Modern Physics

Solids

Ionic bonding

Types of binding

- Ionic bonding
- Hydrogen bridge bond
- van der Waals bond
- Covalent bond
- Metallic bond

Types of binding: Comment

There are different forces that bind atoms to molecules and solids.

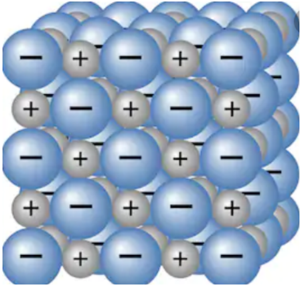
Quantum mechanics is involved in almost all interactions between atoms.

Very often different types of binding occur together, so the strict division of this section is academic in nature.

Ionic bonding

Coulomb force between positively and negatively charged ions

e.g. NaCl (Na: $[\mathrm{Ne}]3s^1$ and Cl: $[\mathrm{Ne}]3s^2\,3p^5$)



Ionic bonding

Comment 1

A common example of ionic bonds is table salt, i.e. sodium chloride.

The electronic configuration of sodium results from the noble gas configuration of neon and a valence electron in the 3s orbital.

The electronic configuration of chloride results from the noble gas configuration of neon and two electrons in the 3s orbital and five electrons in the 3p orbital.

The total energy can be reduced if the 3s valence electron of sodium fills the electron hole of the chloride configuration, so that the noble gas configuration of argon is created.

The charge density of both ions is spherical and the crystal structure of sodium chloride is a close packing of spheres.

Ionic bonding

Comment 2

With sodium chloride, the electrons are stably localized on the sodium and chlorine ions.

It doesn’t always have to be that way.

Often there is a mixture of ionic bonding and covalent bonding.

Hydrogen bridge bond

Types of binding

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- Hydrogen bridge bond
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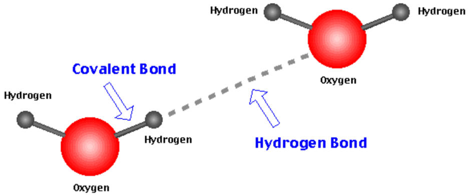
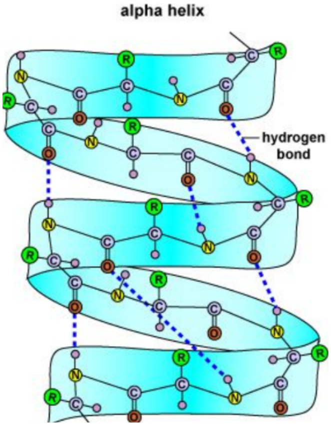
- Metallic bond

Hydrogen bridge bond

Coulomb force between positively charged hydrogen atoms, i.e. protons and negatively charged atoms





Hydrogen bridge bond

Comment

The crystals of water molecules, i.e. ice, are typical examples of hydrogen bonds.

The negative electron cloud of the hydrogen atoms is shifted nearly completely to the oxygen atom.

The water molecule is strongly polar and the positive and negative areas of the water molecule form the hydrogen bond.

There are many examples in chemistry and biology of molecules linked by ionized hydrogen atoms.

van der Waals bond

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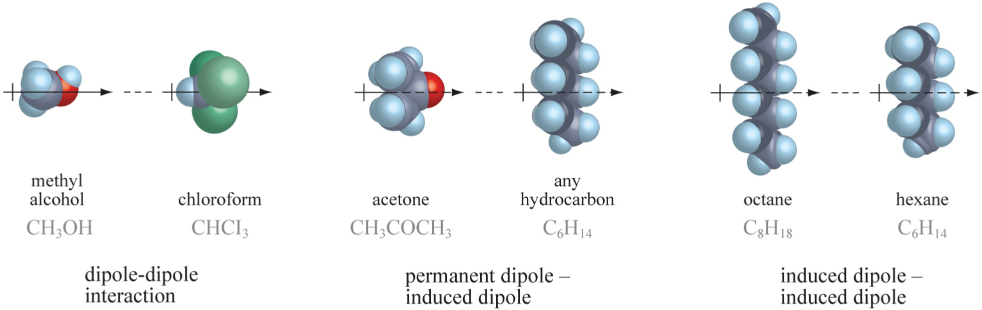
- Metallic bond

van der Waals bond

The reason for van der Waals forces lies in the interaction between permanent and induced electrical dipole moments.



van der Waals bond Comment 1

Electric dipoles experience attractive or repulsive forces depending on their orientation.

This is analogous to the interaction between magnetic dipole moments.

The interaction is limited to a short range because the potential energy is proportional to $1/r^3$.

For comparison, the potential energy of the Coulomb interaction between charges is proportional to $1/r$.

The case of induced dipole moments is particularly interesting.

The picture of a negatively charged electron cloud around an atomic nucleus is not entirely correct, since the cloud is formed by electrons that are constantly moving.

van der Waals bond

Comment 2

The nucleus and the electrons form fluctuating electrical dipole moments due to the movement of the electron.

The movement of the electrons is influenced by neighboring atoms, so that the mean value of the fluctuating dipoles is not zero.

The mere presence of a neighboring atom leads to induced dipole moments in the atoms, leading to an attraction force between the atoms.

For example, the noble gases form crystals at low temperatures due to van der Waals bonds.

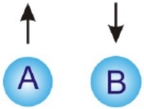
Covalent bond

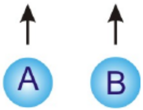
Types of binding

- Ionic bonding
- Hydrogen bridge bond
- van der Waals bond
- Covalent bond
- Metallic bond

Covalent bond 1

The covalent bond is a special form of exchange interaction





atoms can form common molecular orbitals if the atomic orbitals overlap

two electrons can occupy a molecular orbital if they differ in the spin quantum number m_s

Covalent bond 1

Comment 1

Within an atom, the exchange interaction is a consequence of the Coulomb repulsion force between the electrons and the entanglement of the electron states.

Within an atom, the electrons can reduce the effect of the repulsive force if the spins of the electrons are aligned in parallel.

One can imagine that electrons with parallel spins avoid each other and thereby reduce the influence of the repulsive force.

With two neighboring atoms, an additional aspect becomes important.

The figure outlines the case in which the spins of the electrons on the neighboring atoms are aligned parallel or antiparallel.

When the spins of the electrons are antiparallel, the two electrons can jump into the orbital of the electron on the neighboring atom.

Covalent bond 1 Comment 2

This increases the available volume for the electron and the kinetic energy can be reduced due to the uncertainty relations $\Delta x \Delta p \geq \hbar/2$ etc. .

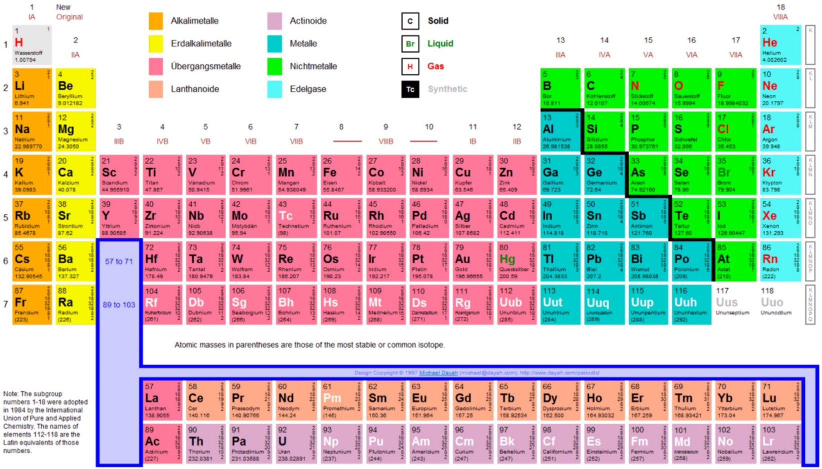
This allows the electrons to increase their binding energy despite the Coulomb repulsion.

This energy gain binds the two atoms together.

If the spins of the two electrons are parallel, they have to avoid each other due to the Pauli principle.

The atoms do not form a bond.

Covalent bond 2



New
Original

🟧 Alkalimetalle
🟨 Erdalkalimetalle
🟥 Übergangsmetalle
🟧 Lanthanoide
🟪 Actinoide
🟦 Metalle
🟩 Nichtmetalle
🟦 Edelgase

C Solid
Br Liquid
H Gas
Tc Synthetic

	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 —	9 VIIIB	10 —	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA	
1	1 H Wasserstoff 1.00794																	2 He Helium 4.002602	K
2	3 Li Lithium 6.941	4 Be Beryllium 9.012182											5 B Bor 10.811	6 C Kohlenstoff 12.0107	7 N Stickstoff 14.00674	8 O Sauerstoff 15.9994	9 F Fluor 18.9984032	10 Ne Neon 20.1797	K L
3	11 Na Natrium 22.989770	12 Mg Magnesium 24.3050											13 Al Aluminium 26.981538	14 Si Silizium 28.0855	15 P Phosphor 30.973761	16 S Schwefel 32.066	17 Cl Chlor 35.453	18 Ar Argon 39.948	K L M
4	19 K Kalium 39.0983	20 Ca Kalzium 40.078	21 Sc Scandium 44.955910	22 Ti Titan 47.867	23 V Vanadium 50.9415	24 Cr Chrom 51.9961	25 Mn Mangan 54.938049	26 Fe Eisen 55.8457	27 Co Kobalt 58.933200	28 Ni Nickel 58.6934	29 Cu Kupfer 63.546	30 Zn Zink 65.409	31 Ga Gallium 69.723	32 Ge Germanium 72.64	33 As Arsen 74.92160	34 Se Selen 78.96	35 Br Brom 79.904	36 Kr Krypton 83.798	K L M N
5	37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirkonium 91.224	41 Nb Niob 92.90638	42 Mo Molybdän 95.94	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.90550	46 Pd Palladium 106.42	47 Ag Silber 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Zinn 118.710	51 Sb Antimon 121.760	52 Te Tellur 127.60	53 I Iod 126.90447	54 Xe Xenon 131.293	K L M N O
6	55 Cs Cäsium 132.90545	56 Ba Barium 137.327	57 to 71	72 Hf Hafnium 178.49	73 Ta Tantal 180.9479	74 W Wolfram 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platin 195.078	79 Au Gold 196.96655	80 Hg Quecksilber 200.59	81 Tl Thallium 204.3833	82 Pb Blei 207.2	83 Bi Wismut 208.98038	84 Po Polonium (209)	85 At Astat (210)	86 Rn Radon (222)	K L M N O P
7	87 Fr Francium (223)	88 Ra Radium (226)	89 to 103	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (266)	107 Bh Bohrium (264)	108 Hs Hassium (269)	109 Mt Meitnerium (268)	110 Ds Darmstadtium (271)	111 Rg Roentgenium (272)	112 Uub Ununbium (285)	113 Uut Ununtrium (284)	114 Uuq Ununquadium (289)	115 Uup Ununpentium (288)	116 Uuh Ununhexium (292)	117 Uus Ununseptium	118 Uuo Ununoctium	K L M N O P Q

Atomic masses in parentheses are those of the most stable or common isotope.

57 La Lanthan 138.9055	58 Ce Cer 140.116	59 Pr Praseodym 140.90765	60 Nd Neodym 144.24	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92534	66 Dy Dysprosium 162.500	67 Ho Holmium 164.93032	68 Er Erbium 167.259	69 Tm Thulium 168.93421	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967
89 Ac Actinium (227)	90 Th Thorium 232.0381	91 Pa Protactinium 231.03588	92 U Uran 238.02891	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)

Note: The subgroup numbers 1-18 were adopted in 1984 by the International Union of Pure and Applied Chemistry. The names of elements 112-118 are the Latin equivalents of those numbers.

Covalent bond 2

Comment

In the periodic table of the elements, the elements marked in green form covalent bonds.

N, O, F and Cl form diatomic molecules.

The other elements (with the exception of bromine) form crystals at room temperature due to covalent bonds.

The electrical conductivity increases with the number of electrons.

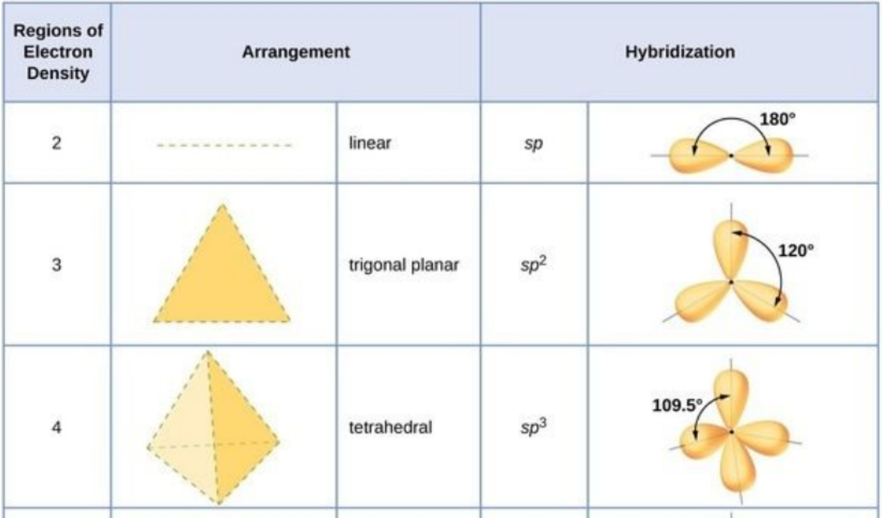
Carbon forms insulating crystals.

Silicon, germanium form semiconductors.

Arsenic and tellurium form semimetals.

Covalent bond 3

sp^n hybrid orbitals:



Regions of Electron Density	Arrangement		Hybridization	
2		linear	sp	180°
3		trigonal planar	sp^2	120°
4		tetrahedral	sp^3	109.5°

Covalent bond 3 Comment 1

The elements highlighted in green are characterized by the fact that the p-shell is not completely occupied by electrons.

However, the covalent bonds are not formed directly by the p orbitals, but by so-called sp^n-hybrid orbitals, i.e. linear combinations of s and p orbitals.

The table shows the sp hybrid orbital first.

The sp orbital is very similar to a normal p orbital and is called a π orbital.

The sp^2 hybrid orbital is planar and has three lobes as shown in the figure.

This is a σ orbital.

Covalent bond 3 Comment 2

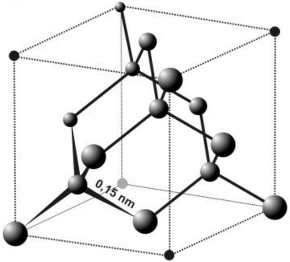
The honeycomb structure of graphite is created by σ orbitals.

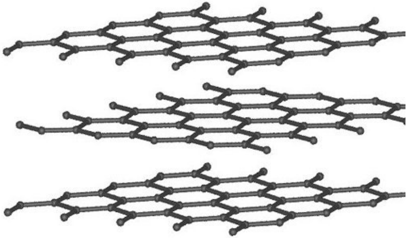
The sp^3 hybrid orbital is displayed in the last line.

The lobes of the orbital point to the corners of a tetrahedron.

The sp^3 hybrid orbitals form the diamond structure, which is realized by carbon, silicon and germanium.

Covalent bond 4





(Diamantstruktur.mp4)

Covalent bond 4

Comment

The illustration compares diamond and graphite, both of which are made up of carbon atoms.

The diamond structure is formed by the sp^3 hybrid orbitals, while the honeycomb structure of graphite results from the sp^2 hybrid orbitals.

In graphite, the hexagonal planes are held together by the weak van der Waals forces.

Metallic bond

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- Hydrogen bridge bond
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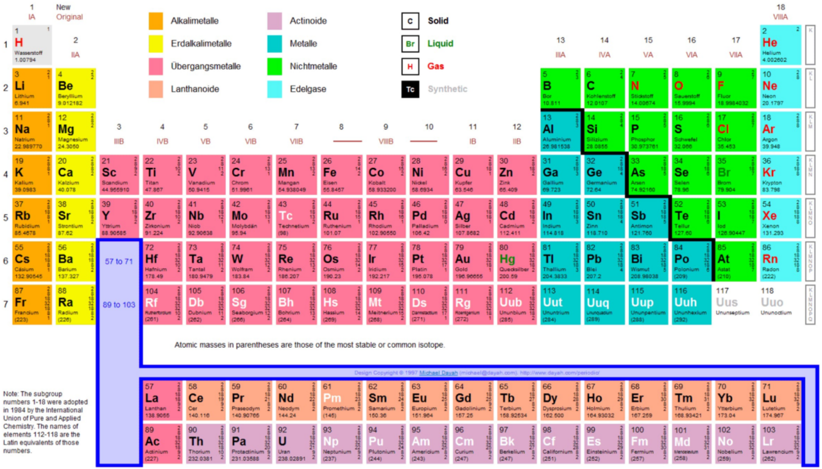
- Metallic bond

Metallic bond 1



Atomic masses in parentheses are those of the most stable or common isotope.

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Metallic bond 1

Comment

Most of the elements in the periodic table form metals when in the solid phase.

Exceptions are the noble gases and the diatomic gases of H_2, N_2, O_2, F_2, Cl_2.

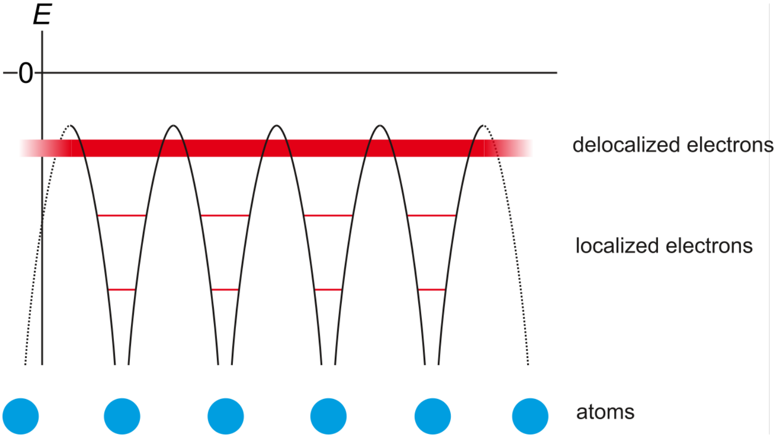
These atoms and molecules form insulating crystals due to the van der Waals forces.

Helium is special because it does not crystallize under ambient pressure.

Due to the uncertainty relations helium is a quantum liquid between 0 and 4.23 K (^4He) and 3.19 K (^3He) with special properties (e.g. superfluidity).

The elements highlighted in green form insulating crystals, semiconductors and semimetals in the solid phase.

Metallic bond 2



Metallic bond 2

Comment 1

The illustration outlines the situation of the metallic bond.

Most electrons are bound in the potential wells of their atoms.

The energy levels of the localized orbitals are indicated by thin red lines.

Overlapping orbitals of neighboring atoms form covalent bonds and the electrons can jump from one atom to another.

The delocalization of the electrons increases with the overlap of the orbitals.

Finally, the electrons no longer occupy the standing waves of localized orbitals, but traveling waves.

Metallic bond 2

Comment 2

The delocalization of the electrons over the entire volume of a crystal reduces the uncertainty of the momentum and thus of the kinetic energy.

Electrons that can move through the crystal are called conduction electrons.

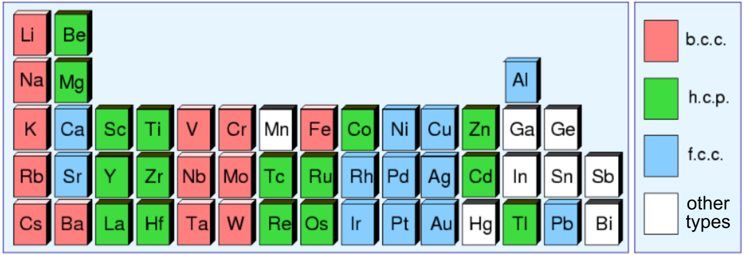
The decrease in the kinetic energy of the conduction electrons contributes to the binding energy of the metal.

Since an electron wave can be occupied by two electrons due to the Pauli principle, many waves of different energies must be occupied.

Therefore, the conduction electrons are marked by a thick red bar in the sketch.

Metallic bond 3

Crystal structures of simple metals



🟥 Li	🟩 Be													
🟥 Na	🟩 Mg											🟦 Al		
🟥 K	🟦 Ca	🟩 Sc	🟩 Ti	🟥 V	🟥 Cr	⬜ Mn	🟥 Fe	🟩 Co	🟦 Ni	🟦 Cu	🟩 Zn	⬜ Ga	⬜ Ge	
🟥 Rb	🟦 Sr	🟩 Y	🟩 Zr	🟥 Nb	🟥 Mo	🟩 Tc	🟩 Ru	🟦 Rh	🟦 Pd	🟦 Ag	🟩 Cd	⬜ In	⬜ Sn	⬜ Sb
🟥 Cs	🟥 Ba	🟩 La	🟩 Hf	🟥 Ta	🟥 W	🟩 Re	🟩 Os	🟦 Ir	🟦 Pt	🟦 Au	⬜ Hg	🟩 Tl	🟦 Pb	⬜ Bi

🟥	b.c.c.
🟩	h.c.p.
🟦	f.c.c.
⬜	other types

b.c.c.	body-centred cubic
h.c.p.	hexagonal close packing
f.c.c.	face-centred cubic

Metallic bond 3

Comment

Since the binding energy of the electrons in the fully occupied orbitals is particularly large, the conduction electrons result from the valence electrons that are less strongly bound to the atomic nucleus.

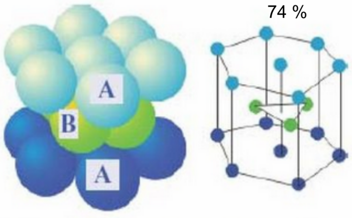
The fully occupied orbitals bound to the atoms lead to a spherical charge distribution.

It is therefore not surprising that the crystal structure of most metals in the periodic table of the elements is described by the closest packing of spheres.

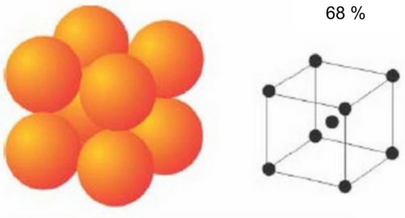
There are three different types of closest packing of spheres (b.c.c, f.c.c., and h.c.p).

There are a few exceptions where the structure of the closest packing of spheres is somewhat distorted (e.g. Hg) or where the crystal structure is determined by covalent bonds of sp hybrid orbitals.

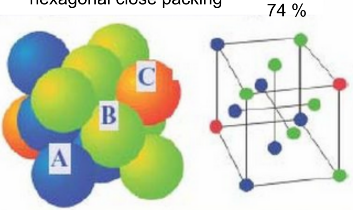
Metallic bond 4



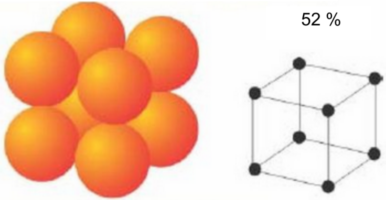
hexagonal close packing



body-centred cubic



face-centred cubic



simple cubic

Metallic bond 4

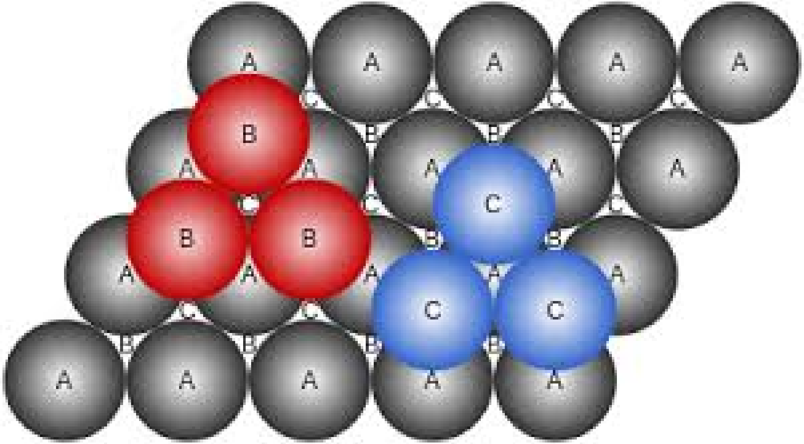
Comment

This figure illustrates the close packing of identical spheres in detail.

The space filling is greatest in the fcc and hcp structures with 74 %.

The space filling of the bcc and sc structures is lower at 68 % and 52 %, respectively.

Metallic bond 5



Metallic bond 5

Comment

This figure illustrates the difference between the AB packing of the hcp structure and the ABC packing of the fcc structure.

The threefold symmetry axis is perpendicular to the plane of the drawing.

In the AB packing, the axis of symmetry corresponds to the six-fold axis of symmetry of a hcp lattice.

In the ABC packing, the axis of symmetry corresponds to the diagonal of the cubic unit cell of an fcc lattice.

Solids

Bravais lattice

Crystal lattices

- Bravais lattice and Wigner-Seitz cell
- Reciprocal lattice
- Brillouin zones

Crystal lattices

Comment

In the introductory chapter “Classical Wave Optics”, X-rays were considered in crystal lattices.

The structure of crystals can be determined using the diffraction of X-rays.

In the following vibrations of crystal lattices and electron waves in crystal lattices are considered.

Knowing some basic properties, especially of cubic crystals, is very helpful or even mandatory.

Bravais lattice and Wigner-Seitz cell 1

Bravais lattice and Wigner-Seitz cell 1

Comment

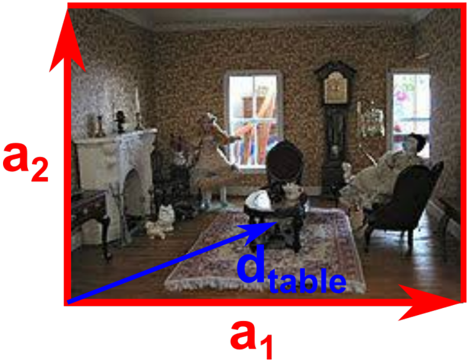
A crystal lattice is formed by the periodic repetition of a primitive unit cell.

The figure illustrates this fact by repeating the room of a doll’s house.

Each red rectangle is a primitive unit cell of the lattice.

Bravais lattice and Wigner-Seitz cell 2

A primitive unit cell is defined by three linearly independent vectors $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$



The position of the objects within the primitive unit cell is described by the vectors $\vec{d}_i$ with respect to the vectors $\vec{a}_1$, $\vec{a}_2$ and $\vec{a}_3$ of the primitive unit cell.

Bravais lattice and Wigner-Seitz cell 2 Comment

The primitive unit cell is spanned by the three linearly independent vectors $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$.

The position of each object within the primitive unit cell is given by a vector $\vec{d}_i$.

The totality of the vectors $\vec{d}_i$ is called the basis of the lattice.

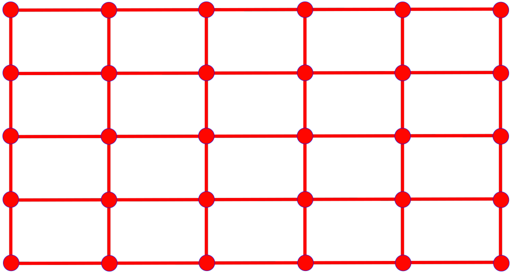
The angles at which the diffraction maxima are observed in X-ray diffraction are determined by the primitive unit cell of the crystal lattice, i.e. the vectors $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$.

The intensity of the diffraction peaks is determined by the so-called structure factor, which is a function of the vectors $\vec{d}_i$ (for details see 3rd lecture).

Bravais lattice and Wigner-Seitz cell 3

The position of the primitive units cell is given by the vectors

$$\vec{R}_{n_1,n_2,n_3} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3 + \vec{r}_{\text{offset}}$$



The vectors $\vec{R}_{n_1,n_2,n_3}$ define a point lattice, which is called the **Bravais lattice**

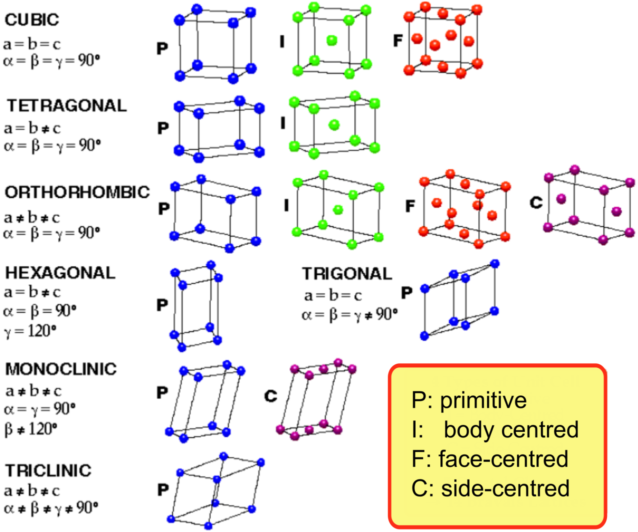
Bravais lattice and Wigner-Seitz cell 3 Comment

The position of the primitive unit cell is indicated by the formula underlined in red.

The numbers $n_{1,2,3}$ are integers.

The vectors $\vec{R}_{n_1,n_2,n_3}$ define a mathematical point lattice which is called the Bravais lattice.

Bravais lattice and Wigner-Seitz cell 4



P: primitive
I: body centred
F: face-centred
C: side-centred

Bravais lattice and Wigner-Seitz cell 4

Comment 1

There are 14 different types of Bravais lattices.

The translation of the primitive unit cell can be combined with rotations of 60°, 90°, 120° and 180°, as well as with reflections and inversions

These symmetry operations limit the number of different Bravais lattices to 14.

The types of Bravais lattices can be divided into so-called crystal classes, e.g. the cubic class, the tetragonal class, etc.

The figure illustrates the various types of Bravais lattices.

Bravais lattice and Wigner-Seitz cell 4 Comment 2

But attention: in some cases the shown unit cells are not the primitive unit cells.

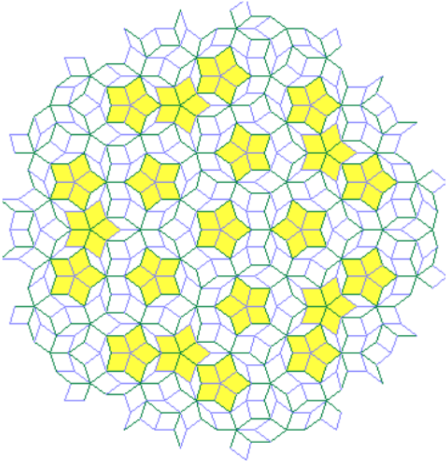
The primitive unit cell always encloses one point of the Bravais lattice.

E.g. the shown cubic cell of the bcc lattice encloses two points of the Bravais lattice and the shown cubic cell of the fcc lattice encloses four points of the Bravais lattice.

Of the three cubic cells shown, only the simple cubic lattice cell is a primitive unit cell!

Bravais lattice and Wigner-Seitz cell 5

Penrose tiling



Bravais lattice and Wigner-Seitz cell 5 Comment

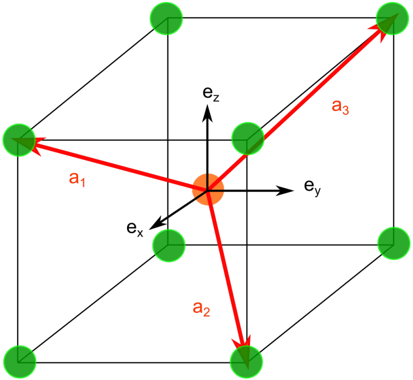
From tiling it is known that even with two or more primitive unit cells, area-filling periodic and aperiodic structures result.

The figure shows an aperiodic, but nevertheless highly symmetrical structure that results from two primitive unit cells.

Such structures also occur in nature, albeit rarely, so that they do not have to be considered in the context of this lecture.

Bravais lattice and Wigner-Seitz cell 6

bcc lattice



possible vectors of a primitive unit cell

$$\vec{a}_1 = \frac{a}{2}(\vec{e}_x - \vec{e}_y + \vec{e}_z)$$
$$\vec{a}_2 = \frac{a}{2}(\vec{e}_y - \vec{e}_z + \vec{e}_x)$$
$$\vec{a}_3 = \frac{a}{2}(\vec{e}_z - \vec{e}_x + \vec{e}_y)$$

Bravais lattice and Wigner-Seitz cell 6 Comment

Many elements crystallize in the bcc and fcc lattice.

The figure shows the cubic unit cell of the bcc lattice.

The cubic unit cell of the bcc lattice encloses two points of the Bravais lattice.

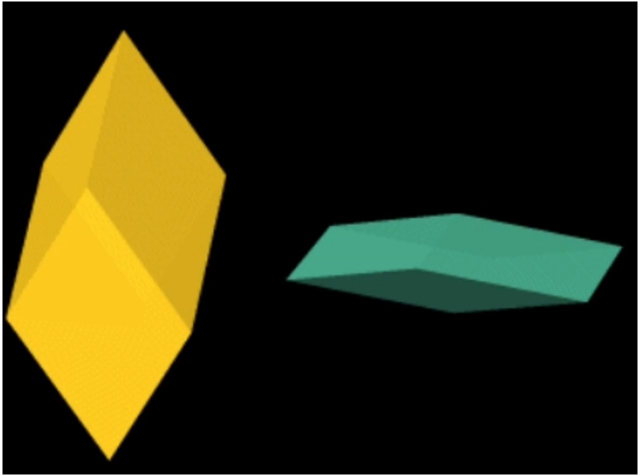
E.g. the red vectors can be used to span a primitive unit cell.

The formulas show the vectors $\vec{a}_{1,2,3}$ in the basis of the orthogonal unit vectors $\vec{e}_{x,y,z}$.

The primitive unit cell has the shape of a rhombohedron.

This primitive unit cell is simple but unfortunately does not show the symmetries of the cubic unit cell of the bcc lattice.

Bravais lattice and Wigner-Seitz cell 7



(Rhombohedron.mp4)

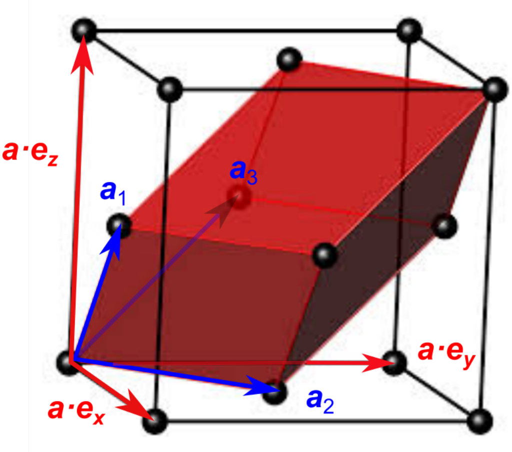
Bravais lattice and Wigner-Seitz cell 7

Comment

The video gives a spatial impression of two rhombohedrons.

Bravais lattice and Wigner-Seitz cell 8

fcc lattice



possible vectors of a primitive unit cell

$$\vec{a}_1 = \frac{a}{2}\left(\vec{e}_x + \vec{e}_z\right)$$
$$\vec{a}_2 = \frac{a}{2}\left(\vec{e}_y + \vec{e}_x\right)$$
$$\vec{a}_3 = \frac{a}{2}\left(\vec{e}_z + \vec{e}_y\right)$$

Bravais lattice and Wigner-Seitz cell 8 Comment

The figure shows the cubic unit cell of the fcc lattice.

The cubic unit cell of the fcc lattice encloses four lattice points of the Bravais lattice.

The vectors $\vec{a}_{1,2,3}$ can be used to span a primitive cell of the fcc lattice.

The result is a rhombohedron which is drawn in red in the cubic unit cell of the fcc lattice.

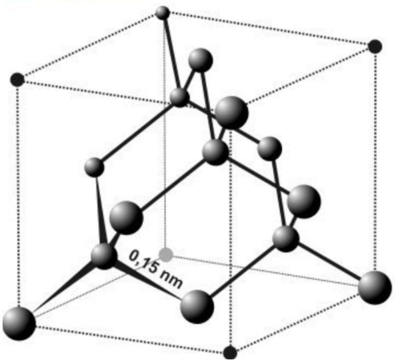
The rhombohedron of the primitive unit cell encloses one point of the Bravais lattice.

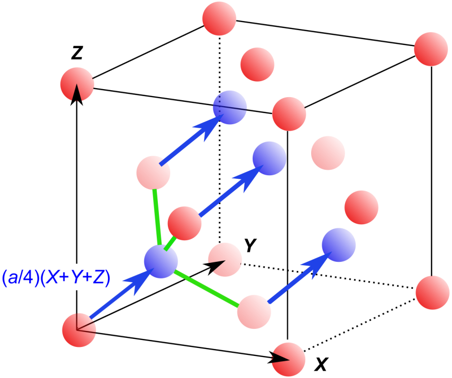
So the volume of the primitive unit cell is $V_{\text{cubic cell}}/4 = a^3/4$.

The formulas give the vectors $\vec{a}_{1,2,3}$ in the basis of the orthogonal unit vectors $\vec{e}_{x,y,z}$.

Bravais lattice and Wigner-Seitz cell 9

diamond lattice (fcc with basis of two atoms)





Bravais lattice and Wigner-Seitz cell 9 Comment 1

The figure shows the cubic unit cell of the diamond structure.

The diamond lattice is important because the semiconductors silicon and germanium crystallize in the diamond lattice.

In the left figure the tetrahedra of the sp^3 hybrid orbitals are easy to see.

The figure on the right shows the unit cell again, with the atoms that lie on the corners and surfaces of the cubic unit cell being marked in red.

The primitive unit cell of the diamond structure contains a second atom, which is marked in blue in the right figure.

Bravais lattice and Wigner-Seitz cell 9

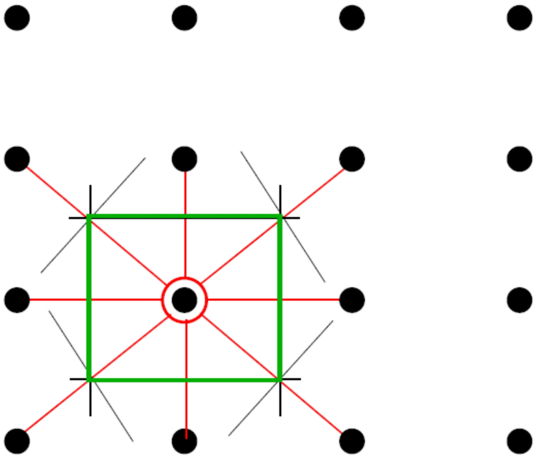
Comment 2

The blue points results when the points marked in red are shifted along a diagonal of the cubic unit cell.

The diamond structure is an fcc lattice with a base of two atoms, labeled red and blue in the right figure.

Bravais lattice and Wigner-Seitz cell 10

construction of the Wigner-Seitz cell



Bravais lattice and Wigner-Seitz cell 10 Comment 1

The primitive unit cell formed by the three vectors $\vec{a}_{1,2,3}$ has the disadvantage that the resulting rhombohedron does not show the symmetry of the crystal lattice at all.

In describing experimental results, it is important that data can be plotted within a primitive unit cell that shows the symmetry of the lattice.

For example, the cubic unit cells of the bcc and fcc lattice show the symmetry of the lattice.

The disadvantage of these cells is that they contain two or four primitive unit cells.

In these unit cells, the same experimental results would be displayed two or four times.

Bravais lattice and Wigner-Seitz cell 10 Comment 2

The Wigner-Seitz cell is a primitive unit cell that shows the symmetry of the lattice.

The figure shows the construction principle of the Wigner-Seitz cell for a planar square lattice.

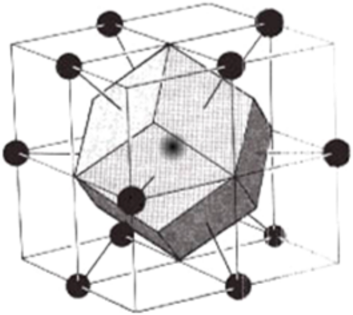
One point of the Bravais lattice is selected and connected to the nearest neighboring points by vectors.

These vectors are perpendicular to planes that intersect the vectors in the middle.

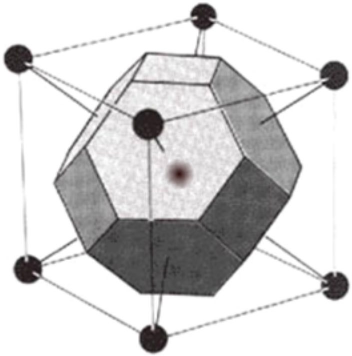
The volume enclosed by these planes is the Wigner-Seitz cell.

In the case of a cubic lattice, the Wigner-Seitz cell is a cube.

Bravais lattice and Wigner-Seitz cell 11



f.c.c Wigner-Seitz cell



b.c.c Wigner-Seitz cell

Bravais lattice and Wigner-Seitz cell 11 Comment

The figure shows the Wigner-Seitz cells of the fcc lattice and the bcc lattice.

With the bcc lattice, the central point in the cubic unit cell is the starting point of the construction.

The resulting Wigner-Seitz cell shows the symmetry of the cubic unit cell, i.e. the rotations of 60° around the diagonal, or the rotations of 90° around the axes through the centers of the cube faces.

With the fcc lattice, one center point on the surface of the cubic cell is chosen as the starting point.

In the figure on the left, this point is shifted to the center of a cubic cell.

The resulting Wigner-Seitz cell shows all symmetries of the cubic unit cell.

Reciprocal lattice

Crystal lattices

- Bravais lattice and Wigner-Seitz cell
- Reciprocal lattice
- Brillouin zones

Reciprocal lattice 1

The vectors of the primitive unit cell are $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$

Bravais lattice

$$\underline{\vec{R}_{n_1,n_2,n_3} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3}$$

Definition of the reciprocal lattice $\boxed{\vec{a}_i\vec{b}_j = 2\pi\delta_{ij}}$

$$\vec{b}_1 = \frac{2\pi}{V_{\text{Cell}}}(\vec{a}_2 \times \vec{a}_3), \quad \vec{b}_2 = \frac{2\pi}{V_{\text{Cell}}}(\vec{a}_3 \times \vec{a}_1), \quad \vec{b}_3 = \frac{2\pi}{V_{\text{Cell}}}(\vec{a}_1 \times \vec{a}_2)$$

volume of the primitive unit cell $V_{\text{Cell}} = \vec{a}_1(\vec{a}_2 \times \vec{a}_3)$

Reciprocal lattice 1

Comment

The vectors R of the equation underlined in red indicate the points of the Bravais lattice.

The vectors $\vec{a}_{1,2,3}$ span the rhombohedral primitive unit cell of the Bravais lattice and are the basis vectors of the Bravais lattice.

The equation outlined in red gives the definition of the reciprocal lattice.

The vectors $\vec{b}_{1,2,3}$ are orthogonal to the vectors $\vec{a}_{1,2,3}$ and can easily be calculated with the vector products of the next line.

Reciprocal lattice 2

reciprocal lattice

$$\underline{\vec{K}_{hk\ell} = h\vec{b}_1 + k\vec{b}_2 + \ell\vec{b}_3}$$

Miller indices

$$h, k, \ell = 0, \pm 1, \pm 2 \ldots$$

$$V_{\mathrm{BZ}} = \vec{b}_1(\vec{b}_2 \times \vec{b}_3) = \frac{(2\pi)^3}{\vec{a}_1(\vec{a}_2 \times \vec{a}_3)} = \frac{(2\pi)^3}{V_{\mathrm{Cell}}}$$

Reciprocal lattice 2 Comment 1

The vectors K of the underlined equation indicate the points of the reciprocal lattice.

The vectors $\vec{b}_{1,2,3}$ span a primitive unit cell of the reciprocal lattice and are the basis vectors of the reciprocal lattice.

There is a simple relationship between the volumes of the primitive unit cells of the Bravais lattice V_{Cell} and the reciprocal lattice V_{BZ}, which is given in the last line.

With the orthogonal vectors $\vec{a}_1$, $\vec{a}_2$ and $\vec{a}_3$ of a simple cubic lattice this formula results directly.

If the vectors are not perpendicular to each other, the calculation is more laborious, but leads to the same result.

Reciprocal lattice 2

Comment 2

The Wigner-Seitz cell of the reciprocal lattice is called the 1st Brillouin zone.

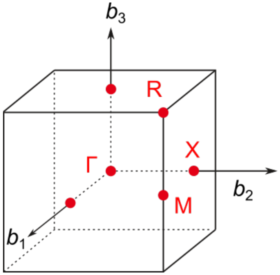
Since the volume of the primitive unit cell is independent of the shape of the cell, I simply denote the volume of the primitive unit cell of the reciprocal lattice with V_{BZ}.

Reciprocal lattice 3

$$\vec{b}_1 = \frac{2\pi}{V_{\text{Cell}}}(\vec{a}_2 \times \vec{a}_3), \quad \vec{b}_2 = \frac{2\pi}{V_{\text{Cell}}}(\vec{a}_3 \times \vec{a}_1), \quad \vec{b}_3 = \frac{2\pi}{V_{\text{Cell}}}(\vec{a}_1 \times \vec{a}_2)$$

the vectors $\vec{b}_{1,2,3}$ of the simple cubic lattice

with $\vec{a}_1 = a\vec{e}_x$, $\vec{a}_2 = a\vec{e}_y$, and $\vec{a}_3 = a\vec{e}_z$



$$\vec{b}_1 = \frac{2\pi}{a^3}(a\vec{e}_y \times a\vec{e}_z) = \frac{2\pi}{a}\vec{e}_x$$

$$\vec{b}_2 = \frac{2\pi}{a}\vec{e}_y$$

$$\vec{b}_3 = \frac{2\pi}{a}\vec{e}_z$$

Reciprocal lattice 3 Comment

This page shows the calculation of the vectors $\vec{b}_{1,2,3}$ of the simple cubic lattice.

The $\vec{b}_{1,2,3}$ are parallel to the vectors $\vec{a}_{1,2,3}$ and the primitive unit cell of the reciprocal lattice is also a cube.

The figure shows the 1st Brillouin zone of the simple cubic lattice.

The lattice point of the reciprocal lattice is in the center of the cube.

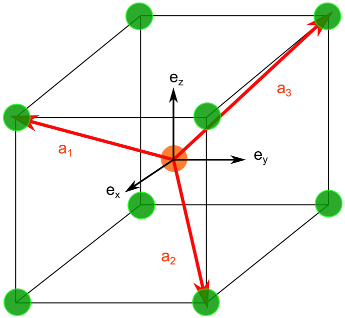
The center of the 1st Brillouin zone is always designated with the letter Γ.

Important points of the 1st Brillouin zone are also marked with letters.

The corners of the cube are denoted by R and the center of the edges by M.

The centers of the faces of the cube are denoted by X.

Reciprocal lattice 4



cubic cell of the bcc lattice

basis vectors of the Bravais lattice

$$\vec{a}_1 = \frac{a}{2}(\vec{e}_x - \vec{e}_y + \vec{e}_z)$$
$$\vec{a}_2 = \frac{a}{2}(\vec{e}_y - \vec{e}_z + \vec{e}_x)$$
$$\vec{a}_3 = \frac{a}{2}(\vec{e}_z - \vec{e}_x + \vec{e}_y)$$

basis vectors of the reciprocal lattice

$$\vec{b}_1 = \frac{2\pi}{V_{\text{Cell}}}(\vec{a}_2 \times \vec{a}_3) = \frac{2\pi}{a}(\vec{e}_x + \vec{e}_z)$$
$$\vec{b}_2 = \frac{2\pi}{V_{\text{Cell}}}(\vec{a}_3 \times \vec{a}_1) = \frac{2\pi}{a}(\vec{e}_y + \vec{e}_x)$$
$$\vec{b}_3 = \frac{2\pi}{V_{\text{Cell}}}(\vec{a}_1 \times \vec{a}_2) = \frac{2\pi}{a}(\vec{e}_z + \vec{e}_y)$$

Reciprocal lattice 4

Comment

To illustrate various aspects of solid-state physics, the substances Cu, Pd, Si and Ge are considered in the following.

These elements crystallise in an fcc lattice.

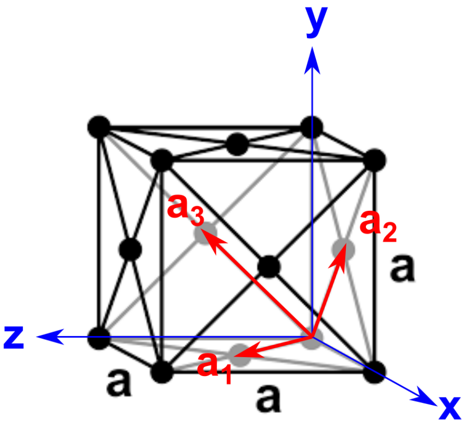
There is an important relationship between the fcc and bcc lattices that one needs to know.

The figure shows the cubic unit cell of the bcc lattice.

The first three formulas on the right give the basis vectors of the Bravais lattice $\vec{a}_{1,2,3}$, which are shown in the figure.

The basis vectors of the reciprocal lattice $\vec{b}_{1,2,3}$ can be calculated with the vectors $\vec{a}_{1,2,3}$ and it turns out that the vectors $\vec{b}_{1,2,3}$ are the basis vectors of an fcc lattice.

Reciprocal lattice 5



cubic cell of the fcc lattice

basis vectors of the Bravais lattice

$$\vec{a}_1 = \frac{a}{2}\left(\vec{e}_x + \vec{e}_z\right)$$
$$\vec{a}_2 = \frac{a}{2}\left(\vec{e}_y + \vec{e}_x\right)$$
$$\vec{a}_3 = \frac{a}{2}\left(\vec{e}_z + \vec{e}_y\right)$$

basis vectors of the reciprocal lattice

$$\vec{b}_1 = \frac{2\pi}{a}(\vec{e}_x - \vec{e}_y + \vec{e}_z)$$
$$\vec{b}_2 = \frac{2\pi}{a}(\vec{e}_y - \vec{e}_z + \vec{e}_x)$$
$$\vec{b}_3 = \frac{2\pi}{a}(\vec{e}_z - \vec{e}_x + \vec{e}_y)$$

Reciprocal lattice 5

Comment

This figure shows the cubic unit cell of the fcc lattice.

The first three formulas on the right give the basis vectors of the Bravais lattice $\vec{a}_{1,2,3}$, which are shown in the figure.

These vectors are collinear with the basis vectors, which were previously calculated for the reciprocal lattice of the bcc lattice.

So the reciprocal lattice of the bcc lattice has the fcc structure.

The formulas written in blue give the basis vectors of the reciprocal lattice of the fcc lattice.

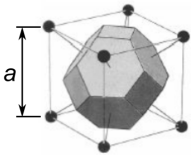
These vectors are collinear to the vectors $\vec{a}_{1,2,3}$ of the bcc lattice.

The reciprocal lattice of the fcc lattice has a bcc structure.

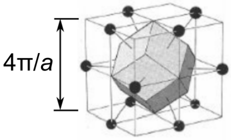
Reciprocal lattice 6

Real lattice

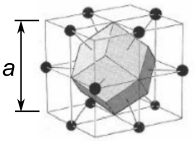
Reciprocal lattice



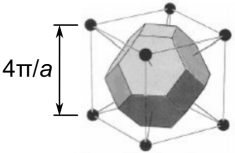
bcc Wigner-Seitz cell



fcc Brillouin zone



fcc Wigner-Seitz cell



bcc Brillouin zone

Reciprocal lattice 6 Comment

This page summarizes these results.

The reciprocal lattice of the bcc lattice is an fcc lattice.

The reciprocal lattice of the fcc lattice is a bcc lattice.

The images on the left show the Wigner-Seitz cells of the bcc and fcc lattice.

The images on the right show the 1st Brillouin zone of the bcc and fcc lattice.

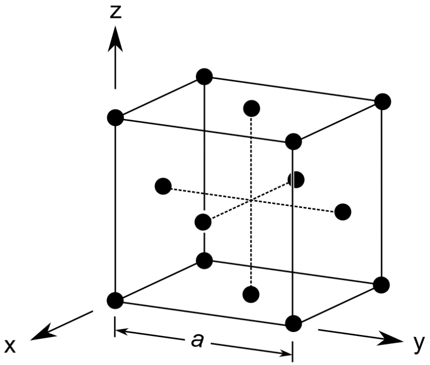
The 1st Brillouin zone is the most important Brillouin zone and is simply referred to as the Brillouin zone in the figures to the right.

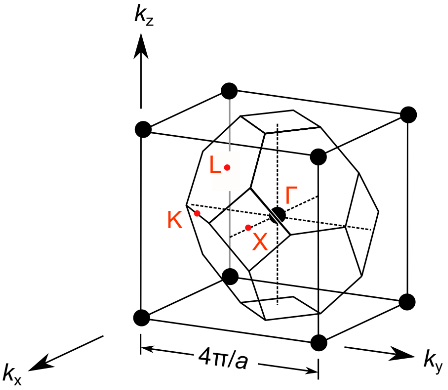
It is also useful to note that the lattice parameter of the cubic unit cell of the reciprocal lattice is $4\pi/a$ if a denotes the lattice parameter of the cubic cell of the Bravais lattice.

Reciprocal lattice 7

Notice

The reciprocal lattice of an fcc lattice is a bcc lattice!





Reciprocal lattice 7

Comment

The left figure shows the cubic unit cell of the fcc lattice again.

The right figure shows the cubic unit cell of the reciprocal lattice.

It’s a bcc lattice.

The right figure also shows the 1st Brillouin zone.

Important points of symmetry are marked with letters.

Brillouin zones

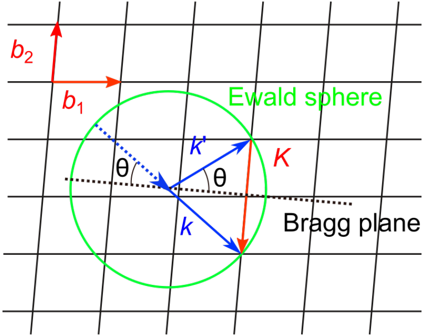
Crystal lattices

- Bravais lattice and Wigner-Seitz cell
- Reciprocal lattice
- Brillouin zones

Brillouin zones 1

Laue condition for elastic scattering, i.e. $|\vec{k}| = |\vec{k}'|$

$$\boxed{(\vec{k} - \vec{k}') = \vec{K}}$$



Laue condition

$$\underline{k \sin\theta = \frac{K}{2}}$$

Bragg's law (1st order)

$$\underline{2d \sin\theta = \lambda}$$

distance between the Bragg planes

$$\underline{d = \frac{2\pi}{K}}$$

Brillouin zones 1 Comment 1

The figure shows a sketch of a reciprocal lattice with the basis vectors $\vec{b}_1$ and $\vec{b}_2$.

The formula outlined in red shows the Laue condition for constructive interference in the case of elastic scattering.

The difference between the wave vector of the incident and the scattered wave gives a vector of the reciprocal lattice.

Since the scattering is elastic, the wavelengths of the incident and scattered waves are the same and consequently the wave numbers of the incident and scattered waves are also the same.

The sketch shows the situation of elastic scattering.

The green circle corresponds in three dimensions to the Ewald sphere.

Brillouin zones 1

Comment 2

Elastic scattering is possible between all points of the reciprocal lattice that lie on the surface of the Ewald sphere.

The sketch also shows the Bragg plane on which the elastic scattering takes place.

The Bragg planes are perpendicular to the reciprocal lattice vector K and intersect the reciprocal lattice vector in the middle.

The first formula underlined in red follows from the geometry of the Laue condition.

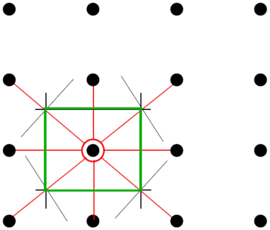
The second equation underlined in red shows the Bragg condition for the first-order constructive interference.

The last equation underlined in red gives the relationship between the distance between the Bragg planes and the length of the corresponding reciprocal lattice vector K.

Brillouin zones 2

The first Brillouin zone is enclosed by the Bragg planes of the shortest vectors of the reciprocal lattice

→ The construction scheme of the 1st Brillouin zone is similar to the construction scheme of the Wigner-Seitz cell of the Bravais lattice



Brillouin zones 2

Comment

The first Brillouin zone is the Wigner-Seitz cell of the reciprocal lattice.

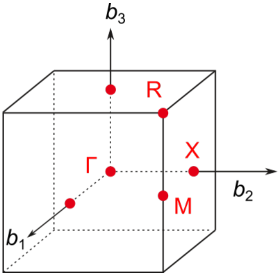
The first Brillouin zone is enclosed by the Bragg planes of the shortest vectors of the reciprocal lattice.

The illustration shows for a simple cubic lattice how the 1^{st} Brillouin zone is constructed.

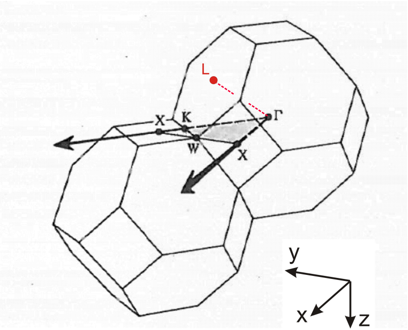
Brillouin zones 3

1st Brillouin zones of the sc and the fcc lattices

sc lattice



fcc lattice



important symmetry points of the 1st Brillouin zones are denoted by capitals

Brillouin zones 3

Comment

The figures show the 1st Brillouin zones of the simple and the face centred cubic lattices.

The reciprocal lattice of a face centred cubic lattice is a body centred lattice.

This has to be noted, in order to understand the shape of the 1st Brillouin zone of the fcc lattice.

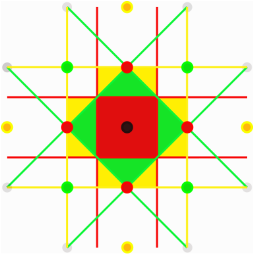
Important symmetry points are denoted by capitals.

The center of the Brillouin zones is always denoted by Γ.

These capitals will be latter used to present the experimental results.

Brillouin zones 4: Higher order Brillouin zones

some Bragg planes and Brillouin zones of the sc lattice



Starting from the Γ-point the nth Brillouin zone is reached by crossing n – 1 Bragg planes, but no fewer

Waves are reflected on Bragg-planes → formation of standing waves

Brillouin zones 4

Comment 1

Bragg planes are barriers to waves.

Waves are reflected on Bragg planes.

The incident and reflected waves superpose and can interfere.

Standing waves can develop in the process.

The figure shows a square lattice.

The Bragg planes are indicated by colored lines.

The Bragg planes are perpendicular to the reciprocal lattice vectors that connect the Γ point with the lattice points.

The lattice points have the color of the corresponding Bragg planes.

Brillouin zones 4 Comment 2

The Bragg planes intersect the associated reciprocal lattice vectors in the middle.

The space between the Bragg-planes is divided into Brillouin zones.

Starting from the Γ point, the n^{th} - Brillouin zone is reached by crossing $(n-1)$ - Bragg planes.

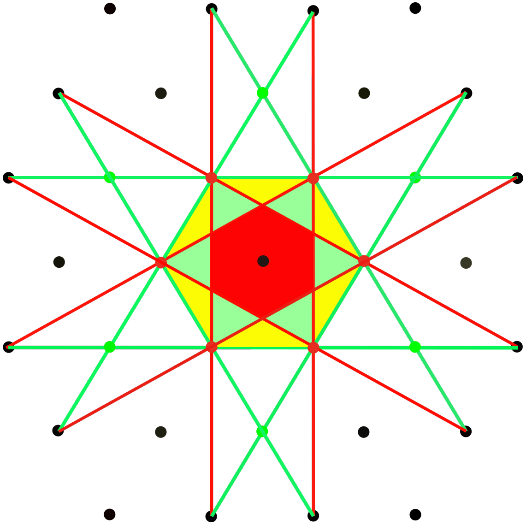
For the 1st Brillouin zone, no Bragg planes have to be crossed.

The 1st Brillouin zone is indicated in red.

The 2nd Brillouin zone in indicated in green and one red Bragg-plane has to be crossed.

The 3rd Brillouin zone is indicated in yellow and a red and a green Bragg-plane must be crossed.

Brillouin zones 5



Brillouin zones 5

Comment

The figure shows some Bragg-planes and the 1st, 2nd, and 3rd Brillouin zones of the hexagonal lattice.

The 1st Brillouin zone is highlighted in red.

The 2nd Brillouin zones is highlighted in green.

To reach the 2nd Brillouin zone, a red Bragg planes has to be crossed.

The 3rd Brillouin zones is highlighted in yellow.

To reach the 3rd Brillouin zone, two red Bragg planes have to be crossed.

Higher-order Brillouin zones become important for electron waves in crystal lattices.

Revision

Summary in Questions 1

1. Explain the conditions for the formation of a covalent bond between two atoms.
2. Why do most of the elements of the periodic table form metals in the solid state?
3. Give the definition of the Bravais lattice.
4. Give the definition of the primitive unit cell of a crystal lattice.
5. Give the definition of the reciprocal lattice.
6. Give the relationship between the basis vectors of the Bravais lattice and the reciprocal lattice.
7. Describe the reciprocal lattice of a bcc lattice.

Summary in Questions 2

8. What is the relationship between the lattice parameters of the cubic unit cells of the Bravais and the reciprocal lattice in a bcc lattice?

9. Describe the reciprocal lattice of an fcc lattice.

10. Give the definition of the 1st Brillouin zone.
11. Write down Bragg's law and the Laue condition for constructive interference.

12. Make a sketch that shows the relationship between Bragg's law and Laue's condition.

13. Give the definition of the nth Brillouin zone.