Crystal Lattices

Outline

1. Bravais Lattice: definitions and examples
2. Unit cell: primitive, conventional and Wigner-Seitz
3. Crystal structure: lattices with basis

The Crystalline state

Cristallinity

- Metals, like quartz, diamond, rock salts, are crystalline in their natural forms
- long range microscopical order (periodic array of ions/atoms)
  - macroscopical regularities (angles between faces of specimens)
- Experimentally verified by Bragg (1913)
  - X-ray crystallography

Crystal of rutilated quartz

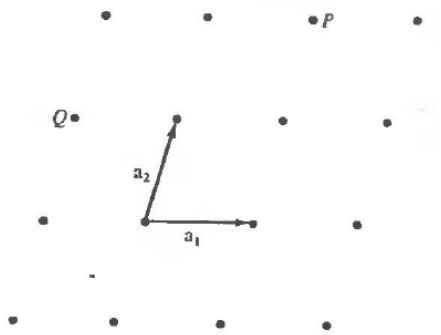
Bravais lattice

Two equivalent definitions

- Describes the underlying periodic arrangements of the repeating units
- A 2D Bravais lattice is called net

Definition/1

- Infinite array of points with arrangement and orientation that appears exactly the same from whichever of the points the array is viewed. Every point has an identical surroundings



A 2D net without symmetry (oblique net). $P = \boldsymbol{a}_1 + 2\boldsymbol{a}_2$; $Q = -\boldsymbol{a}_1 + \boldsymbol{a}_2$

Bravais lattice

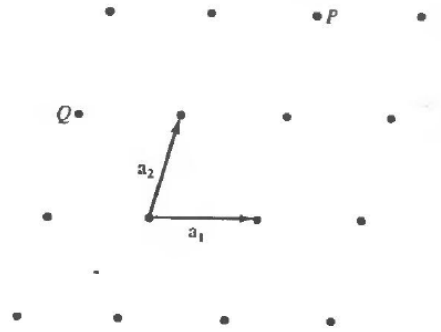
Two equivalent definitions

Definition/2

- All points with position vectors $\boldsymbol{R}$ of the form

$$\boldsymbol{R} = n_1\boldsymbol{a}_1 + n_2\boldsymbol{a}_2 + n_3\boldsymbol{a}_3$$

- $\{\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{a}_3\}$: primitive lattice vectors (generators of the lattice)
- $\{n_1, n_2, n_3\}$: (integers, positive, negative or zero)



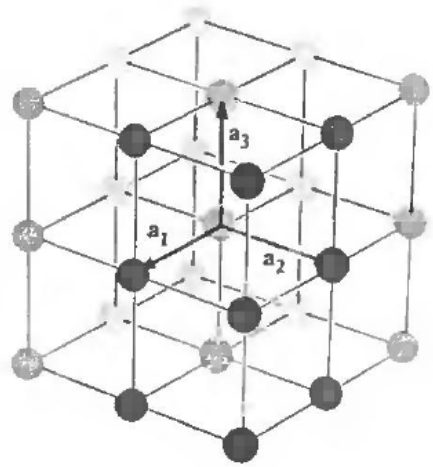
A 2D net without symmetry (oblique net). $P = \boldsymbol{a}_1 + 2\boldsymbol{a}_2$; $Q = -\boldsymbol{a}_1 + \boldsymbol{a}_2$

Bravais lattice

Examples

A Bravais lattice: simple cubic lattice

- All definitions are satisfied
- Lattice spanned by $\{\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{a}_3\}$
  - mutually $\perp$ primitive vectors
  - same length



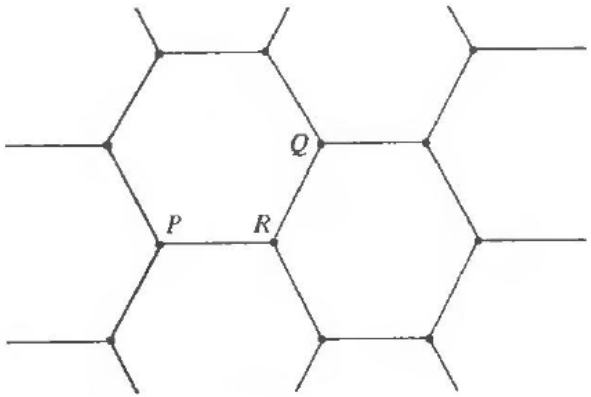
A 3D simple cubic lattice

Bravais lattice

Examples

NOT a Bravais lattice: vertices of a honeycomb lattice

- Structural relations are identical
- Orientational relations are not identical
  - ***P*** and ***Q*** are equivalent points
  - ***P*** and ***R*** are not equivalent
- A 3D example is the Hexagonal close-packed lattice



A honeycomb lattice is not a Bravais lattice

Bravais lattice

A note on finite/infinite crystals and Bravais lattices

- A Bravais lattice is infinite: integers are an infinite (countable) set
- Real crystals are finite
- The concept of infinite Bravais lattice (and crystal) is still useful because
  - Realistic assumption for finite crystals (not sheets, nanowires etc.) since most of the points will be in the bulk
  - Convenient for computational purposes (periodic boundary conditions)
- If surface effects are important
  - The notion of Bravais lattice is still retained
  - Only a finite portion of the ideal lattice is used

Bravais lattice

A note on finite/infinite crystals and Bravais lattices

Periodic boundary conditions (PBC)

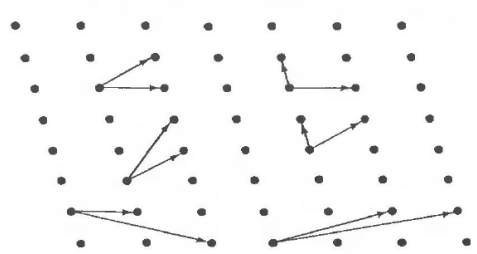
- Use the simples possible form of the finite lattice (cubic)
- Given the primitive vectors $\{\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{a}_3\}$ consider
  - N_1 cells along $\boldsymbol{a}_1$
  - N_2 cells along $\boldsymbol{a}_2$
  - N_3 cells along $\boldsymbol{a}_3$
- Includes all points $\boldsymbol{R} = n_1\boldsymbol{a}_1 + n_2\boldsymbol{a}_2 + n_3\boldsymbol{a}_3$ where
  - $0 \leq n_1 < N_1$, $0 \leq n_2 < N_2$,$0 \leq n_3 < N_3$
  - $N_1 N_2 N_3 = N$ primitive cells
  - N is assumed to be large (of the order of Avogadro's number)

Bravais lattice

Further thoughts about the definitions

Definition/3

- Definition 1 is intuitive, but not useable in analytic works
- Definition 2 is useful and more precise but:
  - Primitive vectors are not unique for a given Bravais lattice
  - It is difficult to prove that a given lattice is a Bravais lattice (existence of a set of primitive vectors)
- Discrete set of vectors $\boldsymbol{R}$, not all in a plane, closed under addition and subtraction



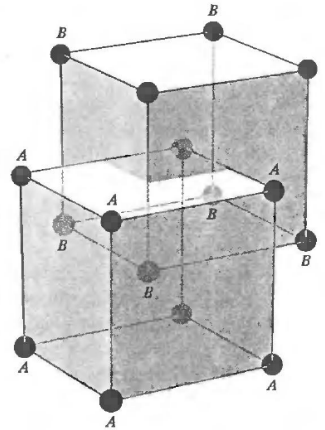
Different choices of primitive vectors of a net

Examples of Bravais lattices

Body-centered cubic lattice (bcc)

bcc Bravais lattice

- Add a lattice point to the center of each cube of a simple cubic lattice
  - Points ***A*** mark the simple cubic lattice
  - Points ***B*** mark the newly added points
- Points ***A*** and ***B*** equivalent
  - Points ***B*** constitute a simple cubic sublattice with ***A*** at the center
  - The roles of ***A*** and ***B*** can be reversed



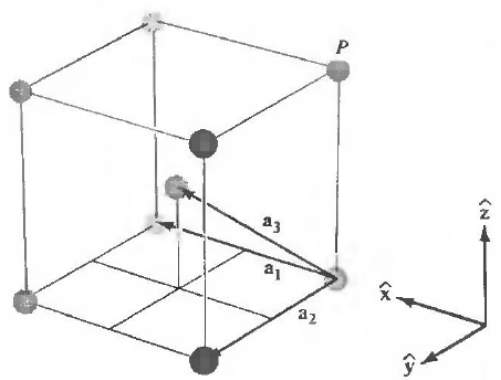
A bcc lattice is a Bravais lattice

Examples of Bravais lattices

Body-centered cubic lattice (bcc)

Choice of primitive lattice vectors

$$\begin{cases} \boldsymbol{a}_1 = & a\hat{\boldsymbol{x}} \\ \boldsymbol{a}_2 = & a\hat{\boldsymbol{y}} \\ \boldsymbol{a}_3 = & \frac{a}{2}(\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}} + \hat{\boldsymbol{z}}) \end{cases}$$



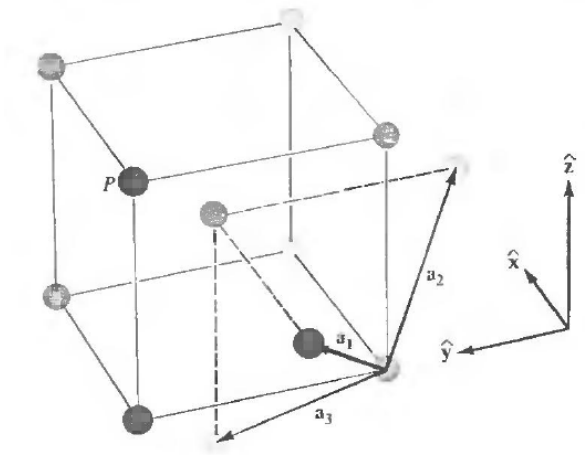
Three primitive vectors for the bcc lattice. $\boldsymbol{P} = -\boldsymbol{a}_1 - \boldsymbol{a}_2 + 2\boldsymbol{a}_3$

Examples of Bravais lattices

Body-centered cubic lattice (bcc)

Standard choice of primitive lattice vectors

$$\begin{cases} \boldsymbol{a}_1 = & \frac{a}{2}(\hat{\boldsymbol{y}} + \hat{\boldsymbol{z}} - \hat{\boldsymbol{x}}) \\ \boldsymbol{a}_2 = & \frac{a}{2}(\hat{\boldsymbol{x}} + \hat{\boldsymbol{z}} - \hat{\boldsymbol{y}}) \\ \boldsymbol{a}_3 = & \frac{a}{2}(\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}} - \hat{\boldsymbol{z}}) \end{cases}$$



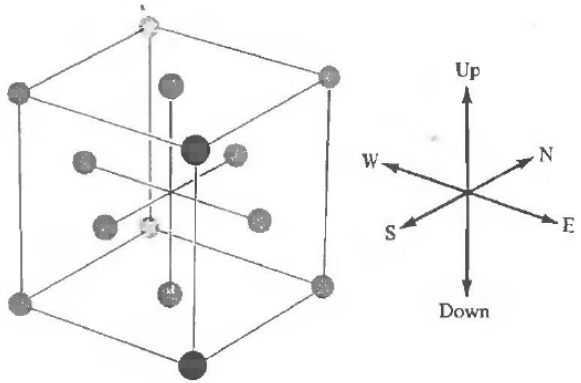
Primitive vectors for the bcc lattice. $\boldsymbol{P} = 2\boldsymbol{a}_1 + \boldsymbol{a}_2 + \boldsymbol{a}_3$

Examples of Bravais lattices

Face-centered cubic lattice (fcc)

fcc Bravais lattice

- Add a lattice point to the center of each cube's face of a simple cubic lattice
- All points are equivalent
- Consider points centering Up and Down faces:
  - They form a simple cubic lattice
  - The original scc lattice points are now centering the horizontal faces
  - The added S-N centering points now center W-E faces
  - The added W-E centering points now center N-S faces

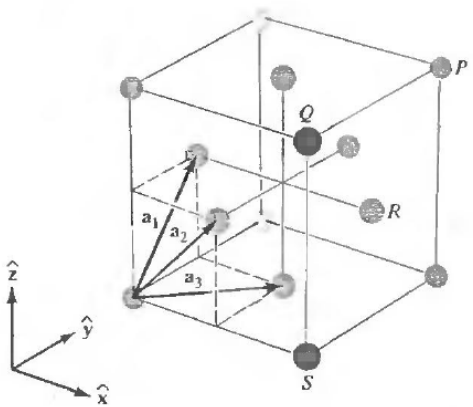


Examples of Bravais lattices

Face-centered cubic lattice (fcc)

Standard choice of primitive lattice vectors

$$\begin{cases} \boldsymbol{a}_1 = \frac{a}{2}(\hat{\boldsymbol{y}} + \hat{\boldsymbol{z}}) \\ \boldsymbol{a}_2 = \frac{a}{2}(\hat{\boldsymbol{x}} + \hat{\boldsymbol{z}}) \\ \boldsymbol{a}_3 = \frac{a}{2}(\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}}) \end{cases}$$



Primitive vectors for the fcc lattice. $\boldsymbol{P} = \boldsymbol{a}_1 + \boldsymbol{a}_2 + \boldsymbol{a}_3$; $\boldsymbol{Q} = 2\boldsymbol{a}_2$; $\boldsymbol{R} = \boldsymbol{a}_2 + \boldsymbol{a}_3$; $\boldsymbol{S} = -\boldsymbol{a}_1 + \boldsymbol{a}_2 + \boldsymbol{a}_3$

Elemental solids with the fcc crystal structure

Atom or ion at each lattice site

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

Elemental solids with the bcc crystal structure

Atom or ion at each lattice site

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)		

More on terminology and notation

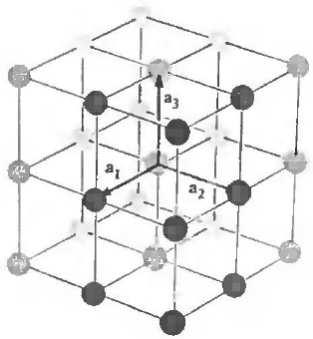
Bravais lattice

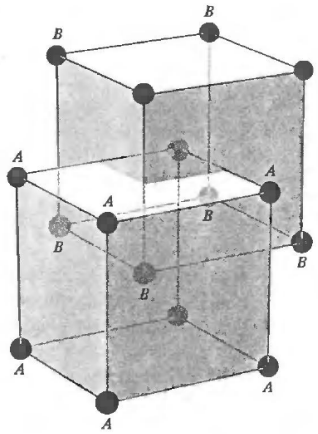
- The term can equally apply to:
  - the set of points constituting the lattice
  - the set of vectors $\boldsymbol{R}$ joining a given point (origin) to all others
  - the set of translations or displacements in the direction of $\boldsymbol{R}$

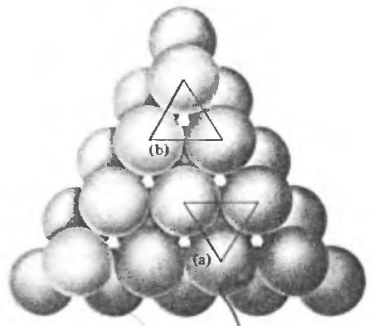
More on terminology and notation

Coordination number of the lattice

- It is the number of nearest neighbours to a given point of the lattice
  - a property of the lattice
  - sc lattice: 6
  - bcc lattice: 8
  - fcc lattice: 12







Unit cell

Primitive unit cell

Definition

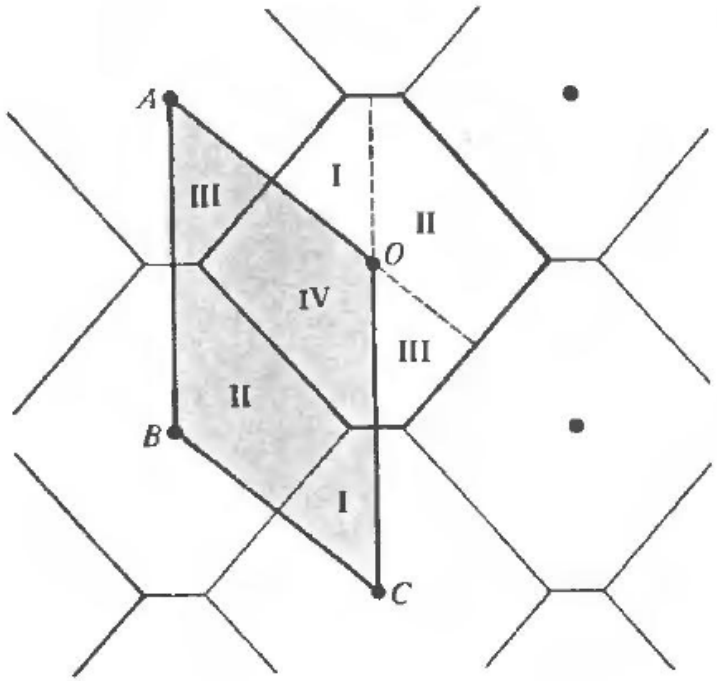
- A volume that when translated through all the vectors $\boldsymbol{R}$ of the Bravais lattice fills all space
  - without overlapping (overlapping regions have zero volume)
  - or leaving voids
- contains one lattice point: $v = \frac{1}{n}$
  - n: density of points in the lattice
- All primitive cells have the same volume (area for a net)
- not uniquely defined

Unit cell

Primitive unit cell

Properties

- Two primitive cells of different shape can be re-assembled into one another
  - by translation with appropriate lattice vectors
  - since their volume is the same



Unit cell

Primitive unit cell

Definition

- It is associated with all points $\boldsymbol{r}$ such that

$$\boldsymbol{r} = x_1 \boldsymbol{a}_1 + x_2 \boldsymbol{a}_2 + x_3 \boldsymbol{a}_3$$

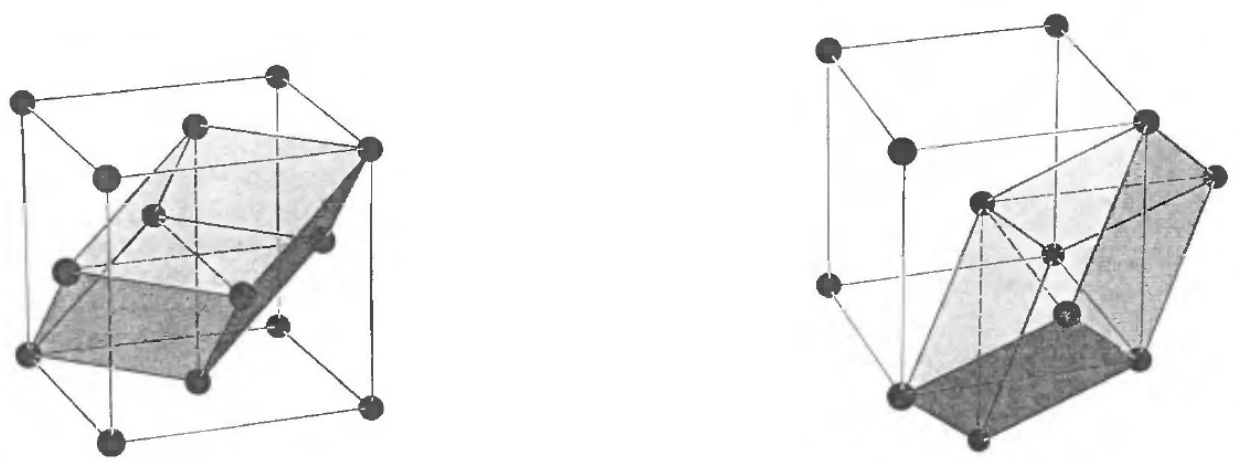
- $0 \leq x_i < 1$
- The parallelepiped spanned by the primitive vectors $\{\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{a}_3\}$
- Sometimes does not display the full symmetry of the lattice
- It is convenient to work with cells that display the full symmetry:
  - conventional cell
  - Wigner-Seitz cell

Unit cell

Conventional unit cell

A nonprimitive unit cell

- Fills up the region when translated by only a subset of the vectors $\boldsymbol{R}$
- It displays the required symmetry (Cubic for bcc and fcc lattices)
- Twice as large for bcc, four times as large for fcc
- Its size is specified by lattice constants:
  - The side of the cube (a) for cubic crystals



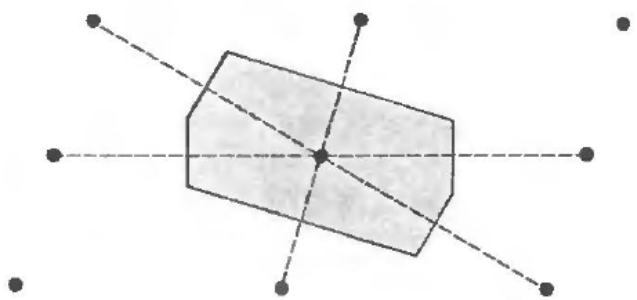
Primitive and conventional cells for the fcc (left) and bcc (right) lattice

Unit cell

Wigner-Seitz cell

A primitive unit cell

- All points that are closer to a given lattice point than to any other lattice points
- Displays the full symmetry of the Bravais lattice
  - Voronoi cell for sets that are not Bravais lattices
- Operationally:
  - draw lines connecting the point to all others in the lattice
  - draw planes bysecting the lines
  - the smallest polyhedron bounded by these planes



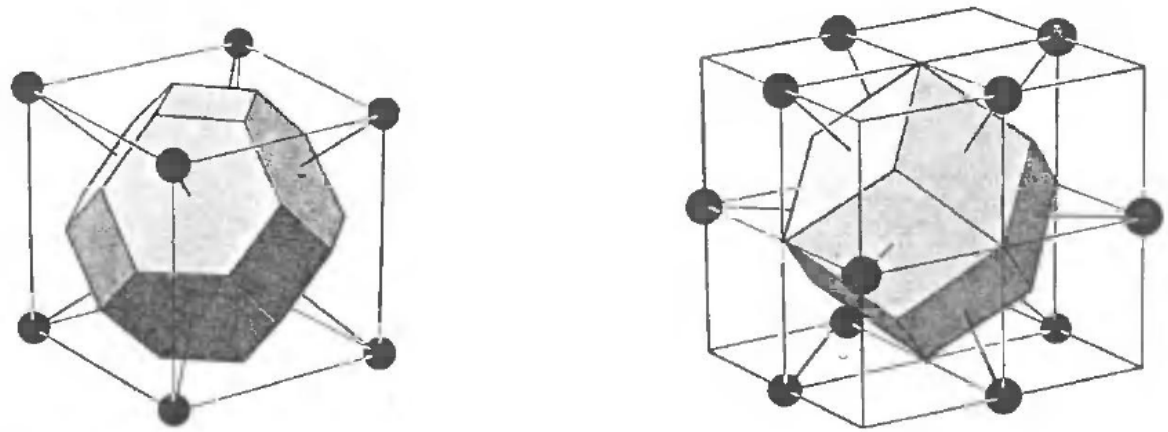
Wigner-Seitz cell for a 2D Bravais lattice

Unit cell

Wigner-Seitz cell

Wigner-Seitz cell for bcc and fcc lattices

- bcc lattice: truncated octahedron
  - faces are squares and regular hexagons
- fcc lattice: rhombic dodecahedron
  - 12 congruent faces
  - $\perp$ to lines joining the edge's midpoints



Wigner-Seitz cells for bcc (left) and fcc (right) lattices

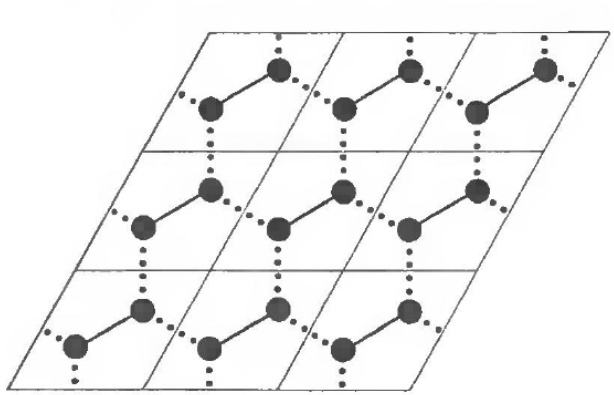
Crystal Structure

Lattice with a basis

- A crystal structure can be described by giving:
  - The underlying Bravais lattice
  - The physical unit associated with each lattice point (basis)
  - lattice with a basis

Example: vertices of a honeycomb net

- 2D Bravais lattice
- two point basis

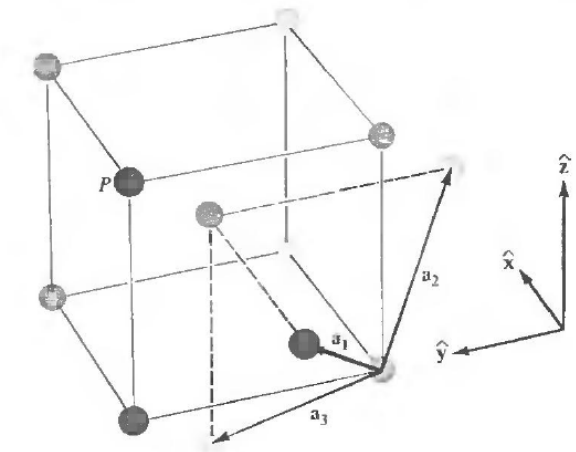


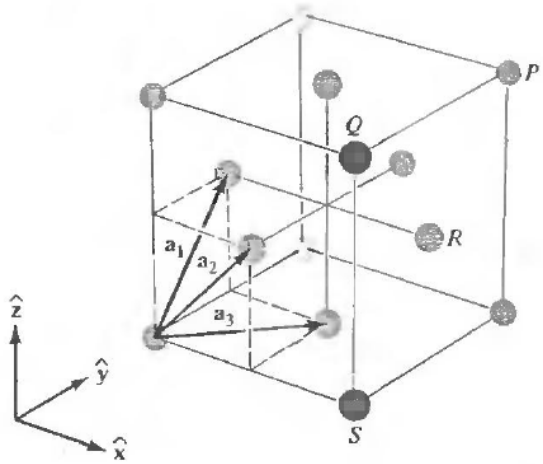
Crystal Structure

Alternative description of Bravais lattices

bcc and fcc Bravais lattices

- bcc Bravais lattice:
  - Can be described as a sc Bravais lattice with a two-point basis
  - $0, \frac{a}{2}(\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}} + \hat{\boldsymbol{z}})$
- fcc Bravais lattice:
  - Can be described as a sc Bravais lattice with a four-point basis
  - $0, \frac{a}{2}(\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}}), \frac{a}{2}(\hat{\boldsymbol{y}} + \hat{\boldsymbol{z}}), \frac{a}{2}(\hat{\boldsymbol{z}} + \hat{\boldsymbol{x}})$



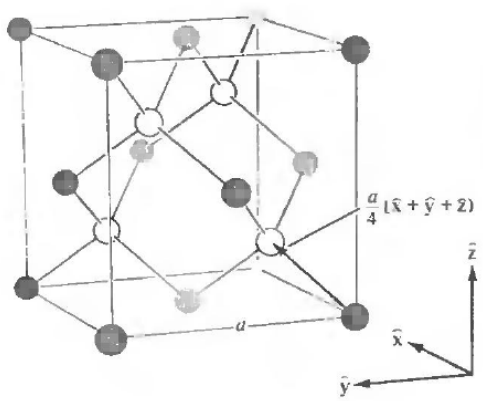


Important examples

Diamond structure

Diamond lattice

- Two interprenetating fcc lattices
  - Displaced along the cube's diagonal by $\frac{1}{4}$ its length
- Described as a lattice with a basis
  - fcc Bravais lattice
  - a two-point basis: $0, \frac{a}{4}(\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}} + \hat{\boldsymbol{z}})$



conventional cubic cell of the diamond lattice

Important examples

Diamond structure

Diamond lattice

- Each lattice point has a tetrahedral environment
  - coordination number is 4
  - bond angles of 109°28′
- Not a Bravais lattice
  - differently oriented environments for nearest-neighbouring points

Table 4.3
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

Important examples

Hexagonal closed packed structure

hcp structure

ELEMENTS WITH THE HEXAGONAL CLOSE-PACKED CRYSTAL STRUCTURE

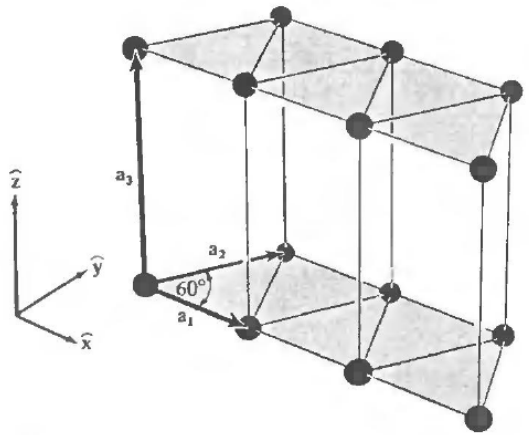
ELEMENT	a (Å)	c	c/a	ELEMENT	a (Å)	c	c/a
Be	2.29	3.58	1.56	Os	2.74	4.32	1.58
Cd	2.98	5.62	1.89	Pr	3.67	5.92	1.61
Ce	3.65	5.96	1.63	Re	2.76	4.46	1.62
α-Co	2.51	4.07	1.62	Ru	2.70	4.28	1.59
Dy	3.59	5.65	1.57	Sc	3.31	5.27	1.59
Er	3.56	5.59	1.57	Tb	3.60	5.69	1.58
Gd	3.64	5.78	1.59	Ti	2.95	4.69	1.59
He (2 K)	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

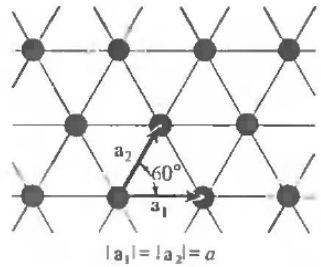
Hexagonal closed packed structure

Underlying Bravais lattice

Simple hexagonal Bravais lattice

- Two triangular nets above each other
- Direction of stacking: c axis
- Two lattice constants
- $\boldsymbol{a}_1 = a\hat{\boldsymbol{x}}$; $\boldsymbol{a}_2 = \frac{a}{2}\hat{\boldsymbol{x}} + \frac{\sqrt{3}a}{2}\hat{\boldsymbol{y}}$; $\boldsymbol{a}_3 = c\hat{\boldsymbol{z}}$

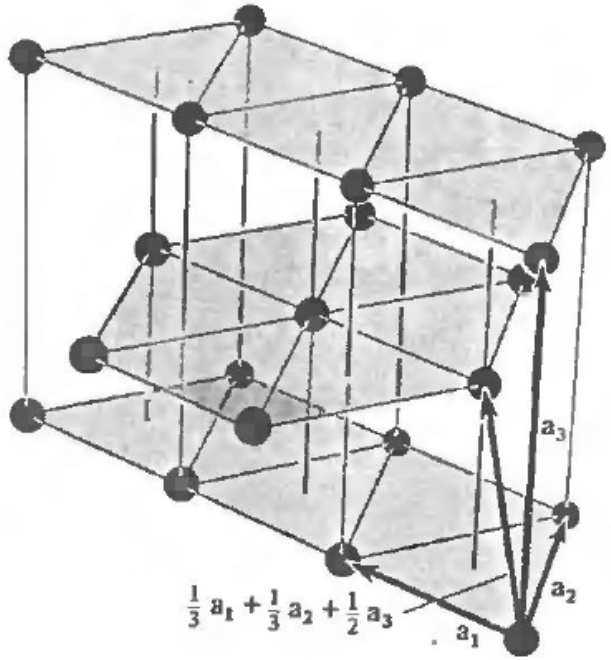




simple hexagonal lattice

Hexagonal closed packed structure

- Two interpenetrating simple hexagonal lattices
- Displaced one another by $\frac{\boldsymbol{a}_1}{3} + \frac{\boldsymbol{a}_2}{3} + \frac{\boldsymbol{a}_3}{2}$
- Close-packed hard spheres can be arranged in such a structure
- Not a Bravais lattice

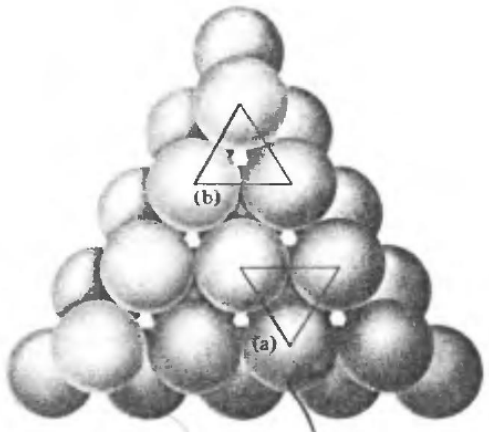


close-packed hexagonal structure

Closed packed structures

hcp structure: ABABAB... sequence

- First layer: plane triangular lattice
- Second layer: spheres placed at the depressions of every other triangles of the first layer
- Third layer: directly above the spheres of the first layer
- Ideal $\frac{c}{a}$ ratio: $\sqrt{\frac{8}{3}}$



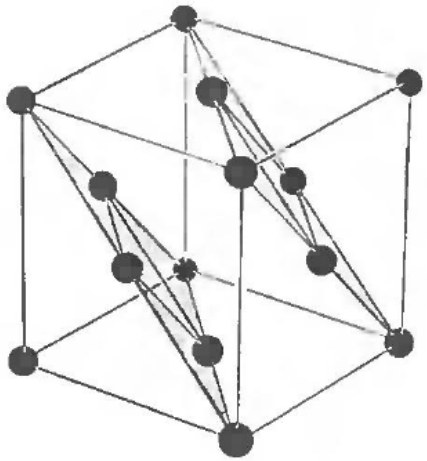
Stack of hard spheres

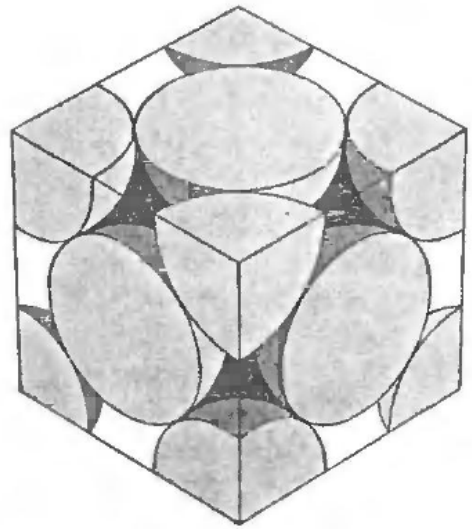
Other closed packed structures

fcc close-packing: ABCABCABC... sequence

The only closed packed Bravais lattice

- Third layer: spheres at sites (b)
- Fourth layer: directly above the spheres of the first layer



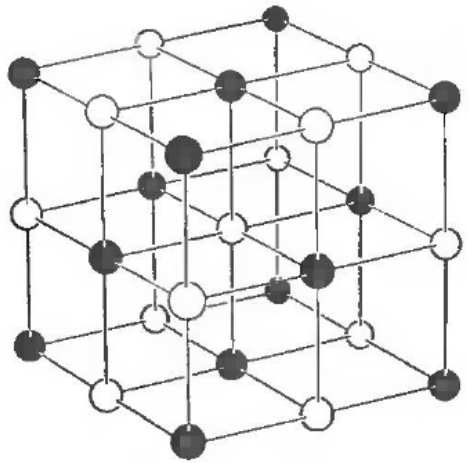


Sections of fcc closed packed spheres

Sodium-Chloride structure

Rock-salt structure: lattice with a basis

- Necessary here because:
  - Two different kind of species (ions)
  - Full translational symmetry of the Bravais lattice is lacking
- Bravais lattice: fcc
- Basis: 0 (Na), $\frac{a}{2}(\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}} + \hat{\boldsymbol{z}})$ (Cl)



The sodium chloride structure

Sodium-Chloride structure

Rock-salt structure

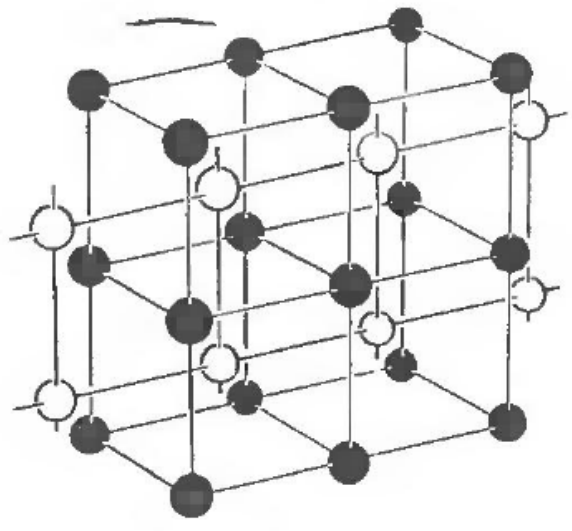
Table 4.5
SOME COMPOUNDS WITH THE SODIUM CHLORIDE STRUCTURE

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		

Other important examples

Cesium-Chloride structure

- Two interpenetrating bcc lattices
  - coordination number is 8
- Bravais lattice: sc
- Basis: 0 (Cs), $\frac{a}{2}(\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}} + \hat{\boldsymbol{z}})$ (Cl)



The sodium chloride structure

Other important examples

Cesium-Chloride structure

Table 4.6
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

Other important examples

ZnS crystal structure

- Zn and S distributed in a diamond lattice
  - each atom has coordination number 4
  - of the opposite kind

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		