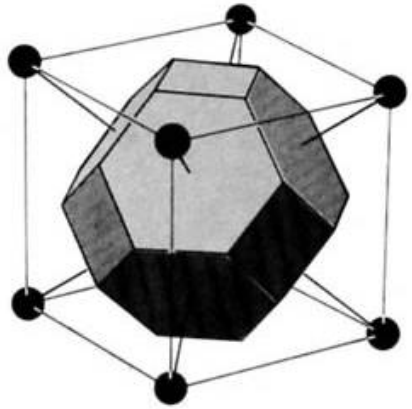


a set of primitive vectors

$$\mathbf{a}_1 = \frac{a}{2}(\mathbf{y}+\mathbf{z}-\mathbf{x})$$

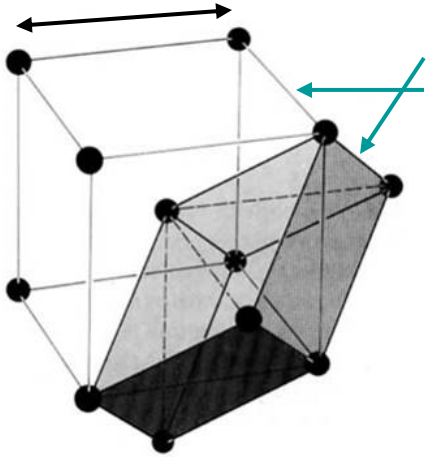
$$\mathbf{a}_2 = \frac{a}{2}(\mathbf{z}+\mathbf{x}-\mathbf{y})$$

$$\mathbf{a}_3 = \frac{a}{2}(\mathbf{x}+\mathbf{y}-\mathbf{z})$$



the Wigner-Seitz cell of the bcc Bravais lattice
a "truncated octahedron"

a – lattice constant



primitive and unit cell or conventional unit cell

generally chosen to have the lattice symmetry

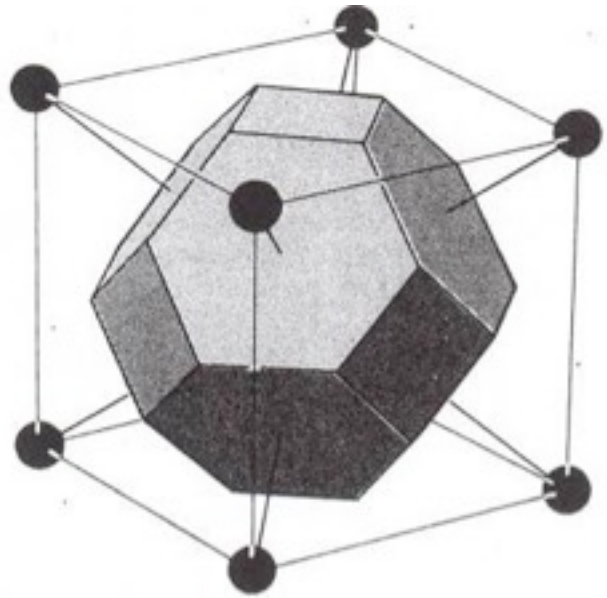
bcc lattices are described by cubic unit cell

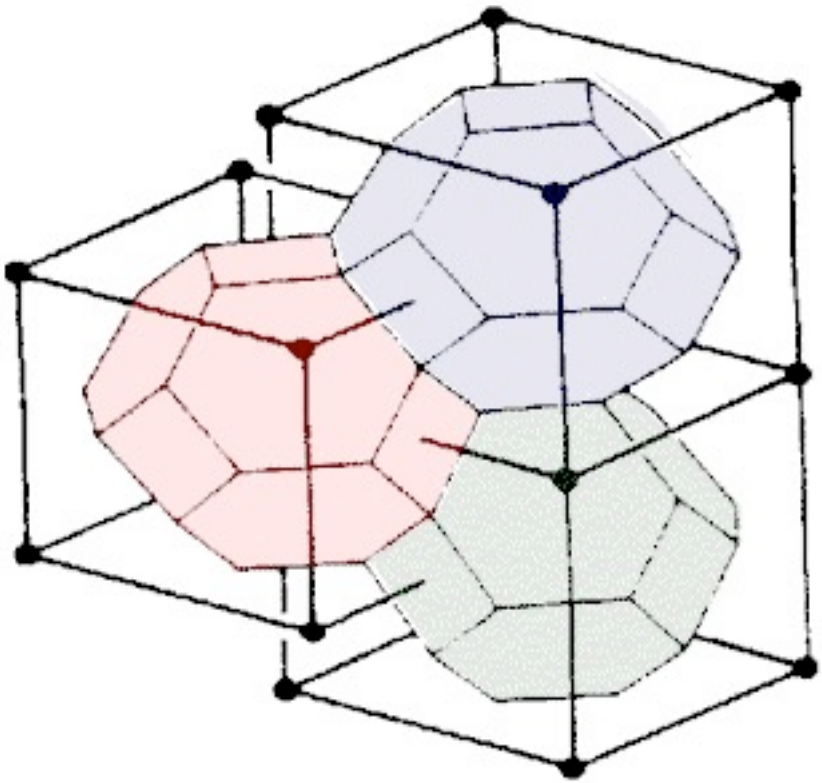
ELEMENTS WITH THE MONATOMIC BODY-CENTERED CUBIC CRYSTAL STRUCTURE

ELEMENT	a (Å)	ELEMENT	a (Å)	ELEMENT	a (Å)
Ba	5.02	Li	3.49 (78 K)	Ta	3.31
Cr	2.88	Mo	3.15	Tl	3.88
Cs	6.05 (78 K)	Na	4.23 (5 K)	V	3.02
Fe	2.87	Nb	3.30	W	3.16
K	5.23 (5 K)	Rb	5.59 (5 K)		

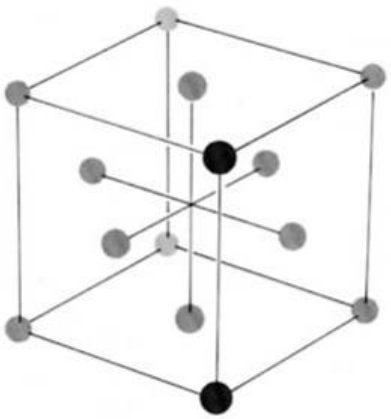
3D examples: Wigner - Seitz cell for BCC

The Wigner-Seitz cell for the body-centered cubic Bravais lattice (a "truncated octahedron"). The surrounding cube is a conventional body-centered cubic cell with a lattice point at its center and on each vertex. The hexagonal faces bisect the lines joining the central point to the points on the vertices (drawn as solid lines). The square faces bisect the lines joining the central point to the central points in each of the six neighboring cubic cells (not drawn). The hexagons are regular (see

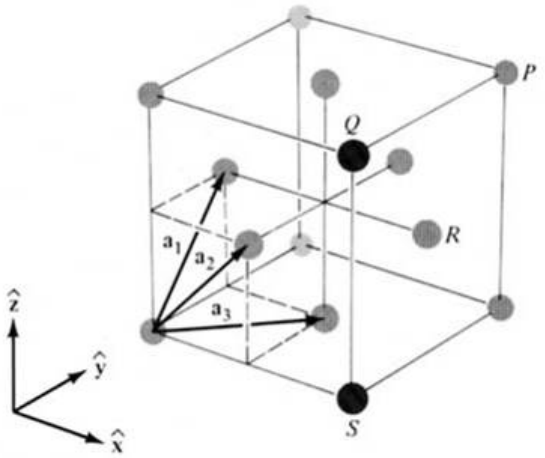




face-centered-cubic (fcc) Bravais lattice



fcc Bravais lattice

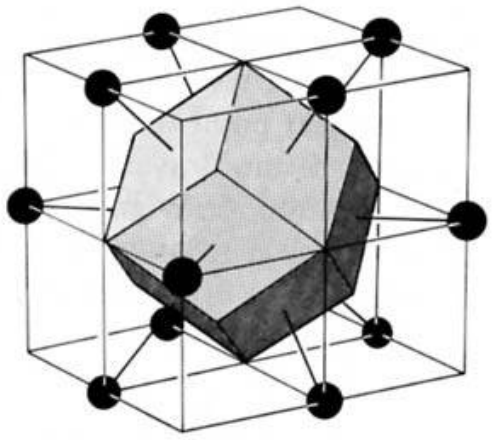


a set of primitive vectors

$$\mathbf{a}_1 = \frac{a}{2}(\mathbf{y}+\mathbf{z})$$

$$\mathbf{a}_2 = \frac{a}{2}(\mathbf{z}+\mathbf{x})$$

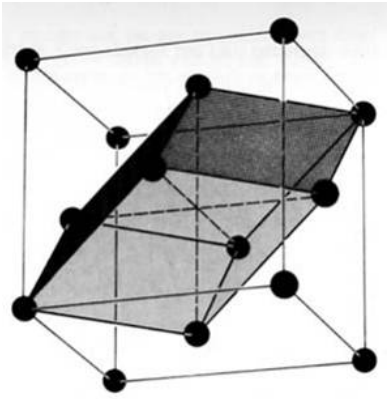
$$\mathbf{a}_3 = \frac{a}{2}(\mathbf{x}+\mathbf{y})$$



the Wigner-Seitz cell of the fcc Bravais lattice

a "rhombic dodecahedron"

the surrounding cube is not the conventional unit cell but one in which lattice points are at the center of the cube



primitive cell and <u>unit cell</u>

fcc lattices are described by cubic unit cell

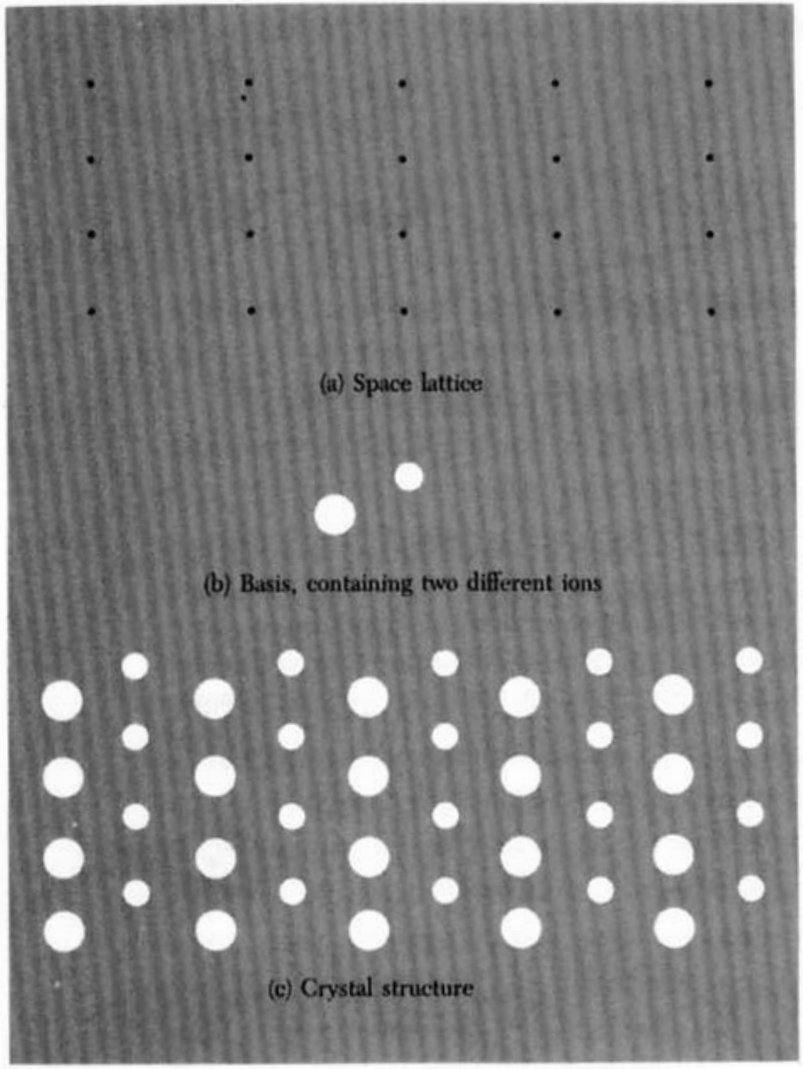
ELEMENTS WITH THE MONATOMIC FACE-CENTERED CUBIC CRYSTAL STRUCTURE

ELEMENT	a (Å)	ELEMENT	a (Å)	ELEMENT	a (Å)
Ar	5.26 (4.2 K)	Ir	3.84	Pt	3.92
Ag	4.09	Kr	5.72 (58 K)	δ-Pu	4.64
Al	4.05	La	5.30	Rh	3.80
Au	4.08	Ne	4.43 (4.2 K)	Sc	4.54
Ca	5.58	Ni	3.52	Sr	6.08
Ce	5.16	Pb	4.95	Th	5.08
β-Co	3.55	Pd	3.89	Xe (58 K)	6.20
Cu	3.61	Pr	5.16	Yb	5.49

Crystalline lattices with basis

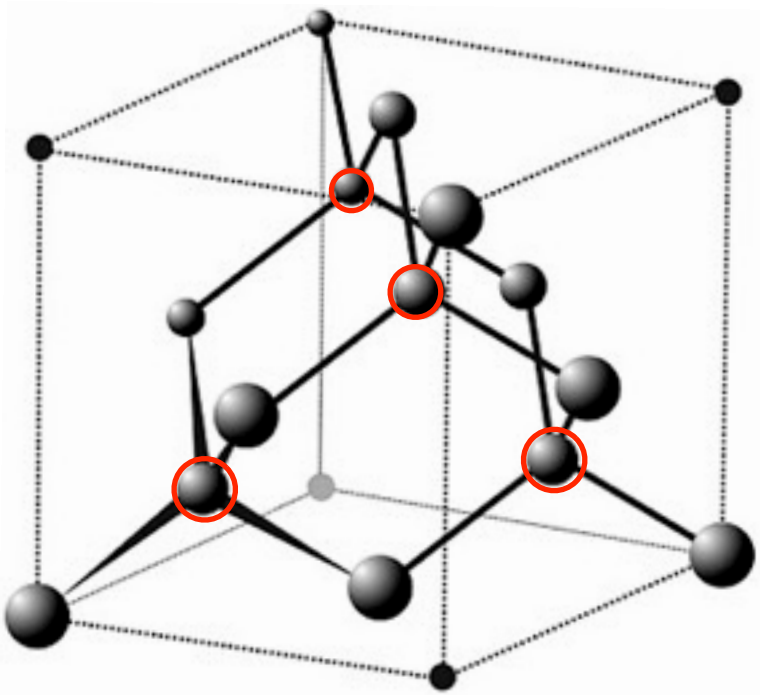
crystal structure consists of identical points of the same physical unit, called the basis, located at all the points of a Bravais lattice

crystal structure is a lattice with a basis

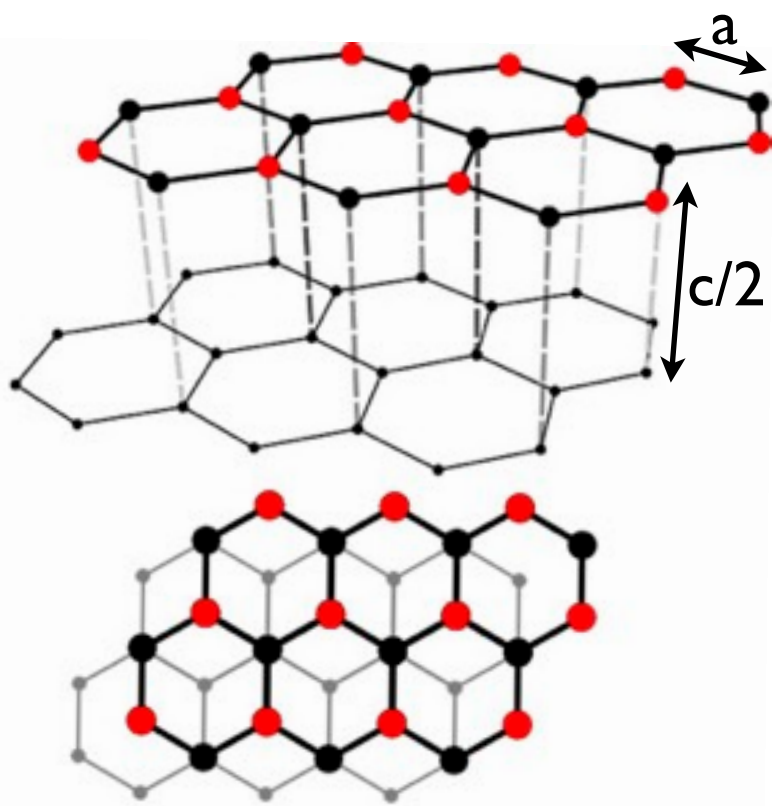


Crystalline lattices with basis

example: two allotropic forms of Carbon (elemental solid - only **one** atomic type)



diamond
(FCC+basis)



graphite
(HEX+basis)

primitive vectors
and
vectors of the basis:

$$a_1 = a\left(\frac{1}{2}, \frac{\sqrt{3}}{2}, 0\right)$$
$$a_2 = a\left(-\frac{1}{2}, \frac{\sqrt{3}}{2}, 0\right)$$
$$a_3 = c\,(0, 0, 1)$$

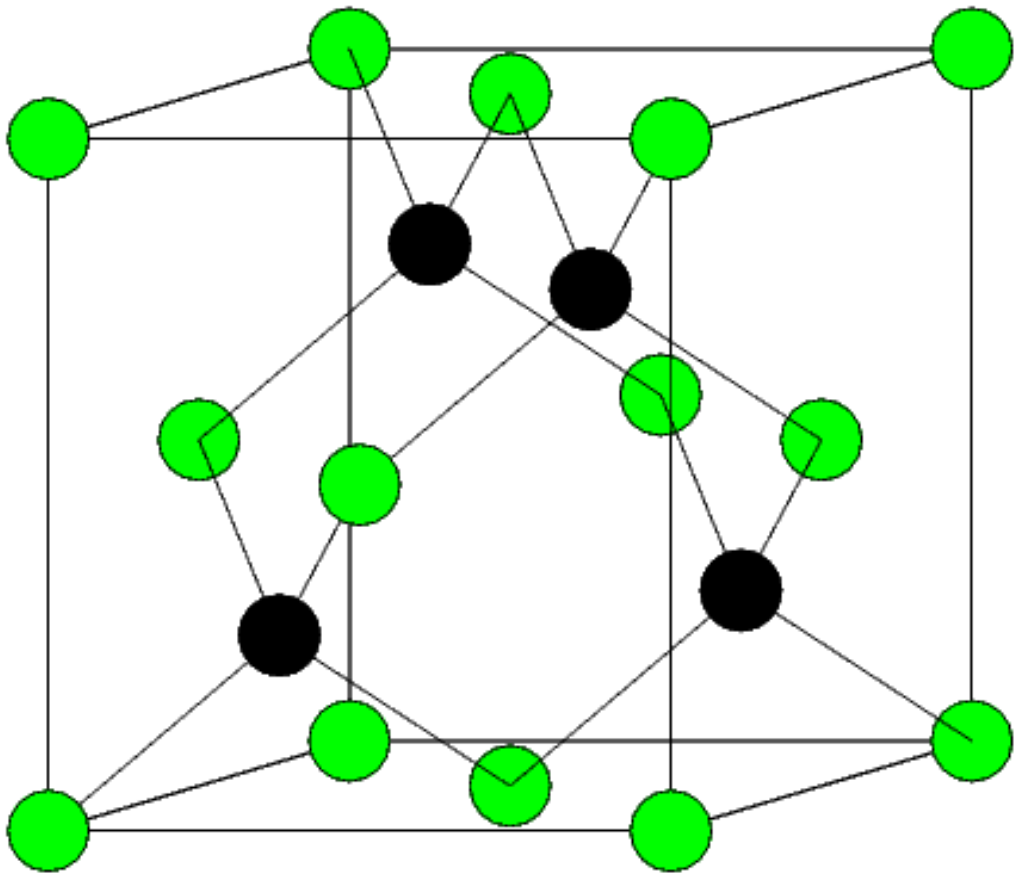
$$d_1 = (0, 0, 0)$$
$$d_2 = \left(0, \frac{a}{\sqrt{3}}, 0\right)$$
$$d_3 = \left(0, 0, \frac{c}{2}\right)$$
$$d_4 = \left(0, \frac{2a}{\sqrt{3}}, \frac{c}{2}\right)$$

zincblende

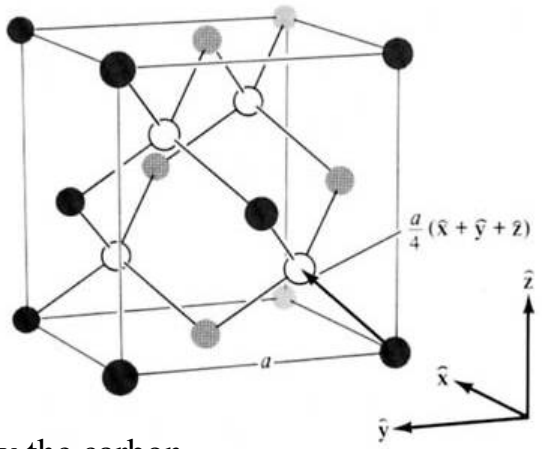
(NOT a Bravais lattice: FCC+basis with 2 different atoms)

reduces to diamond

in case of one atomic type



diamond structure **zincblende structure**



formed by the carbon in a diamond crystal

the diamond lattice consists of two interpenetrating fcc Bravais lattices displaced by $(a/4)(\mathbf{x}+\mathbf{y}+\mathbf{z})$

diamond lattice is fcc lattice with the two point basis 0 and $(a/4)(\mathbf{x}+\mathbf{y}+\mathbf{z})$

ZnS consists of equal number of zinc and sulfur ions distributed on a diamond lattice so that each Zn has 4 S as its nearest neighbors
= fcc lattice with a basis consisting of Zn at 0 and S at $(a/4)(\mathbf{x}+\mathbf{y}+\mathbf{z})$

ELEMENTS WITH THE DIAMOND CRYSTAL STRUCTURE

ELEMENT	CUBE SIDE a (Å)
C (diamond)	3.57
Si	5.43
Ge	5.66
α-Sn (grey)	6.49

SOME COMPOUNDS WITH THE ZINCBLENDE STRUCTURE

CRYSTAL	a (Å)	CRYSTAL	a (Å)	CRYSTAL	a (Å)
CuF	4.26	ZnS	5.41	AlSb	6.13
CuCl	5.41	ZnSe	5.67	GaP	5.45
CuBr	5.69	ZnTe	6.09	GaAs	5.65
CuI	6.04	CdS	5.82	GaSb	6.12
AgI	6.47	CdTe	6.48	InP	5.87
BeS	4.85	HgS	5.85	InAs	6.04
BeSe	5.07	HgSe	6.08	InSb	6.48
BeTe	5.54	HgTe	6.43	SiC	4.35
MnS (red)	5.60	AlP	5.45		
MnSe	5.82	AlAs	5.62		

Hexagonal closed packed
(NOT a Bravais lattice: HEX+basis)

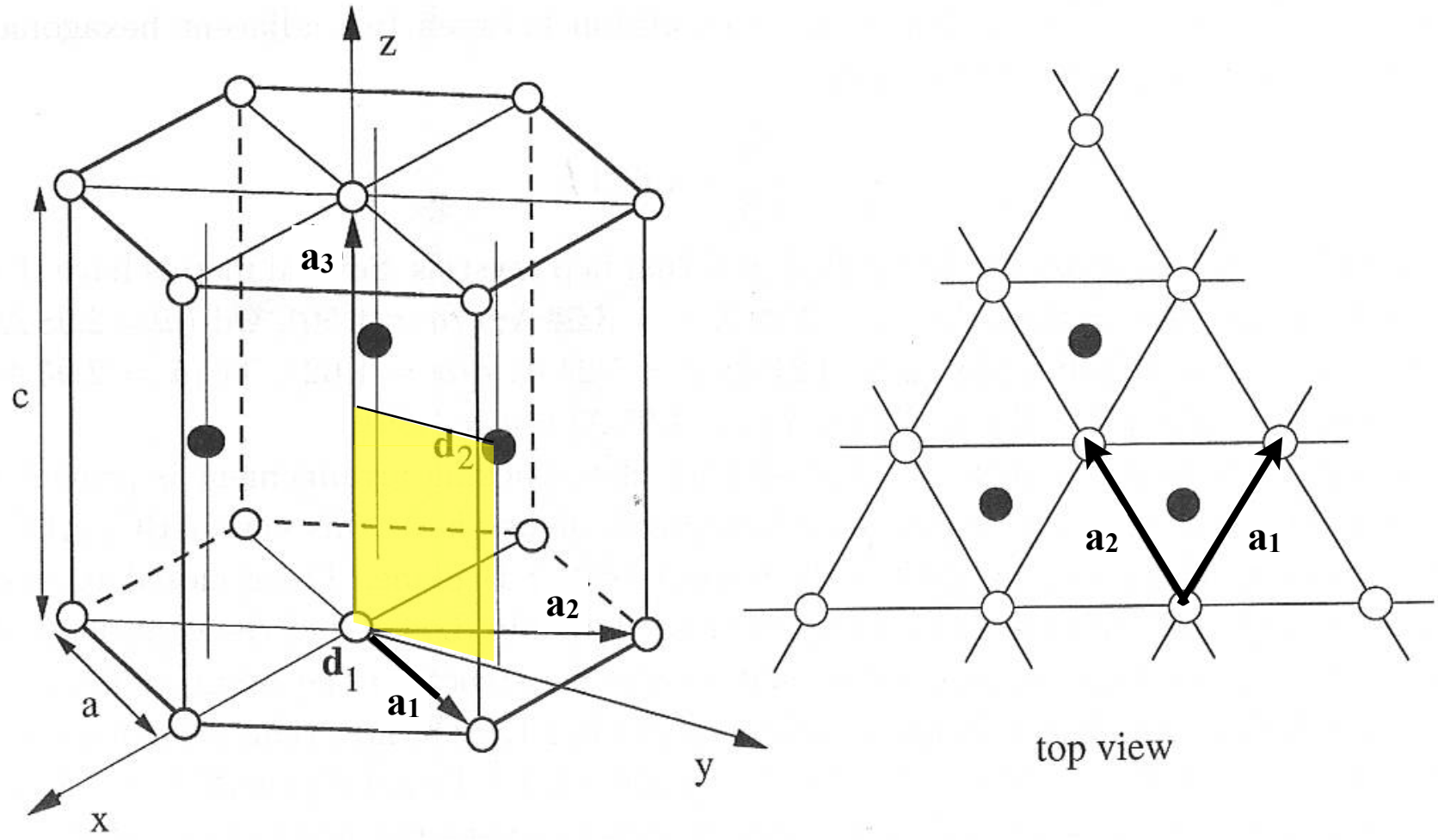
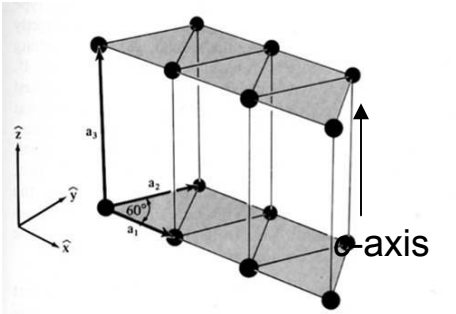
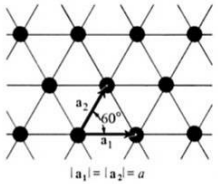
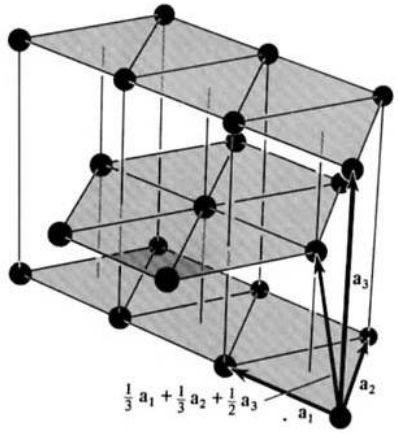


Fig. 13 Hexagonal closed-packed structure. The primitive translation vectors $\mathbf{t}_1, \mathbf{t}_2, \mathbf{t}_3$ and the end points of the basis vectors $\mathbf{d}_1$ and $\mathbf{d}_2$, given in Eqs. (15) of the text, are also indicated. The top view of the structure is also shown for convenience.

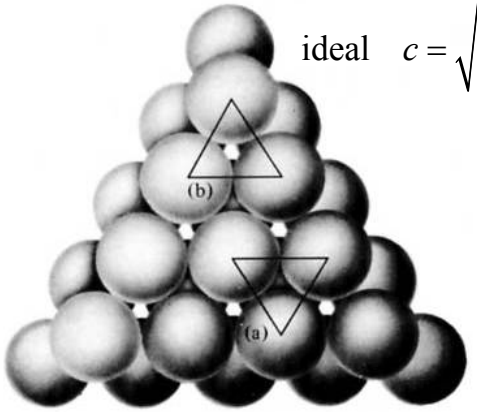
hexagonal close-packed (hcp) structure







ideal $c = \sqrt{\frac{8}{3}}a$



<u>simple hexagonal Bravais lattice</u>

2D triangular nets stacked above one another

a set of primitive vectors

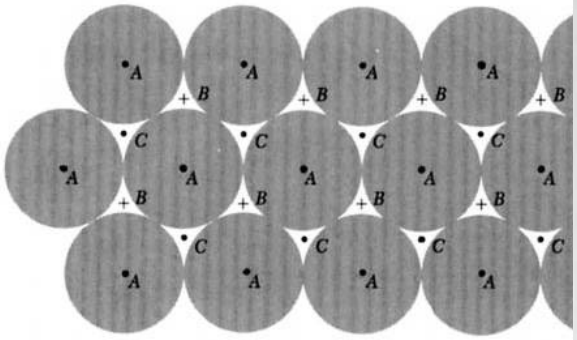
$$\mathbf{a}_1 = a\mathbf{x}$$

$$\mathbf{a}_2 = \frac{a}{2}\mathbf{x} + \frac{\sqrt{3}a}{2}\mathbf{y}$$

$$\mathbf{a}_3 = c\mathbf{z}$$

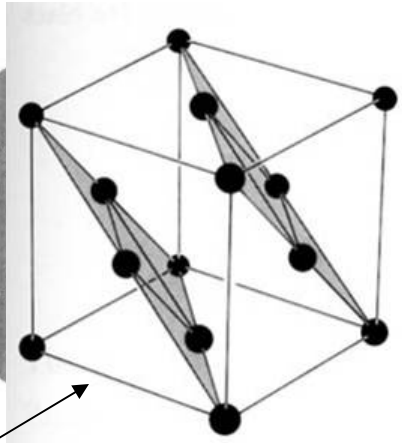
hcp structure consists of two interpenetrating simple hexagonal lattices displaced by $\mathbf{a}_1/3 + \mathbf{a}_2/3 + \mathbf{a}_3/2$

truly close-packed structure with the ideal value of c/a – an <u>ideal hcp structure</u>



hcp – …ABABAB…

fcc - …ABCABCABC…



infinitely many other closed packing arrangements, e.g. …ABACABACABAC…

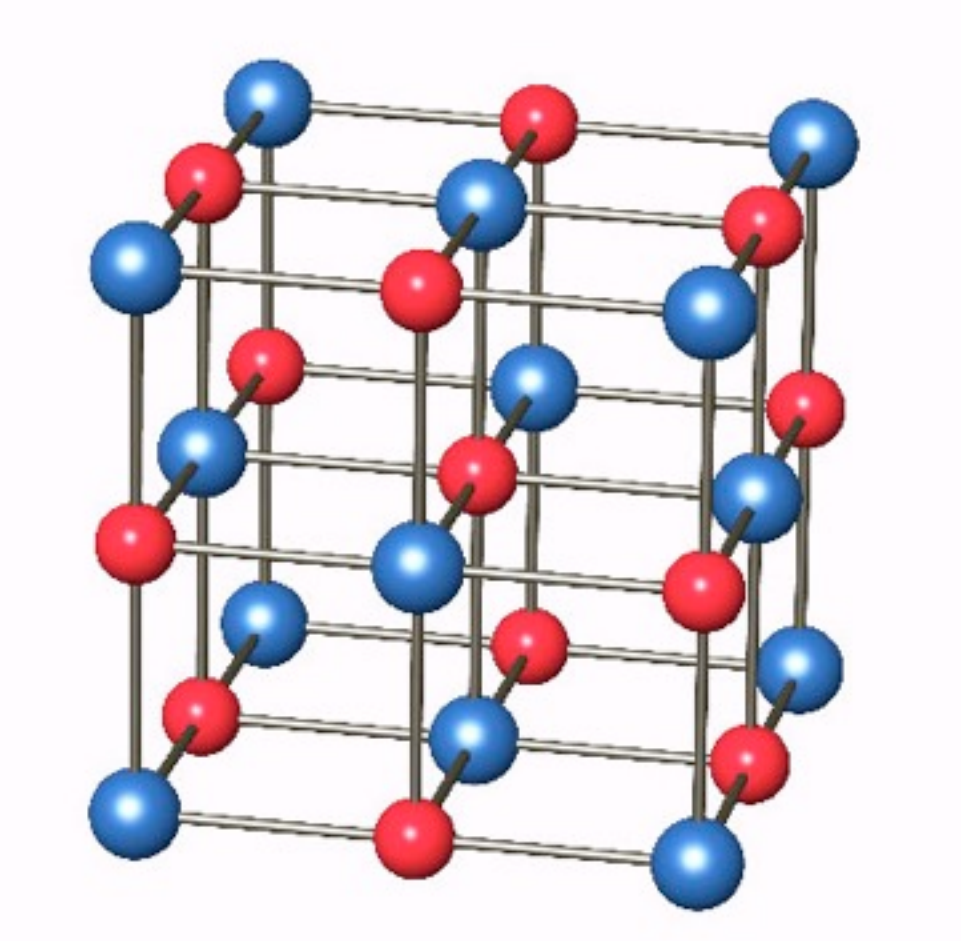
ELEMENTS WITH THE HEXAGONAL CLOSE-PACKED CRYSTAL STRUCTURE

ELEMENT	a (Å)	c	c/a	ELEMENT	a (Å)	c	c/a
Be	2.29	3.58	1.56	Os	2.74	4.32	1.58
Cd	2.98	5.62	1.89	Pr	3.67	5.92	1.61
Ce	3.65	5.96	1.63	Re	2.76	4.46	1.62
α-Co	2.51	4.07	1.62	Ru	2.70	4.28	1.59
Dy	3.59	5.65	1.57	Sc	3.31	5.27	1.59
Er	3.56	5.59	1.57	Tb	3.60	5.69	1.58
Gd	3.64	5.78	1.59	Ti	2.95	4.69	1.59
He (2 K)	3.57	5.83	1.63	Tl	3.46	5.53	1.60
Hf	3.20	5.06	1.58	Tm	3.54	5.55	1.57
Ho	3.58	5.62	1.57	Y	3.65	5.73	1.57
La	3.75	6.07	1.62	Zn	2.66	4.95	1.86
Lu	3.50	5.55	1.59	Zr	3.23	5.15	1.59
Mg	3.21	5.21	1.62		—	—	
Nd	3.66	5.90	1.61	"Ideal"			1.63

rocksalt **(sodium chloride structure)**

(NOT a Bravais lattice: FCC+basis with 2 different atoms)

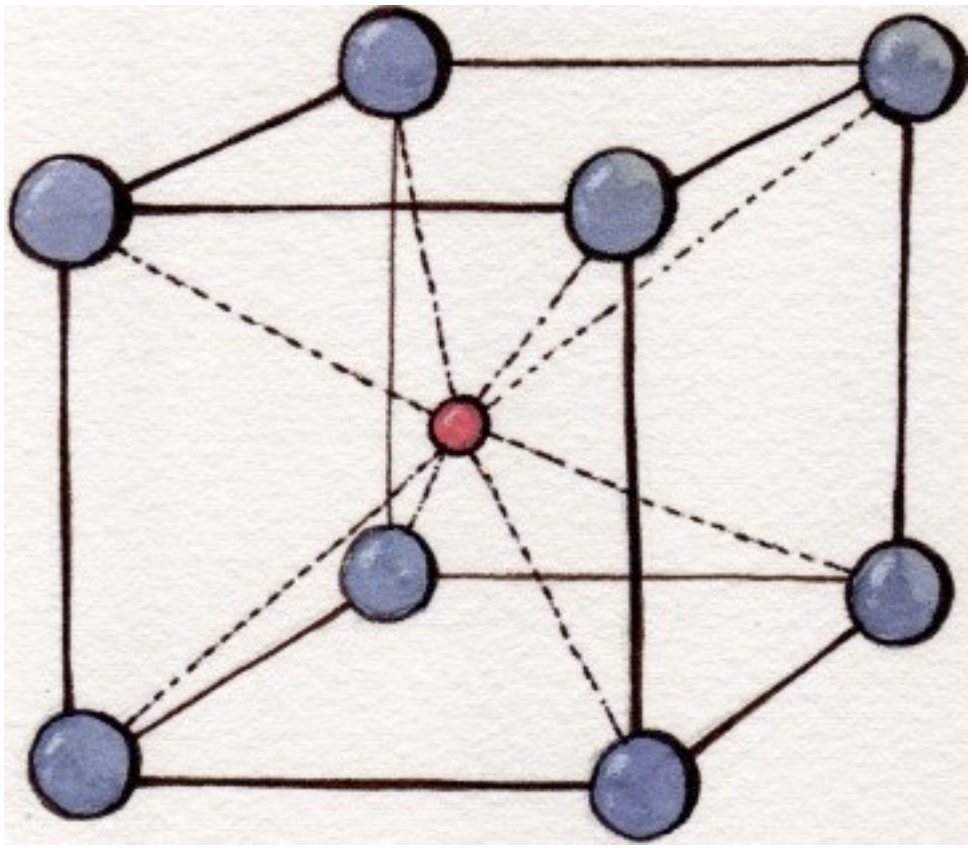
(basis with different positions w.r.t. the zincblende)



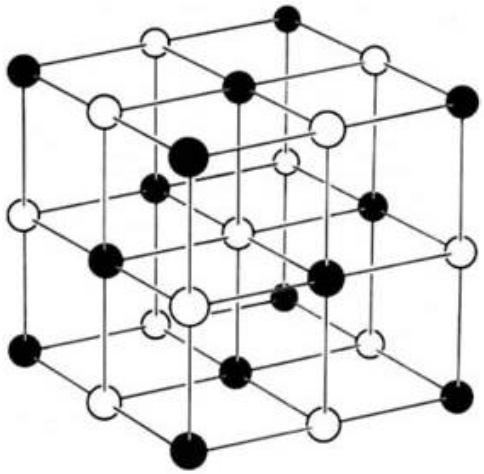
CsCl (cesium chloride structure)

(NOT a Bravais lattice: SC+basis with 2 different atoms)

reduces to the BCC Bravais lattice
in case of one atomic type

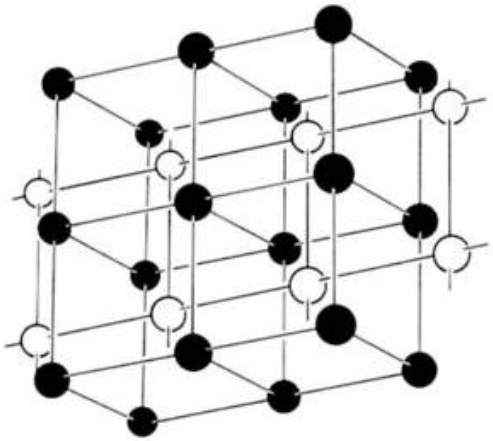


The Sodium Chloride structure



NaCl consists of equal number of Na and Cl ions placed in alternative points of sc lattice so that each Na has 6 Cl as its nearest neighbors
= fcc Bravais lattice with a basis consisting of Na at 0 and Cl at (a/2)(**x** + **y** + **z**)

The Cesium Chloride structure



CsCl consists of equal number of Cs and Cl ions placed at the points of bcc lattice so that each Cs has 8 Cl as its nearest neighbors
= sc Bravais lattice with a basis consisting of Cs at 0 and Cl at (a/2)(**x** + **y** + **z**)

SOME COMPOUNDS WITH THE SODIUM CHLORIDE STRUCTURE

CRYSTAL	a (Å)	CRYSTAL	a (Å)	CRYSTAL	a (Å)
LiF	4.02	RbF	5.64	CaS	5.69
LiCl	5.13	RbCl	6.58	CaSe	5.91
LiBr	5.50	RbBr	6.85	CaTe	6.34
LiI	6.00	RbI	7.34	SrO	5.16
NaF	4.62	CsF	6.01	SrS	6.02
NaCl	5.64	AgF	4.92	SrSe	6.23
NaBr	5.97	AgCl	5.55	SrTe	6.47
NaI	6.47	AgBr	5.77	BaO	5.52
KF	5.35	MgO	4.21	BaS	6.39
KCl	6.29	MgS	5.20	BaSe	6.60
KBr	6.60	MgSe	5.45	BaTe	6.99
KI	7.07	CaO	4.81		

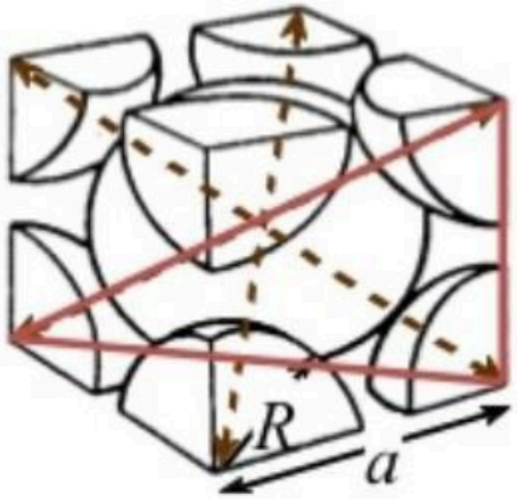
SOME COMPOUNDS WITH THE CESIUM CHLORIDE STRUCTURE

CRYSTAL	a (Å)	CRYSTAL	a (Å)
CsCl	4.12	TlCl	3.83
CsBr	4.29	TlBr	3.97
CsI	4.57	TlI	4.20

coordination number – the number of the nearest neighbors to a given point in the lattice

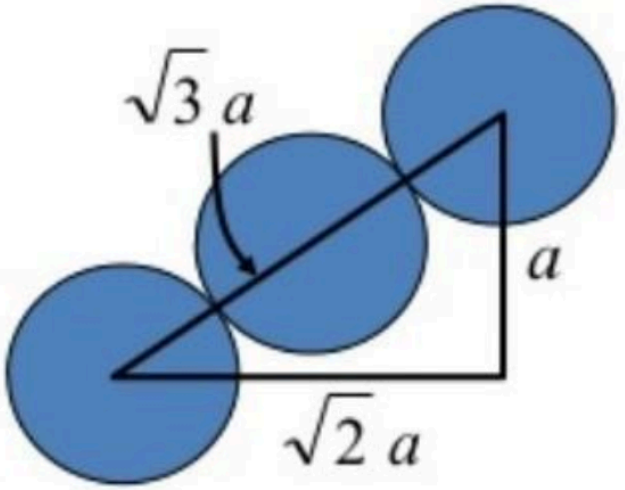
	coordination number
diamond lattice	4
sc	6
bcc	8
hcp	12
fcc	12

packing fraction - the fraction of volume occupied by sphere closely packed with respect to the available volume



Adapted from Fig. 3.2(a), *Callister 7e.*

Example: BCC



Step 1: Number of atoms per unit cell =
1 atom at center + 1/8 th of 8 corner atoms = 2 atoms

Step 2: Identify close packed direction

$$\sqrt{3}\,a = 4R$$

Step 3: Volume of unit cell $= a^3 = \left(\frac{4R}{\sqrt{3}}\right)^3$

packing fraction f $= \dfrac{\textbf{Volume of atoms}}{\textbf{Volume of unit cell}} = \dfrac{2x\frac{4}{3}\pi R^3}{a^3} = \mathbf{0.68}$

packing fraction - the fraction of volume occupied by sphere closely packed with respect to the available volume

$$FCC = \frac{\sqrt{2}}{6}\pi \approx 0.74$$

$$BCC = \frac{\sqrt{3}}{8}\pi \approx 0.68$$

$$SC = \frac{\pi}{6} \approx 0.52$$

$$diam = \frac{\sqrt{3}}{16}\pi \approx 0.34$$