Crystal Lattices

Outline

1. Bravais Lattice: definitions and examples
2. Unit cell: primitive, conventional and Wigner-Seitz
3. Crystal structure: lattices with basis
4. Supercells
5. More on closed packed structures: packing efficiency

The Crystalline state

Crystallinity

- Metals, like quartz, diamond, rock salts, are crystalline in their natural forms
- Long range microscopical order (periodic array of ions/atoms)
  - macroscopical regularities (definite angles between faces of specimens)
- Experimentally verified by Bragg (1913)
  - X-ray crystallography
- Often made of small pieces each large on the macroscopic scale
  - polycrystalline state

Crystal of rutilated quartz

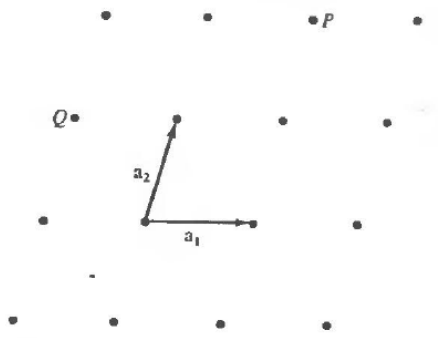
Bravais lattice

Two equivalent definitions

- Describes the underlying periodic arrangements of the repeating units
  - repeating units can be atoms, groups of atoms, molecules, ions ...
- A 2D Bravais lattice is called net

Definition/1

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



A 2D net without symmetry (oblique net).

Bravais lattice

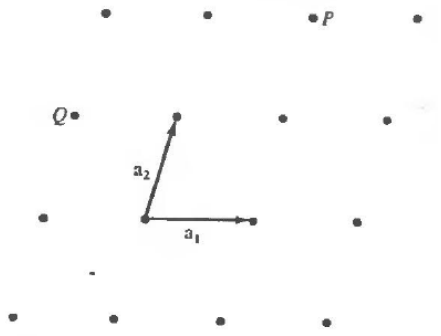
Two equivalent definitions

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
  - the primitive vectors generate (span) the lattice
  - $\{n_1, n_2, n_3\}$: (integers, positive, negative or zero)



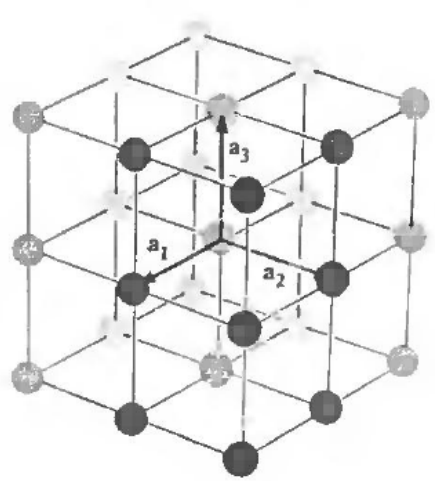
A 2D net without symmetry (oblique net). $P = \boldsymbol{a}_1 + 2\boldsymbol{a}_2$; $Q = -\boldsymbol{a}_1 + \boldsymbol{a}_2$

Bravais lattice

Examples

A 3D 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



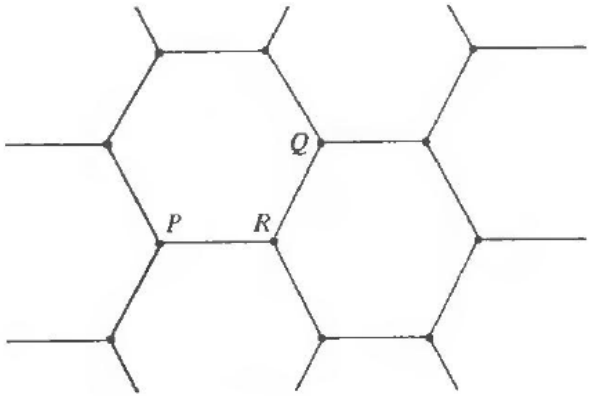
A 3D simple cubic lattice

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 (hcp) 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 filled

Bravais lattice

A note on finite/infinite crystals and Bravais lattices

Periodic boundary conditions (PBC)

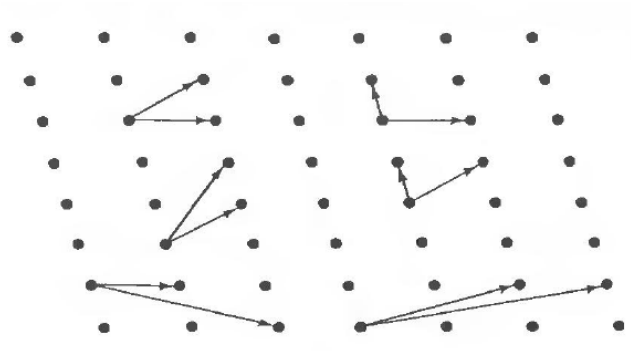
- Use the simples possible form of the finite lattice (cubic)
- Given the primitive vectors $\{\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{a}_3\}$ consider
  - N_1 cells along $\boldsymbol{a}_1$
  - N_2 cells along $\boldsymbol{a}_2$
  - N_3 cells along $\boldsymbol{a}_3$
- Includes all points $\boldsymbol{R} = n_1\boldsymbol{a}_1 + n_2\boldsymbol{a}_2 + n_3\boldsymbol{a}_3$ 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 work
- 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



Different choices of primitive vectors of a net

Bravais lattice

Further thoughts about the definitions

Definition/3

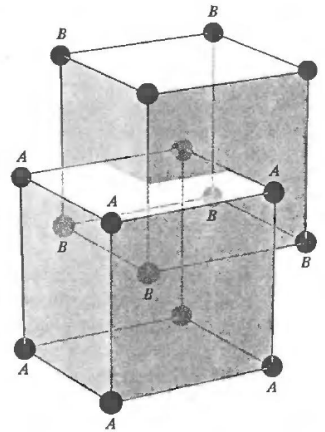
- Given a Bravais lattice $\mathcal{R}$ and two lattice points $\mathbf{R}_1 \in \mathcal{R}$ and $\mathbf{R}_2 \in \mathcal{R}$ then $\mathbf{R}_1 + \mathbf{R}_2 \in \mathcal{R}$
  - $\mathbf{R}_1 = \sum_{i=1}^{d} n_{1,i}\boldsymbol{a}_i,\ n_{1,i} \in \mathbb{Z}, i = 1, \ldots, 3$
  - $\mathbf{R}_2 = \sum_{i=1}^{d} n_{2,i}\boldsymbol{a}_i,\ n_{2,i} \in \mathbb{Z}, i = 1, \ldots, 3$
  - $\rightarrow \mathbf{R}_1 + \mathbf{R}_2 = \sum_{i=1}^{d} (n_{1,i} + n_{2,i})\boldsymbol{a}_i \in \mathcal{R}$
- The term Bravais lattice 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 $\boldsymbol{R}$

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*** are equivalent
  - points ***B*** constitute a simple cubic sublattice with ***A*** at the center
  - the roles of ***A*** and ***B*** can be reversed
  - points ***A*** and ***B*** have identical surroundings

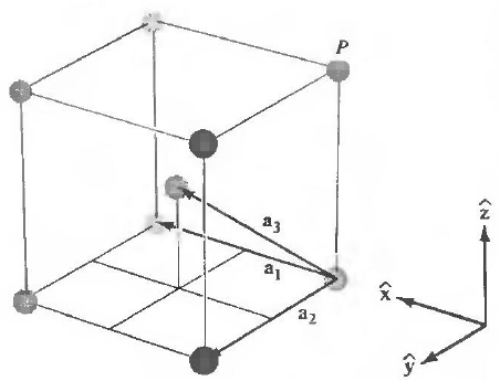


Examples of Bravais lattices

Body-centered cubic lattice (bcc)

Choice of primitive lattice vectors

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



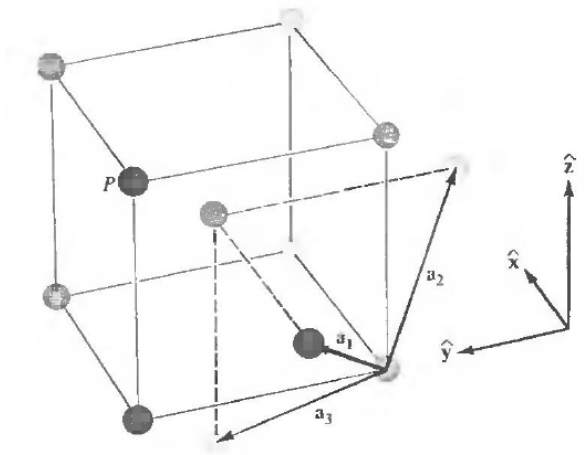
Three primitive vectors for the bcc lattice. $\boldsymbol{P} = -\boldsymbol{a}_1 - \boldsymbol{a}_2 + 2\boldsymbol{a}_3$

Examples of Bravais lattices

Body-centered cubic lattice (bcc)

Standard choice of primitive lattice vectors

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



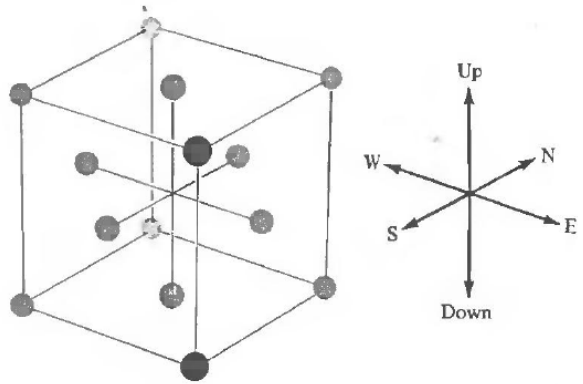
Primitive vectors for the bcc lattice. $\boldsymbol{P} = 2\boldsymbol{a}_1 + \boldsymbol{a}_2 + \boldsymbol{a}_3$

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
- Consider points centering Up and Down faces:
  - they form a simple cubic lattice
  - the original sc 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



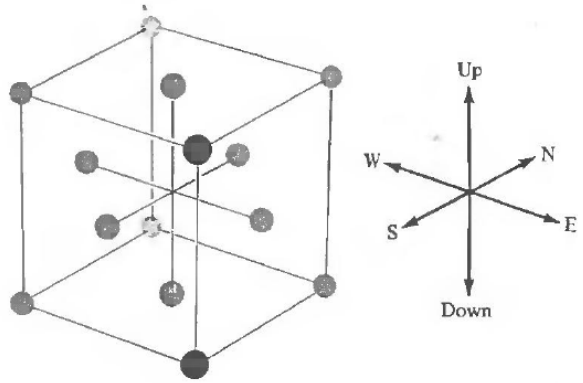
A fcc lattice is a Bravais lattice

Examples of Bravais lattices

Face-centered cubic lattice (fcc)

fcc Bravais lattice

- Consider points centering N and S faces:
  - they also form a sc lattice
  - the other points now center the faces of this new sc lattice.
- All points are equivalent



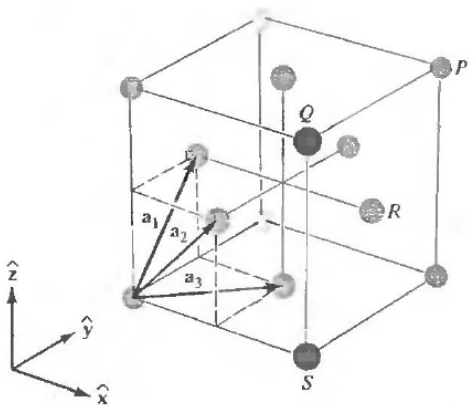
A fcc lattice is a Bravais lattice

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

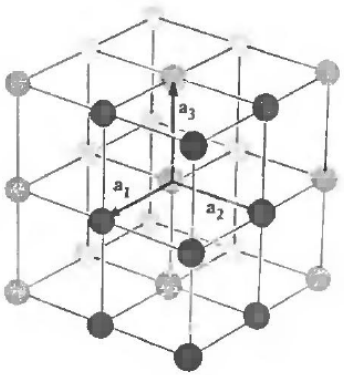
ELEMENTS WITH THE MONATOMIC BODY-CENTERED CUBIC CRYSTAL STRUCTURE

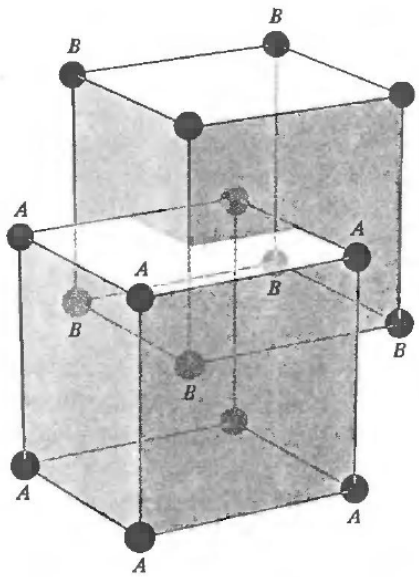
ELEMENT	a (Å)	ELEMENT	a (Å)	ELEMENT	a (Å)
Ba	5.02	Li	3.49 (78 K)	Ta	3.31
Cr	2.88	Mo	3.15	Tl	3.88
Cs	6.05 (78 K)	Na	4.23 (5 K)	V	3.02
Fe	2.87	Nb	3.30	W	3.16
K	5.23 (5 K)	Rb	5.59 (5 K)		

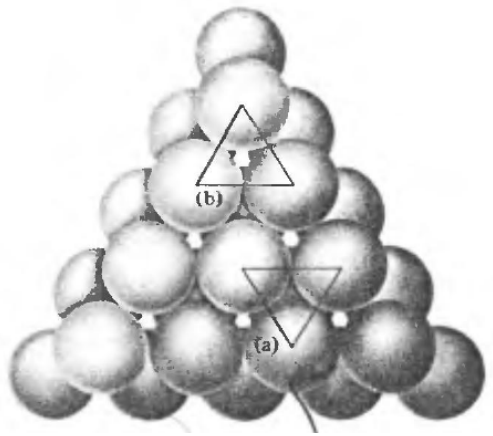
More on terminology and notation

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



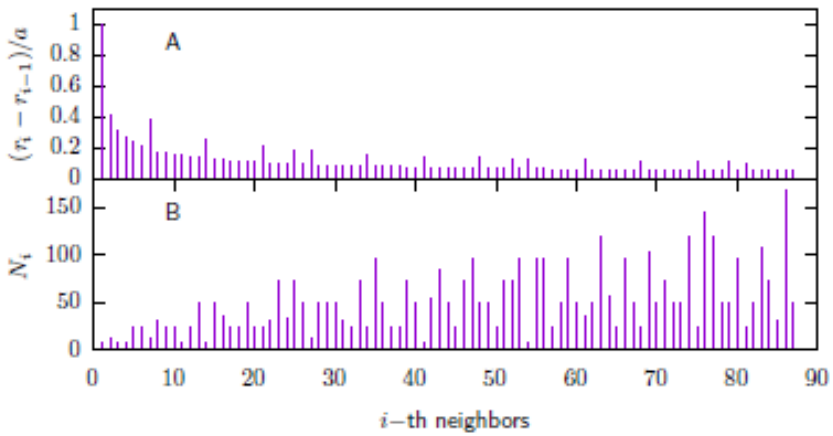




More on terminology and notation

First, second, . . . neighbours

- Every lattice point has the same number of first, second, . . . neighbours.
  - they lay on the surface of a sphere (or on a circle for nets) centering the given lattice point
  - their numbers and distances depend on the given Bravais lattice
  - their numbers increase with increasing order (not monotonically)
  - difference in radii of successive spheres decreases



example of a simple cubic lattice. *a* is the cell constant.

Unit cell

Primitive unit cell

Definition

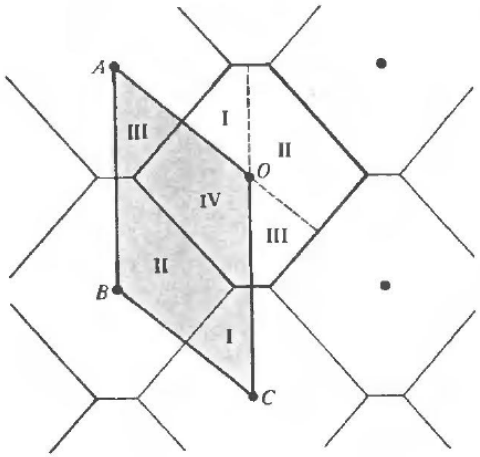
- A volume that when translated through all the vectors $\boldsymbol{R}$ of the Bravais lattice fills all space
  - without overlapping (overlapping regions have zero volume)
  - or leaving voids
- contains one lattice point:
  - n: density of points in the lattice (nr. of lattice points per unit volume)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

Unit cell

Primitive unit cell

Properties

- Two primitive cells of different shape can be re-assembled into one another (their volume is the same)
  - by translation with appropriate lattice vectors
- The following translations recover the parallelogram:
  - region I:***CO***; region II:***BO***, region III:***AO***; region IV:none



Two possible primitive cells for a net

Unit cell

Primitive unit cell

Definition

- It is associated with all points $\boldsymbol{r}$ such that (semi-open set):

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

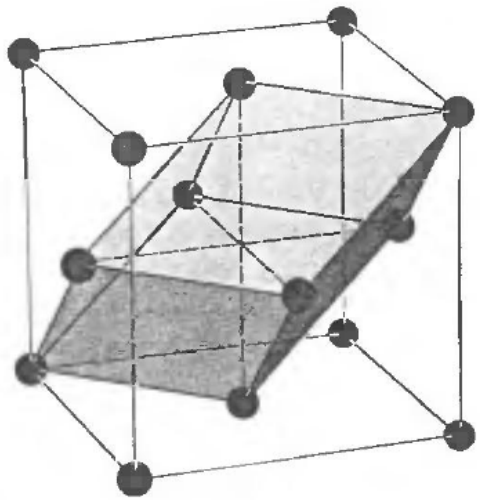
- $0 \leq x_i < 1$
- The parallelepiped spanned by the primitive vectors $\{\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{a}_3\}$
- Sometimes does not display the full symmetry of the lattice
- It is convenient to work with cells that display the full symmetry:
  - conventional cell
  - Wigner-Seitz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

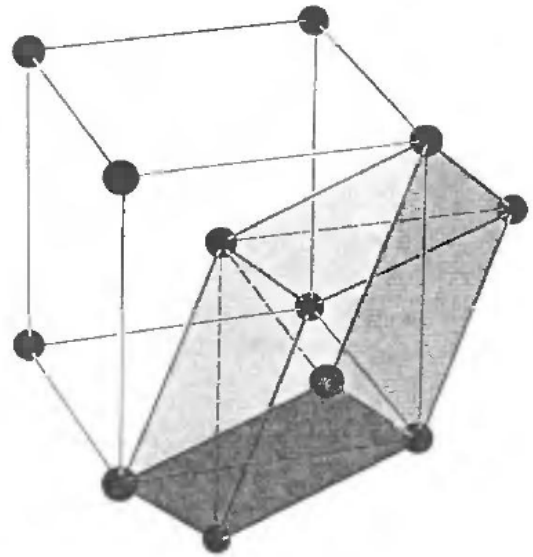
Unit cell

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





Unit cell

Wigner-Seitz cell

A primitive unit cell

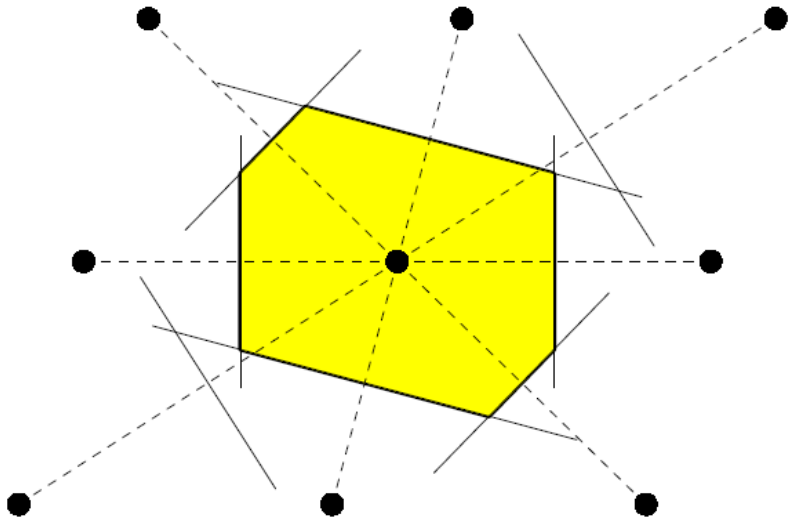
- All points that are closer to a given lattice point than to any other lattice points
- Displays the full symmetry of the Bravais lattice
  - Voronoi cell for sets that are not Bravais lattices
- Operationally:
  - draw lines connecting the point to all others in the lattice
  - draw orthogonal planes bysecting the lines
  - the smallest polyhedron bounded by these planes
- For 2D lattices it is always an hexagon or a rectangle (for rectangular nets)

Unit cell

Wigner-Seitz cell

A primitive unit cell

- A primitive cell (by construction)
- Uniquely defined



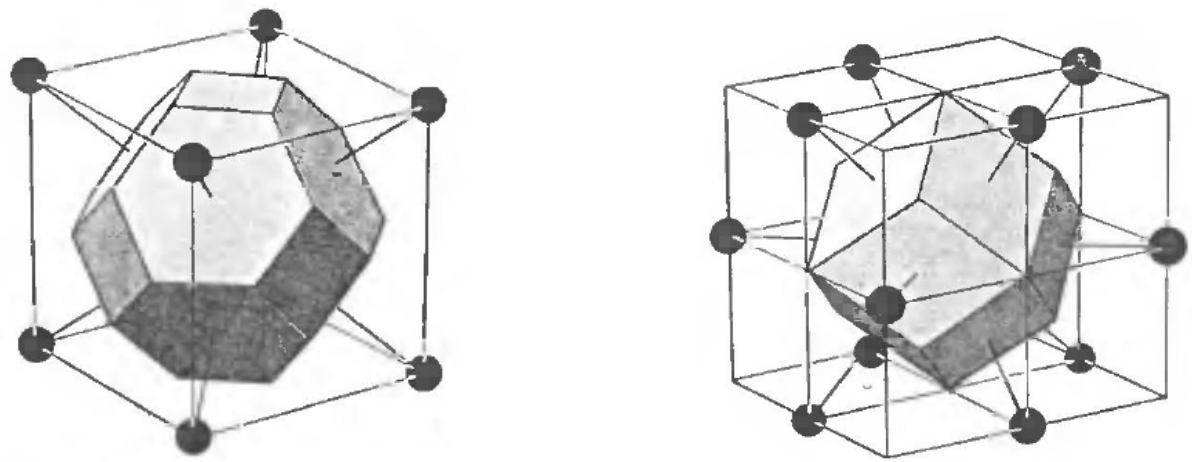
Wigner-Seitz cell for a 2D Bravais lattice

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
  - the surrounding cube is NOT the conventional cell



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

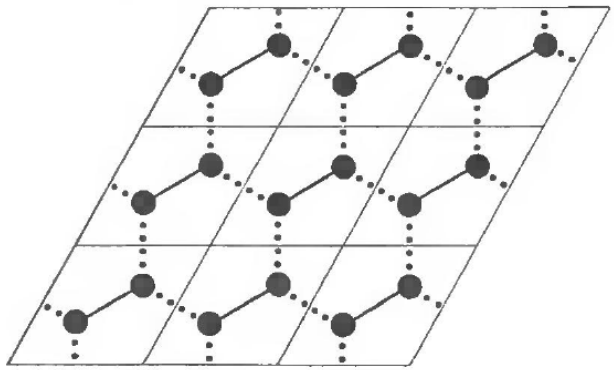
Crystal Structure

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)
- Infinite crystal obtained by translating the basis through all lattice vectors $\boldsymbol{R} \in \mathcal{R}$
- If the basis is a single atom (or ion): monoatomic Bravais lattice

Example: vertices of a honeycomb net

- The Bavais lattice is a triangular net
- two-point basis

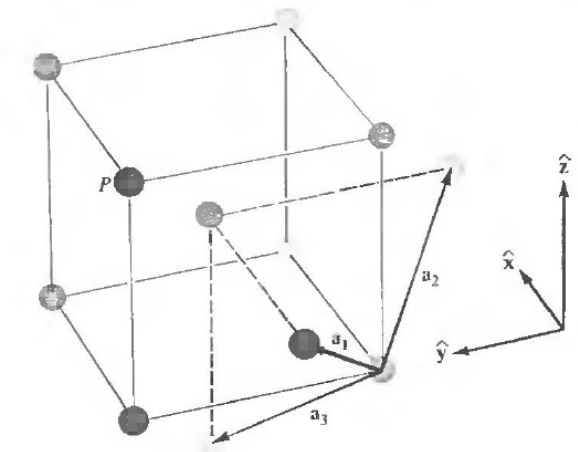


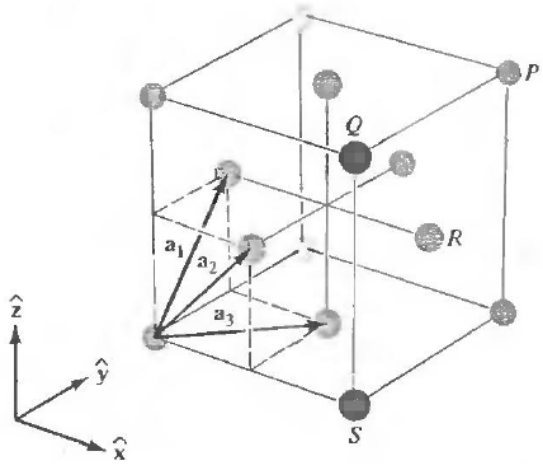
Crystal Structure

Bravais lattices as lattices with a basis

bcc and fcc Bravais lattices

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



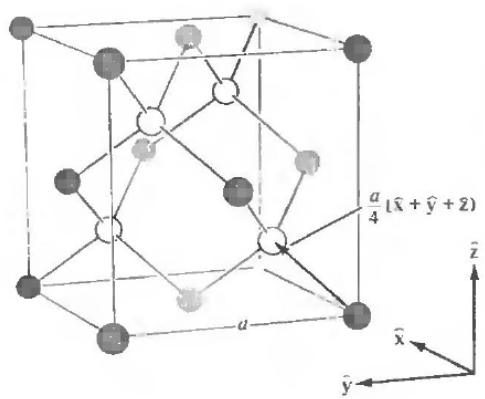


Examples of crystal structures and lattices with basis

Diamond structure

the diamond lattice: NOT a Bravais lattice

- Describes the crystal structure of diamond
- Two interprenetating fcc lattices
  - displaced along the cube's diagonal by $\frac{1}{4}$ its length
- fcc Bravais lattice with a two-point basis
  - $0, \frac{a}{4}(\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}} + \hat{\boldsymbol{z}})$



conventional cubic cell of the diamond lattice

Examples of crystal structures and lattices with basis

Diamond structure

the diamond lattice: NOT a Bravais 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

Examples of crystal structures and lattices with basis

Hexagonal closed packed structure

hcp structure

ELEMENTS WITH THE HEXAGONAL CLOSE-PACKED CRYSTAL STRUCTURE

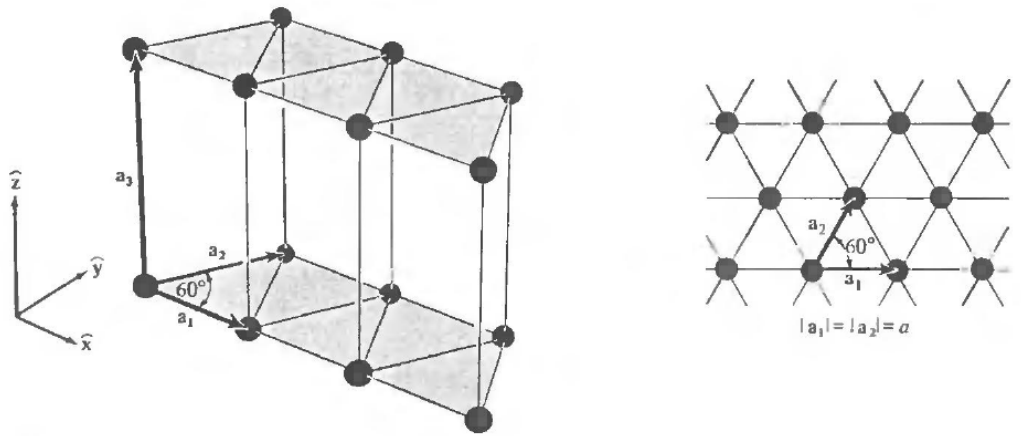
ELEMENT	a (Å)	c	c/a	ELEMENT	a (Å)	c	c/a
Be	2.29	3.58	1.56	Os	2.74	4.32	1.58
Cd	2.98	5.62	1.89	Pr	3.67	5.92	1.61
Ce	3.65	5.96	1.63	Re	2.76	4.46	1.62
α-Co	2.51	4.07	1.62	Ru	2.70	4.28	1.59
Dy	3.59	5.65	1.57	Sc	3.31	5.27	1.59
Er	3.56	5.59	1.57	Tb	3.60	5.69	1.58
Gd	3.64	5.78	1.59	Ti	2.95	4.69	1.59
He (2 K)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

Examples of crystal structures and lattices with basis

Hexagonal closed packed structure

Simple hexagonal Bravais lattice

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

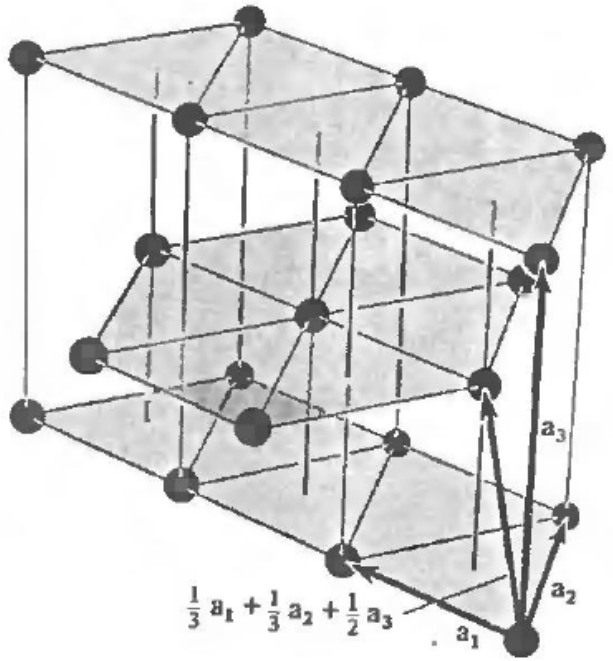


the simple hexagonal Bravais lattice

Examples of crystal structures and lattices with basis

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

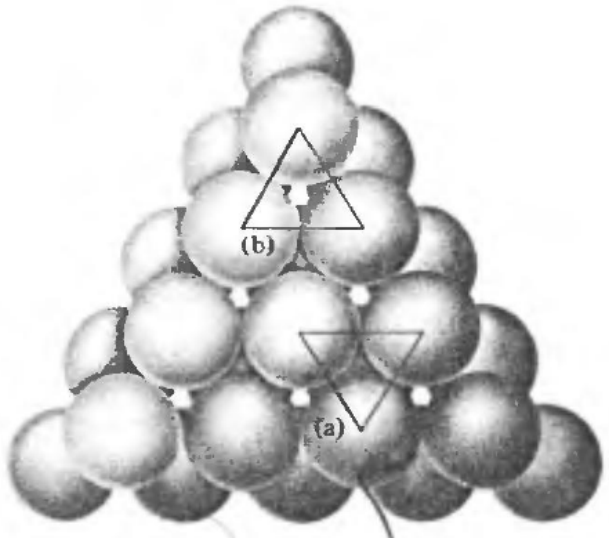


close-packed hexagonal structure (hcp)

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: $\sqrt{\frac{8}{3}}$



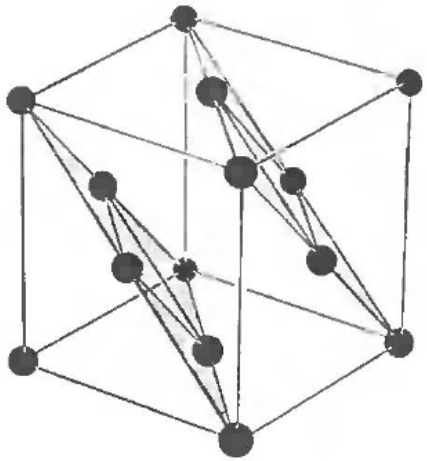
Stack of hard spheres

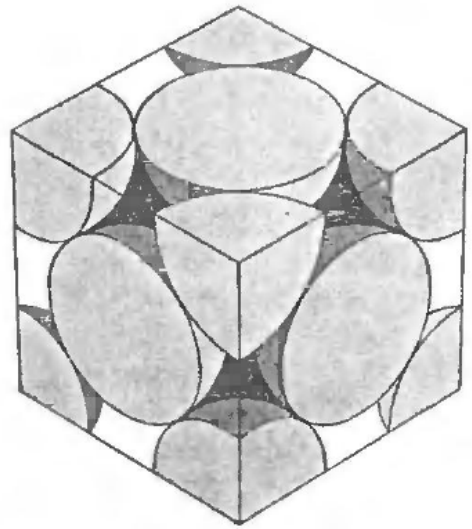
Closed packed structures

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



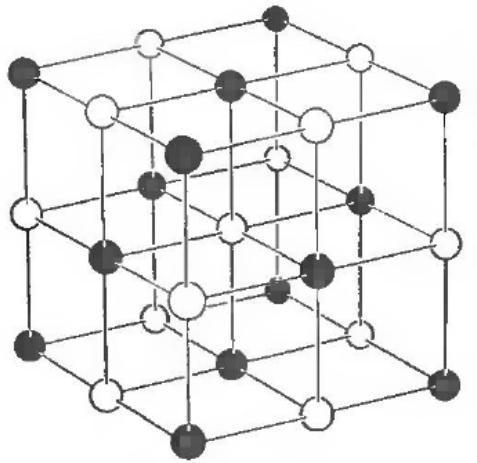


Sections of fcc closed packed spheres

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
- fcc Bravais lattice:
  - basis: 0 (Na), $\frac{a}{2}(\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}} + \hat{\boldsymbol{z}})$ (Cl)
- Each ion is surrounded by six ions of the other kind



The sodium chloride structure

Sodium-Chloride structure

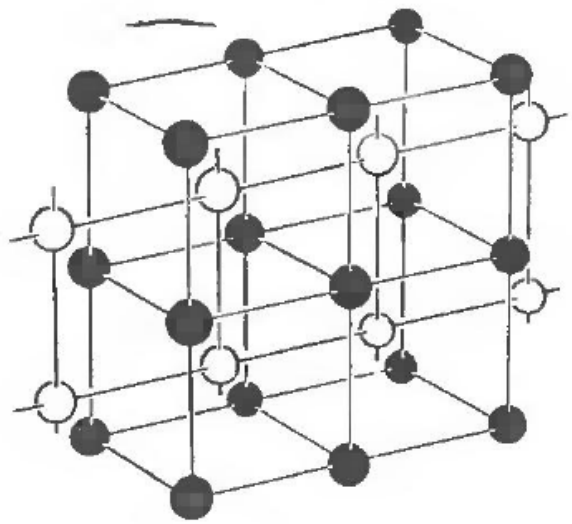
Rock-salt structure: lattice with a basis

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		

Cesium-Chloride structure

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



The cesium chloride structure

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

The Zincblende structure

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		

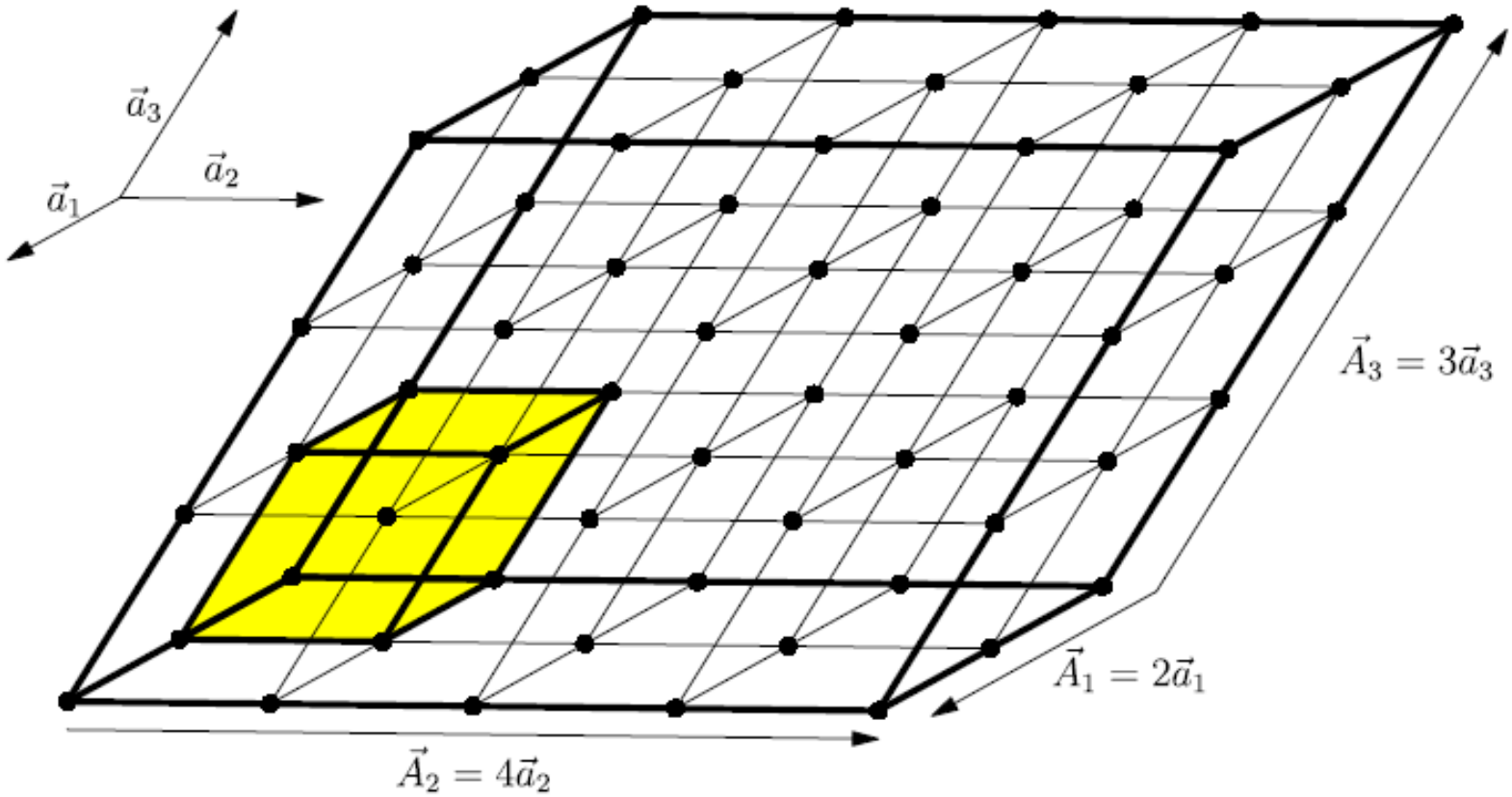
Simple supercells

Non primitive cells

- A $n_1 \times n_2 \times n_3$ supercell is built by keeping:
  - n_1 consecutive primitive cells along $\boldsymbol{a}_1$
  - n_2 consecutive primitive cells along $\boldsymbol{a}_2$
  - n_3 consecutive primitive cells along $\boldsymbol{a}_3$
- Defined by vectors $\boldsymbol{A}_1$, $\boldsymbol{A}_2$, $\boldsymbol{A}_3$
  - $\boldsymbol{A}_1 = n_1\boldsymbol{a}_1$; $\boldsymbol{A}_2 = n_2\boldsymbol{a}_2$; $\boldsymbol{A}_3 = n_3\boldsymbol{a}_3$
  - a new linearly independent set of vectors
- The vectors define a new Bravais lattice $\mathcal{R}_B \subset \mathcal{R}$
  - $\mathcal{R}$ is the underlying original Bravais lattice
- $\mathcal{R}_B$ and $\mathcal{R}$ (and their primitive cells) are commensurate
  - one is obtained from the other by an integer number of times along each primitive direction
  - $\frac{A_i}{a_i} = n_i$

Simple supercells

Non primitive cells

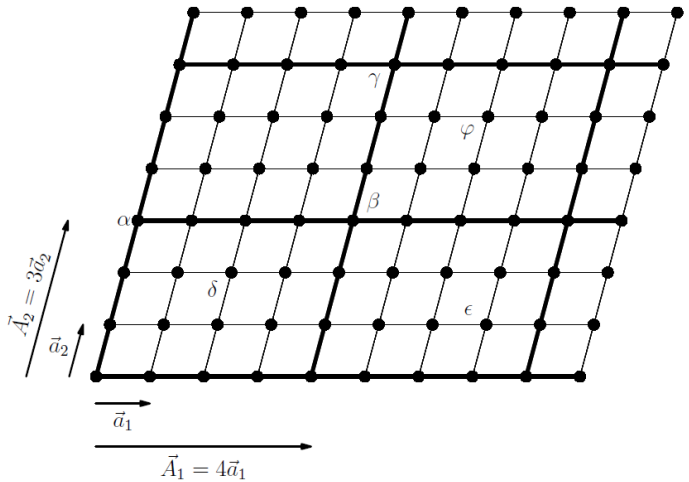


example of a $2 \times 4 \times 3$ supercell

Simple Supercells

Properties

- $N = n_1 n_2 n_3$ lattice points of $\mathcal{R}$ are contained in the primitive cell of $\mathcal{R}_B$
  - the primitive cell of $\mathcal{R}_B$ contains N primitive cells of $\mathcal{R}$
- $V = Nv$
  - v: volume of the primitive cell of $\mathcal{R}$
- $\mathcal{R}_B$ is a subset of $\mathcal{R}$: $\mathcal{R}_B \subset \mathcal{R}$

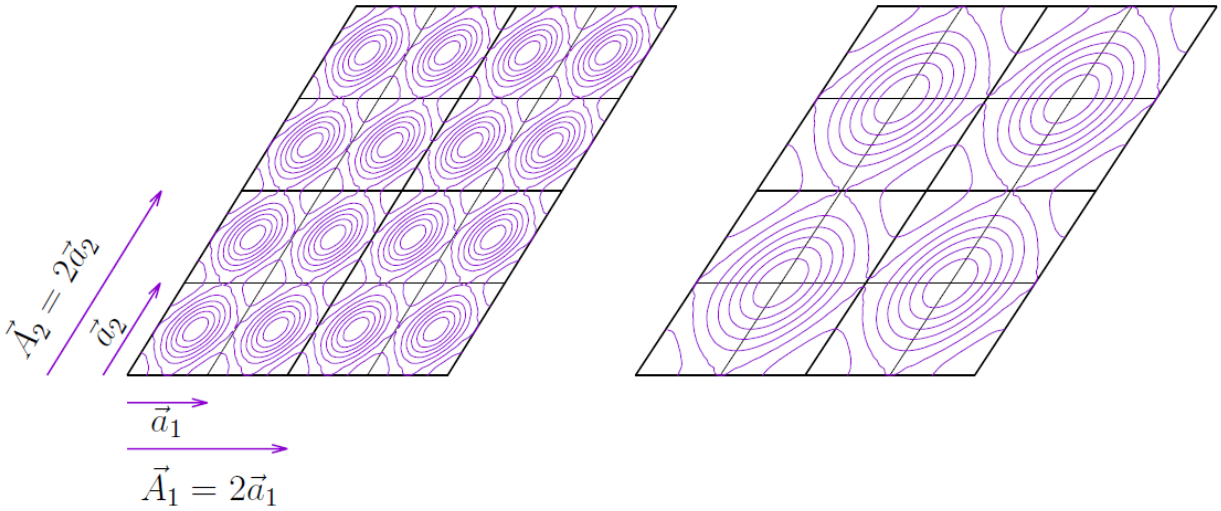


points δ, ϵ, ϕ DO NOT belong to $\mathcal{R}_B$

Simple Supercells

Properties

- $\mathcal{R}$ can be described as $\mathcal{R}_B$ with a basis
  - the lattice points of $\mathcal{R}$ contained in the primitive cell of $\mathcal{R}_B$
- A function periodic on $\mathcal{R}$ is also periodic on $\mathcal{R}_B$
  - the opposite is NOT true in general



left: function periodic on $\mathcal{R}$, right: function periodic on $\mathcal{R}_B$

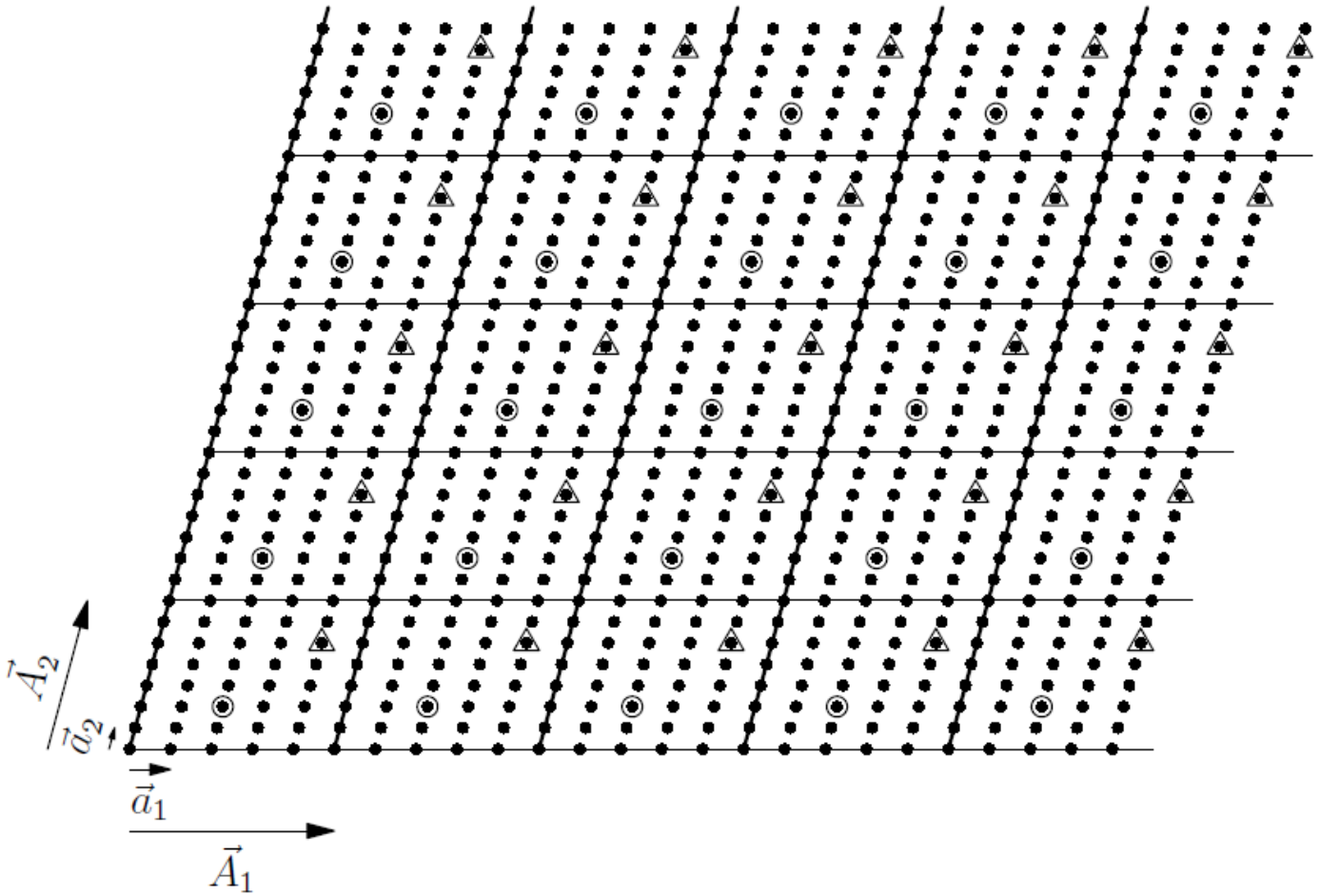
Simple Supercells

Properties

- $\mathcal{R}$ can be partitioned in a finite number of (infinite) subsets:
  - $\mathcal{R} = \bigcup_{i=1}^{N} S_i$
  - $S_i \bigcap S_j = \varnothing$
- Each subset is indexed by the $\mathcal{R}$ point inside the primitive cell of $\mathcal{R}_B$
- Each subset contains all the infinite images obtained by applying the vectors of $\mathcal{R}_B$:
  - $S_j = \{\boldsymbol{r} : \boldsymbol{r} = \boldsymbol{r}_j + \boldsymbol{R}, \forall \boldsymbol{R} \in \mathcal{R}_B\}$
- $\forall (\boldsymbol{r}_i, \boldsymbol{r}_k) \in S_j \ \exists!\ \boldsymbol{R} \in \mathcal{R}_B : \boldsymbol{r}_i - \boldsymbol{r}_k = \boldsymbol{R}$
- $\forall \boldsymbol{R} \in \mathcal{R}_B \ \exists!\ (\boldsymbol{r}_i, \boldsymbol{r}_k) \in S_j : \boldsymbol{r}_i - \boldsymbol{r}_k = \boldsymbol{R}$
- if $\boldsymbol{r}_i$ and $\boldsymbol{r}_k$ belong to different subsets then no vector of $\mathcal{R}_B$ can be found to connect them

Simple supercells

Non primitive cells



supercell with $\boldsymbol{A}_1 = 5\boldsymbol{a}_1$ and $\boldsymbol{A}_2 = 7\boldsymbol{a}_2$

The conventional cell is a supercell

Conventional cell

- The conventional cell vectors $(\boldsymbol{A}_1, \boldsymbol{A}_2, \boldsymbol{A}_3)$ are obtained from the primitive vectors $(\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{a}_3)$ by a linear combination:

$$\begin{pmatrix} \boldsymbol{A}_1 \\ \boldsymbol{A}_2 \\ \boldsymbol{A}_3 \end{pmatrix} = \begin{pmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{23} & c_{23} \\ c_{31} & c_{32} & c_{33} \end{pmatrix} \begin{pmatrix} \boldsymbol{a}_1 \\ \boldsymbol{a}_2 \\ \boldsymbol{a}_3 \end{pmatrix}$$

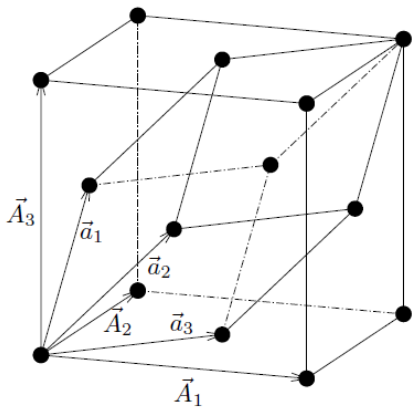
- All non primitive lattices (not of type P) are represented with conventional cells

The conventional cell is a supercell

example: FCC lattive

- The conventional cell vectors $(\boldsymbol{A}_1, \boldsymbol{A}_2, \boldsymbol{A}_3)$ given by:
  - $\boldsymbol{A}_1 = a(1,0,0)$; $\boldsymbol{A}_2 = a(0,1,0)$; $\boldsymbol{A}_3 = a(0,0,1)$
- The primitive vectors $(\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{a}_3)$ can be expressed as:
  - $\boldsymbol{a}_1 = a(0,1/2,1/2)$; $\boldsymbol{a}_2 = a(1/2,0,1/2)$; $\boldsymbol{a}_3 = a(1/2,1/2,0)$
- Therefore:

$$\begin{pmatrix} \boldsymbol{A}_1 \\ \boldsymbol{A}_2 \\ \boldsymbol{A}_3 \end{pmatrix} = \begin{pmatrix} -1 & 1 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{pmatrix} \begin{pmatrix} \boldsymbol{a}_1 \\ \boldsymbol{a}_2 \\ \boldsymbol{a}_3 \end{pmatrix}$$



Packing efficiency

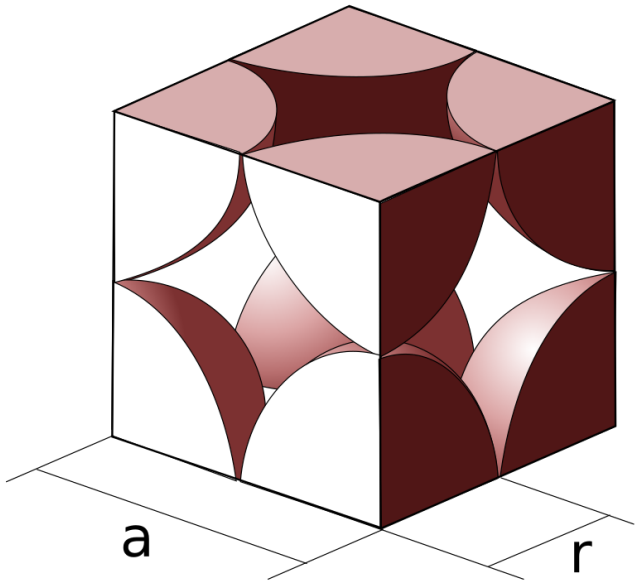
Atomic packing factor (APF)

- Atomic packing factor: fraction of the volume of the unit cell occupied by atoms.
- For simplicity we assume that atoms can be regarded as rigid spheres
  - $V_{atom} = \frac{4}{3}\pi r^3$
  - r radius of the sphere
- depends on:
  - number of atoms in the cell, N
  - its volume, V_{cell}

Packing efficiency

sc lattice

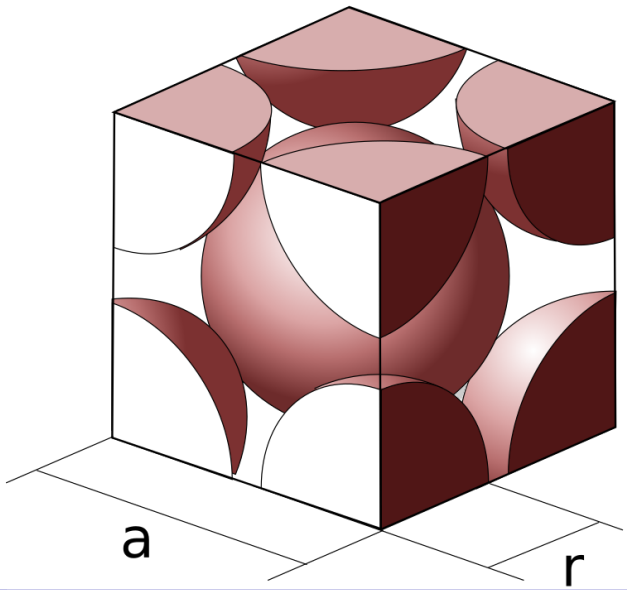
- $N = 1 \times \frac{1}{8} = 1$
  - each corner is shared btw 8 cells
- $V_{cell} = a^3$
- $r = \frac{a}{2}$
  - spheres touch along the cube's sides
- APF$= \frac{\pi}{6} = 0.5236 \sim 52.4\%$



Packing efficiency

bcc lattice

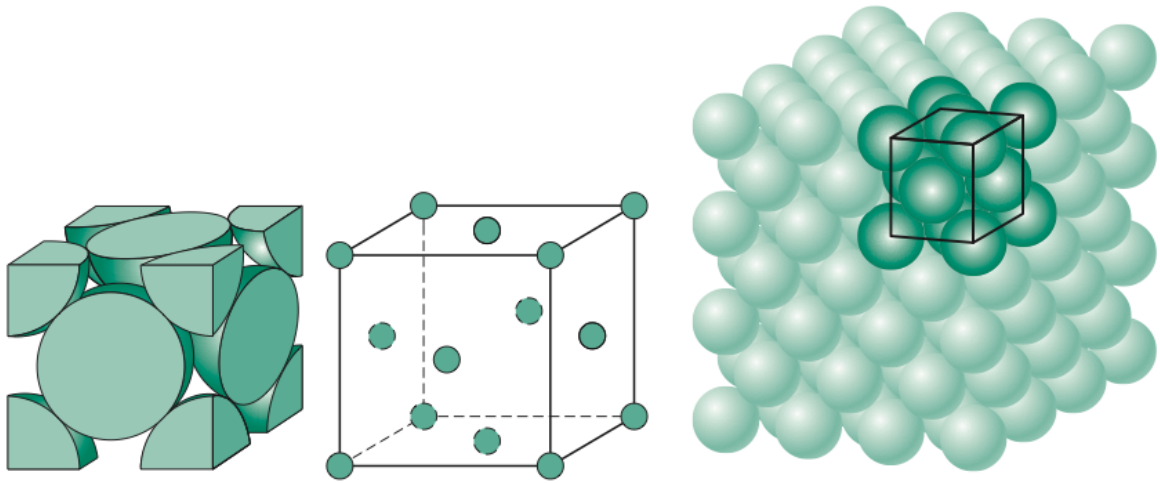
- $N = 1 \times \frac{1}{8} + 1 = 2$
  - one full sphere in the center of the cube
- $V_{cell} = a^3$
- $r = a\frac{\sqrt{3}}{4}$
  - spheres touch along the cube's diagonal
- APF$= \pi\frac{\sqrt{3}}{8} = 0.6802 \sim 68.02\%$



Packing efficiency

fcc lattice

- $N = 1 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$
  - spheres on the faces are shared btw two cells
- $V_{cell} = a^3$
- $r = a\frac{\sqrt{2}}{4}$
  - spheres touch along the cube's faces diagonals
- APF$= \frac{\pi}{3\sqrt{2}} = 0.7405 \sim 74.05\%$



Packing efficiency

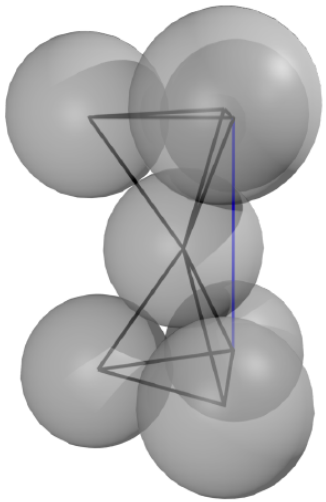
diamond lattice

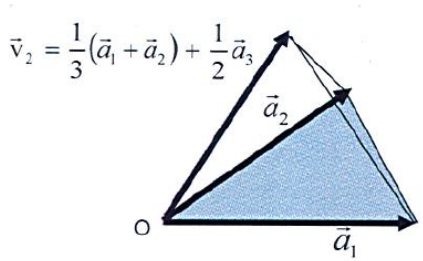
- Obtained from an fcc lattice and adding another fcc lattice:
  - displaced by $\boldsymbol{w}_2 = \frac{a}{4}(\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}} + \hat{\boldsymbol{z}}$
- fcc lattice with a basis: $\boldsymbol{w}_1 = 0$, $\boldsymbol{w}_2$
- N=4+4=8
- $V_{cell} = a^3$
- $r = \frac{|\boldsymbol{w}_2|}{2} = \frac{\sqrt{3}}{8}a$
  - spheres touch along the displacement vector
- APF= $\pi\frac{\sqrt{3}}{16} = 0.3401 \sim 34.01\%$
- lots of empty space due to covalent bonding

Packing efficiency

hcp lattice

- Obtained from a simple exagonal Bravais lattice:
  - $\boldsymbol{a}_1 = a\hat{\boldsymbol{x}}$; $\boldsymbol{a}_2 = \frac{a}{2}\hat{\boldsymbol{x}} + a\frac{\sqrt{3}}{2}\hat{\boldsymbol{y}}$; $\boldsymbol{a}_3 = c\hat{\boldsymbol{z}}$)
- with a two-point basis:
  - $\boldsymbol{v}_1 = 0$, $\boldsymbol{v}_2 = \frac{1}{3}(\boldsymbol{a}_1 + \boldsymbol{a}_2) + \frac{1}{3}\boldsymbol{a}_3$
- $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, and $\boldsymbol{v}_2$ point to the vertex of a tetrahedron:
  - point to the centers of touching perfect spheres
  - $r = \frac{|\boldsymbol{v}_2|}{2} = \frac{a}{2}$





Packing efficiency

hcp lattice

- Ideal $\frac{c}{a}$ ratio when $|\boldsymbol{v}_2| = a \longrightarrow \frac{c}{a} = \sqrt{\frac{8}{3}}$
  - $|\boldsymbol{v}_2|^2 = \boldsymbol{v}_2 \cdot \boldsymbol{v}_2 = \frac{a^2}{3} + \frac{c^2}{4}$
- N=$3 \times 1 + 2 \times 6 \times \frac{1}{6} + 2 \times \frac{1}{2}$=6
- $V_{cell} = 6 \times (\frac{\sqrt{3}}{4} a^2 c) = \frac{3}{2}\sqrt{3} a^2 c$
  - $V_{cell} = 3\sqrt{2} a^3$ for ideal $\frac{c}{a}$ ratio
- APF= $\frac{\pi}{3\sqrt{2}} = 0.7405 \sim 74.05\%$