

28

Solid-state physics

28.1 Structure of solid bodies

28.1.1 Basic concepts of solid-state physics

Solid, matter in the solid physical state. Solids may be classified according to the state of order of their structural constituents (atoms, ions, molecules):

- **Crystalline solid (crystal)**, a solid with periodic order of its structural constituents. Regular, periodically repeating configurations of structural elements occur in all three dimensions.
- **Amorphous solid**, a solid without long-range order of the structural elements. There are no periodically repeating configurations of structural elements.
- Alkali metals have a crystalline structure. Diamond is crystalline carbon. Common salt (sodium chloride, NaCl) exhibits a crystalline structure.
- Alloys and gels are amorphous solids.

Many solid materials (e.g., **glasses** or **polymers**) cannot be included in this scheme. Polymers have a partly periodic order. Solids exist with micro-crystalline structure.

Solids are distinguished from each other by their response to a physical influence:

- **Isotropic solid**, no space direction is preferred over the others. The response of the solid is direction-independent.
- ▲ Frequently, amorphous solids are isotropic.
- **Anisotropic solid**, certain space directions are different from the others. The response of the solid is direction-dependent.
- ▲ The periodic structures in crystals define preferred spatial orientations.

Monocrystal, idealized solid with a periodically repeating atomic structure that extends over the entire volume. The crystal axes have about the same orientation relative to a body-fixed coordinate frame in all regions of the body.

- Salts crystallizing out of **solutions** are often monocrystals.

M **Monocrystal growing** from melts (one component), from solutions (several components) or from the gaseous phase.

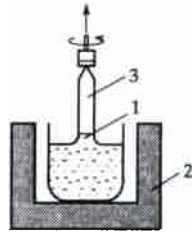


Figure 28.1: Schematic view of the Czochralski method. 1 – melt, 2 – heater, 3 – growing monocrystal.

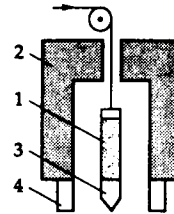


Figure 28.2: Schematic view of the Bridgman method. 1 – melt, 2 – heater, 3 – growing crystal, 4 – cooling.

Czochralski method: The crystal is drawn directly from the melt (Fig. 28.1).

Bridgman method: The crystal grows in a crucible, which descends at a constant speed from the hot zone into the cold zone (Fig. 28.2).

The methods mentioned above have the disadvantage that the crystal is polluted by oxygen incorporated from the crucible walls.

Zone melting method: The impure material is melted by a narrow melting device moving slowly along the sample. A monocrystal forms behind the heating zone. Impurities prefer the liquid phase and are removed.

Lattice defect, deviation from the ideal structure of strict spatial periodicity by lattice defects (dislocations, vacancies, stacking disorders, etc.).

▲ The type and abundance of lattice defects essentially determines the physical properties of a solid.

Polycrystalline solids, the monocrystalline regions (crystallites) frequently extend over few micrometers only, the crystallite orientations vary randomly.

■ Metals crystallized after melting are usually polycrystalline.

Grain, monocrystalline region in a solid.

Grain boundaries, separate the monocrystalline regions of a polycrystalline solid.

Texture, distribution of the orientation of grains in a polycrystalline solid.

28.1.2 Structure of crystals

Crystal lattice, periodic, three-dimensional arrangement of atoms, molecules or ions; their type and geometric structure determines the outward appearance and the physical properties of the crystal.

Space lattice, point lattice, mathematical abstraction of the crystal lattice to a spatially periodic arrangement of points corresponding to the lattice sites. The kind of atoms or molecules at the lattice sites is thereby ignored.

Base, a group of atoms or molecules ascribed to any lattice point or any elementary parallelepiped.

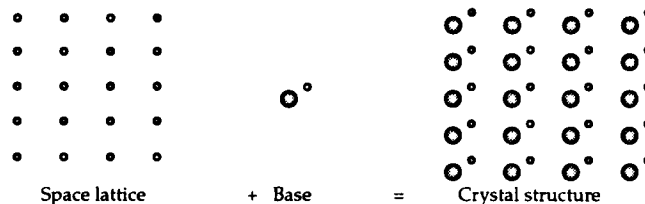


Figure 28.3: On the concept of crystalline structure.

1. Crystal structure,

determined by the symmetry of the structure, the lattice parameters (lengths and angles), and the specification of the center-of-mass positions in the asymmetric unit of the elementary cell.

Elementary cell, element of the crystal lattice from which the complete lattice may be reproduced by translation.

Asymmetric unit, smallest spatial fraction of an elementary cell from which the entire elementary cell may be obtained by symmetry operations.

Translation, displacement of an elementary cell in space by the translation vector \vec{T} .

2. Lattice vectors and crystal axes

Fundamental translation vectors, lattice vectors \vec{a} , \vec{b} , \vec{c} , displacements $\vec{T} = \vec{a}n_1 + \vec{b}n_2 + \vec{c}n_3$ along integral multiples of these vectors map a crystal lattice onto itself.

■ Let \vec{r} be an arbitrary point in space. The lattice at the point

$$\vec{r}' = \vec{r} + n_1\vec{a} + n_2\vec{b} + n_3\vec{c} \quad (n_1, n_2, n_3 \text{ are integers})$$

is identical to the lattice at the point \vec{r} . The lattice vectors \vec{a} , \vec{b} , \vec{c} span a parallelepiped.

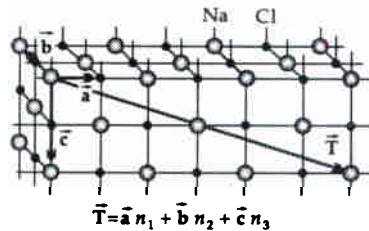


Figure 28.4: On the concept of the translation vector.

▲ A point lattice is uniquely defined by the fundamental translation vectors (lattice vectors) \vec{a} , \vec{b} , \vec{c} .

Crystal axes, directions defined by the fundamental lattice vectors \vec{a} , \vec{b} and \vec{c} .

Lattice constants, magnitudes of the fundamental lattice vectors \vec{a} , \vec{b} and \vec{c} , specify the distances of the bases along the crystal axes.

3. Primitive elementary cell,

elementary cell with the minimum volume for a given lattice structure. The primitive elementary cell contains only one lattice point.

➤ Although the primitive parallelepiped has one lattice point on each of its eight edges, these have to be shared over the eight elementary cells contacting each other there. The lattice vectors shown in Fig. 28.5 each span a primitive elementary cell.

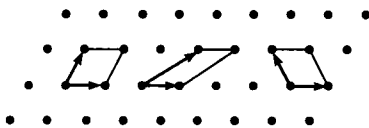


Figure 28.5: Primitive elementary cells.

➤ It is not always suitable, or customary, to choose the elementary cell to be as small as possible. The elementary cells of tungsten and copper shown in the following figure exhibit the cubic symmetry of these metals better.

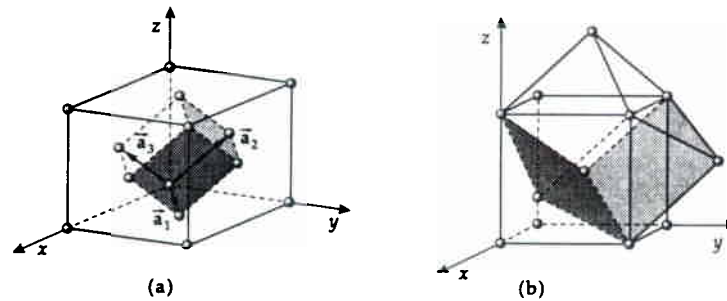


Figure 28.6: Elementary cell. (a): copper (face-centered cubic lattice), (b): tungsten (body-centered cubic lattice).

4. Crystal system and lattice types

Crystal system, subdivision of crystals into seven crystal systems according to the following criteria:

- lattice constants are equal or different,
- angles between the crystal axes.

Lattice types:

- **Primitive lattice:** all lattice points are on the edges of the elementary cell.
- **Face-centered lattice:** additional atoms occur at the intersection points of the face diagonals of the elementary cell.
- **Base-centered lattice:** besides the atoms at the edges, there is one atom at each intersection point of the face diagonals of two opposite faces.
- **Body-centered lattice:** besides the atoms at the edges, there is one atom at the intersection point of the space diagonals of the elementary cell.

28.1.3 Bravais lattices

1. Types of Bravais lattices

Bravais lattice, notation for individual lattice types. In 3D space, there are 14 distinct Bravais lattices:

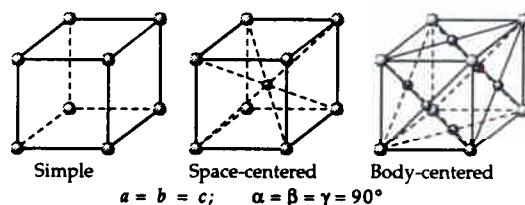


Figure 28.7: Cubic Bravais lattice.

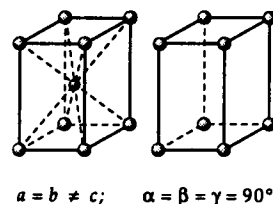


Figure 28.8: Tetragonal Bravais lattice.

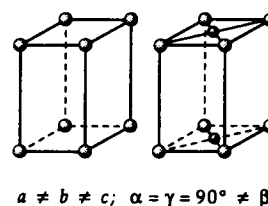


Figure 28.9: Monoclinic Bravais lattice.

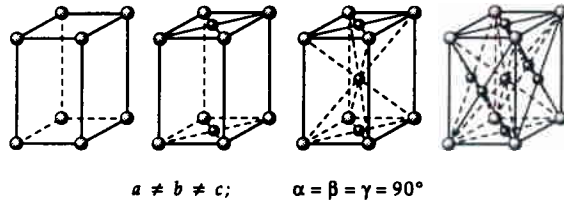


Figure 28.10: Orthorhombic Bravais lattice.

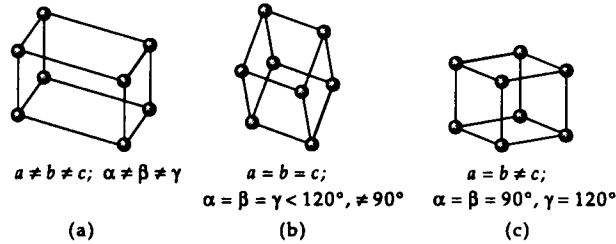


Figure 28.11: Bravais lattices. (a): triclinic, (b): rhombohedral, (c): hexagonal.

The following structures are important for metals:

- the face-centered cubic lattice (fcc),
 - the body-centered cubic lattice (bcc),
 - the hexagonal compact packing of spheres (hcp).
- The lattice types of important elemental crystals are given in the **Periodic Table of elements**.

2. Packing density of the elementary cell

Compact packing of spheres, regular arrangement of spheres of equal size with a minimum of empty space between them. One distinguishes between **hexagonal** and **face-centered** compact packing of spheres.

Fig. 28.12 shows a layer of compact packing of spheres with the centers at A.

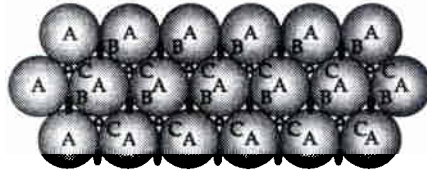


Figure 28.12: Compact packing of spheres.

If the second layer is arranged in the positions B (or in the equivalent positions C), there are two possibilities for arranging the third layer:

- The spheres of the third layer may be placed above the positions A. The result is a sequence $ABABA \dots$ (**hexagonal** structure).
 - The spheres of the third layer occupy the positions above C. The result is a sequence of planes $ABCABC \dots$ (**face-centered cubic**).
- ▲ In the compact packing of spheres, every sphere of a plane touches six other spheres of the same plane and three spheres in each of the two neighboring planes.

Packing density, fraction of space occupied in the elementary cell by the volume of the spheres.

- In both types of structures for the compact packing of spheres, the packing density amounts to 74 %.

- For comparison: the packing density of the bcc-lattice is 68 %.
- Coordination number**, the number of next neighbors of an atom.

3. Lattice planes and Miller indices

Lattice plane, arbitrary plane in a lattice. A plane is uniquely determined by three non-collinear points. The intersection points of the plane with the crystal axes are used to define the lattice plane. **Miller indices**, abbreviation for the specification of lattice planes for given crystal axes. They are fixed as follows:

- The intersection points of the plane with the crystal axes defined by the lattice vectors \vec{a} , \vec{b} , \vec{c} are determined in units of the lattice constants (**Fig. 28.14**).
- The reciprocal values of the numbers obtained in this way are reduced to the least common denominator.
- The numerators of the fractions are the Miller indices of the lattice plane.
- The planes are identified by Miller indices given in brackets: (hkl) .
- If an intersection point is at infinity, the corresponding index is zero.

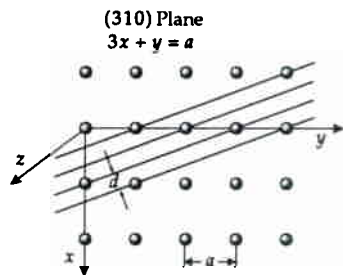


Figure 28.13: Lattice plane perpendicular to the z -axis, lattice sites in the x - y -plane.

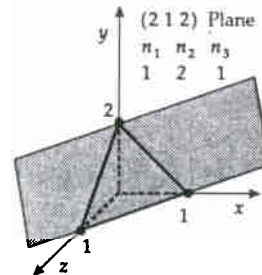


Figure 28.14: Construction scheme of the Miller indices: example $(h, k, l) = (2, 1, 2)$.

- For the plane with intersection points 6, 2, 3, the reciprocal values are $1/6$, $1/2$, $1/3 \rightarrow 1/6$, $3/6$, $2/6$.

Hence, the Miller indices are (132) .

- If the plane intersects one or several crystal axes on the negative side of the origin, the index is specified by an upper horizontal bar.
- $(h\bar{k}l)$ means that the plane intersects the \vec{b} -axis in the negative range.

Crystal direction, direction of a vector in the basis of the fundamental lattice vectors; its components are integer numbers (**Fig. 28.16**).

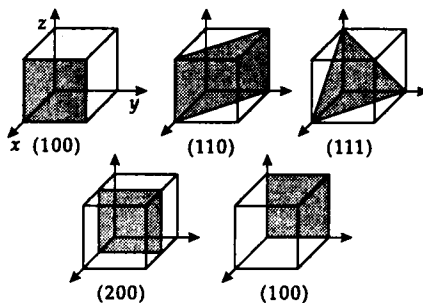


Figure 28.15: Several crystal planes in a cubic lattice.

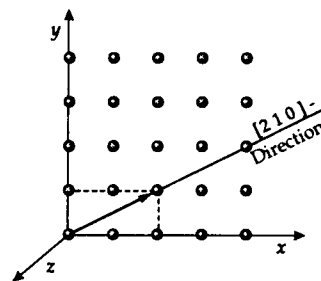


Figure 28.16: Crystal direction.

These integer numbers are put into **square brackets**: $[hkl]$.

- In cubic crystals the **direction** $[hkl]$ is always **perpendicular to the plane** (hkl) with the same indices. In other crystal systems this does not hold in general.

Atomic coordinates u , v , w , determine the positions of lattice points in an elementary cell. They are given as fractions of the lattice constants a , b , c along the crystal axes.

28.1.3.1 Simple crystal structures

1. NaCl

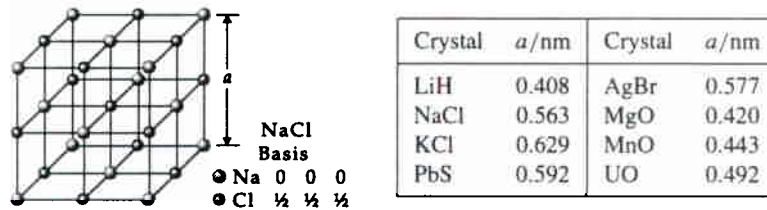


Figure 28.17: NaCl-structure and representative crystals of the NaCl-structure (a : lattice constant).

Bravais lattice: fcc, base: 1 sodium- and 1 chlorine atom (separation: $\frac{1}{2}$ of space diagonal), number of base units per elementary cell: 4, coordination number: 6.

Atomic coordinates:

$$\text{Na: } 000; \frac{1}{2}\frac{1}{2}0; \frac{1}{2}0\frac{1}{2}; 0\frac{1}{2}\frac{1}{2} \quad \text{Cl: } \frac{1}{2}\frac{1}{2}\frac{1}{2}; 00\frac{1}{2}; 0\frac{1}{2}0; \frac{1}{2}00$$

2. CsCl

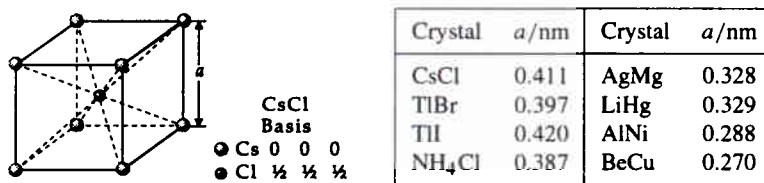


Figure 28.18: CsCl-structure and representative crystals of the CsCl-structure (a : lattice constant).

Bravais lattice: simple cubic, base: 1 cesium- and 1 chlorine atom (separation $\frac{1}{2}$ of space diagonal), number of base units per elementary cell: 1, coordination number: 8.

Atomic coordinates:

$$\text{Cs: } 000 \quad \text{Cl: } \frac{1}{2}\frac{1}{2}\frac{1}{2}$$

28.1.4 Methods for structure investigation

1. X-ray diffraction,

most common method for structure investigation. It is based on the diffraction of x-rays by the lattice atoms. Wavelength of photon (energy E_γ):

$$\lambda_\gamma = \frac{1.24}{E_\gamma/\text{keV}} \text{ nm}.$$

Diffraction occurs on the atomic electrons. Hence, the intensity of diffraction depends strongly on atomic number Z .

X-ray diffraction is not very sensitive for elements of low atomic number. The positions of oxygen atoms or hydrogen atoms may barely be determined by x-ray diffraction. Moreover, elements of neighboring atomic numbers may barely be distinguished from each other.

2. Electron diffraction,

diffraction of electrons by atomic nuclei, therefore sensitively dependent on the atomic number. The wavelength of an electron with energy E_e is

$$\lambda_e = \frac{1.2}{\sqrt{E_e/\text{eV}}} \text{ nm}.$$

Electrons are charged particles and about 2000 times lighter than neutrons. They interact very intensely with matter electromagnetically, hence do not penetrate deeply into the crystal. Electron diffraction is therefore of particular importance for structure investigations of surfaces and thin layers.

3. Neutron diffraction,

exploits the wave property of the neutron for diffraction by periodic structures. Neutron diffraction by a crystal lattice occurs if the de Broglie wavelength of the neutrons (energy E_n) is similar to the separation of the lattice planes in the crystal. The wavelength of the neutron is

$$\lambda_n = \frac{0.028}{\sqrt{E_n/\text{eV}}} \text{ nm}.$$

Coherent scattering of neutrons occurs at the atomic nuclei of the structure components. The intensity of the diffraction depends on the neutron scattering cross-section of the nucleus. Structure analysis may be done with experiments with thermal neutrons ($E_n \approx 0.025 \text{ eV}$).

Neutron diffraction allows both the determination of the position of elements of low atomic number, and also the discrimination between neighboring elements of the Periodic Table.

Magnetic scattering of neutrons, scattering by the magnetic moments of the atoms due to the interaction with the magnetic moment of the neutron.

4. Bragg condition,

premise for constructive interference in the reflection of incident radiation by the lattice planes of the crystal. If the condition is not fulfilled, the radiation interferes destructively.

Bragg condition				L
	Symbol	Unit	Quantity	
$n\lambda = 2d \cdot \sin \Theta$	n	1	integer number	
	λ	m	wavelength	
	d	m	separation of lattice planes	
	Θ	rad	glancing angle	

- The wavelength must be within the range given by the structure of the crystal in order to produce measurable Bragg reflections.

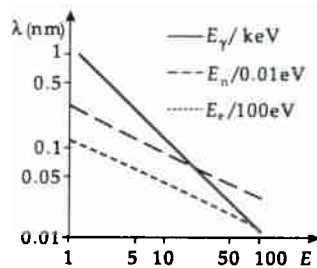


Figure 28.19: Wavelengths of x-ray photons, neutrons and electrons as a function of their energy.

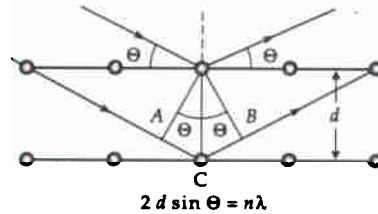


Figure 28.20: Bragg condition. Θ : glancing angle. The angle of incidence relative to the normal to the lattice planes is $\pi/2 - \Theta$. A, B : wave fronts, ABC : path difference $2d \sin \Theta$.

5. Methods of x-ray and neutron scattering

a) Laue method: In this method, a **fixed monocrystal** is irradiated by x-ray or neutron beams with a **continuous, "white" spectrum**. The Bragg condition is fulfilled only for certain wavelengths. Constructive interferences arise at certain angles, producing point-like reflections. The pattern of reflections is determined by the structure of the crystal. This method is particularly convenient for a rapid determination of crystal orientations and crystal symmetries. It is rarely used for structure investigations.

b) Rotating-crystal method: A **monocrystal** in a **mono-energetic** x-ray or neutron beam is **rotated** about a fixed axis. The Bragg condition is fulfilled at certain rotation angles at which point-like constructive interferences occur.

c) Debye-Scherrer method: This method is applied for the investigation of powders. The **powder specimen is irradiated** by a **mono-energetic beam**. The crystallites in the powder sample are statistically oriented. Diffracted beams emerge from crystallites that are randomly oriented in such a way that the primary beam hits several lattice planes at an angle that fulfils the Bragg condition.

The Debye-Scherrer method is applied for measurements of the variation of the lattice constants with the temperature, or the variation of the composition of an alloy. A practical advantage of the method is that monocrystals are not needed.

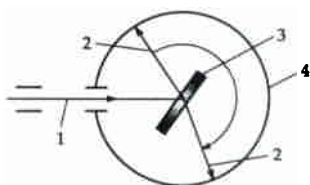


Figure 28.21: Rotating-crystal method.
1 – primary beam, 2 – scattered beam,
3 – rotating monocrystal, 4 – film.

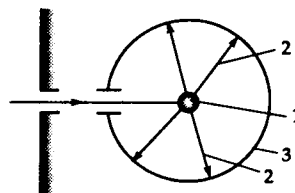
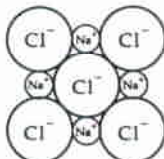
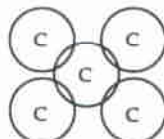
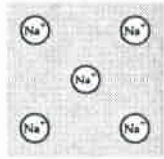
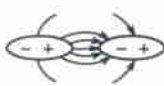


Figure 28.22: Debye-Scherrer method.
1 – polycrystal, 2 – scattered beam, 3 – film.

28.1.5 Bond relations in crystals

1. Survey of the types of bond in crystals

Type of bond	Ionic (heteropolar)	Covalent (unipolar)
properties	insulator at low temperatures, ionic conduction at high temperatures, plastically deformable	insulator, semiconductor, brittle, high melting point
interaction		
examples	alkali halogenides	organic molecules; C; Si; InSb
binding energy (eV/atom)	6 – 20	1 – 7

Type of bond	Metallic	Van der Waals
properties	electric conductor, good thermal conductor, plastic, high reflectance in IR and visible spectrum	insulator, low melting point, easily compressible, transparent in the far UV
interaction		
examples	metals, alloys	noble-gas crystals, H ₂ , O ₂ , polymers, molecular crystals
binding energy (eV/atom)	1 – 5	10 ⁻² – 10 ⁻¹

Lattice energy, difference of energy between the free atoms and the crystal.

- ▲ A crystal is only stable if its total energy is lower than the total energy of the free atoms or molecules of which it is composed.

2. Ionic bond,

caused by the attracting Coulomb force between different charged ions.

■ Common salt, Na^+Cl^- , is a typical ionic crystal.

binding energy in ionic bond			ML^2T^{-2}
$E_B = \frac{Q^2}{4\pi\epsilon_0} \cdot \frac{\alpha}{r}$	Symbol	Unit	Quantity
	E_B	J	binding energy
	Q	A s	charge
	ϵ_0	A s/(V m)	permittivity of free space
	r	m	distance
	α	1	Madelung constant

Ionic binding forces have a long range. Frequently, the effect of not only the next but also of even more distant neighbors has to be taken into account.

Madelung constant, α , determines the strength of the ionic bond by taking into account the more distant ionic charges:

Madelung constant			1
$\alpha = \sum_j \frac{\pm R}{r_j}$	Symbol	Unit	Quantity
	R	m	distance of next neighbors
	r_j	m	distance between ion j and reference ion

For a negative reference ion, positive ions get a sign +, and negative ions a sign −.

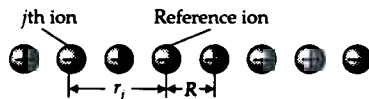


Figure 28.23: On calculating the Madelung constant.

Table of typical values of the Madelung constant α :

Structure	NaCl	CsCl	ZnS (cubic)
α	1.747558	1.747558	1.6381

Repulsive interaction, occurs because of the Coulomb force and the Pauli principle (see p. 844) if two atoms approach each other closely and their electron shells overlap.

- At low temperature, ionic crystals are insulators.
- At high temperature, ionic conduction occurs. Ionic crystals are plastically deformable.

3. Metallic bond,

originates from the electrostatic interaction of the valence electrons released by the atoms with all positive atomic cores of the crystal. The binding partners are not rigidly coupled; the free valence electrons have a high mobility and are not localized.

■ Sodium, aluminum, iron.

Transition metals, metals with an incomplete d-shell (3d-, 4d-, 5d-metals), i.e., all metals beyond the eight main groups of the Periodic Table of elements (see p. 877). They are characterized by a high binding energy. Additional binding forces are generated by the interaction between the inner d-shells.

■ Copper, silver, gold.

The metallic bond is weaker than the ionic bond. Hence, the lattice energy of an alkali metal crystal is significantly lower than that of an ionic alkali halogenide crystal.

Example: NaCl: 8.1 eV/atom, Na: 1.1 eV/atom.

- M** Crystals with a metallic bond are electric conductors and good thermal conductors. They are plastically deformable. They are strongly reflecting in the IR and the visible spectral range.

4. Covalent bond,

unipolar bond, electron pair binding via the exchange interaction. This type of bond is dominant in the elements of the third through the fifth main group of the Periodic Table. The unfilled valence electron shells may organize a closed, noble-gas-like electron configuration that involves the valence electrons of the next neighbors.

- Many carbon compounds are covalently bound, in particular diamond and organic molecules.

Electron exchange, an affiliation of an electron pair to two neighboring atoms.

Exchange interaction of covalent bond, a force mediated by the exchange of electrons between atoms. The spins of the electrons are oriented antiparallel (singlet state), so that (due to the Pauli principle) the spatial wave function of the two electrons is symmetric. For a spatially symmetric electron wave function (antiparallel spins: antisymmetric spin wave function), the probability density of finding the particle at the center between the binding partners is larger than in the case of a spatially antisymmetric wave function for electrons with parallel spins (triplet state – symmetric spin function). The singlet configuration of electrons yields an energy contribution—as compared with separated atoms—which leads to a binding of the two atoms.

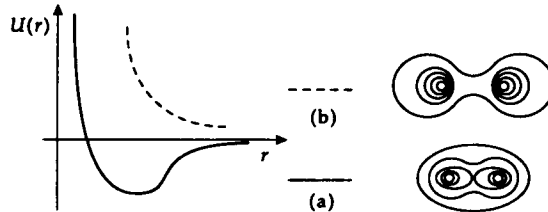


Figure 28.24: Binding potentials as a function of the interatomic distance r for electron pairs with (a) antiparallel spins (bound state), and (b) parallel spins (scattering state). The right side of the figure sketches the contour lines of the electron density distribution: despite the exchange force, the electrons remain closely to the atoms.

- ▲ Covalent bonds are bonds between neutral atoms. A configuration with parallel orientation of the spins of electrons involved in the exchange does not lead to a binding of the atoms.
- ▲ Important examples are covalently bound semiconductors.
- ▲ Besides crystals with ionic or covalent bonds, there are also crystals with a mixed bond.

5. Van der Waals bond,

weakly attracting dipole-dipole interaction occurring when instantaneous dipole moments are mutually induced in the crystal atoms or molecules. The interaction from these induced dipole moments (dipole-dipole interaction) results in a weak attractive electric force.

Van der Waals binding energy			ML^2T^{-2}
$U(r) \approx -\frac{C}{r^6}$	Symbol	Unit	Quantity
	$U(r)$	J	binding potential
	C	J m^6	interaction constant
	r	m	distance

- ▲ C is of the order of magnitude of 10^{-77} J m^6 .
- ▲ The Van der Waals potential is the most important attractive interaction in noble-gas crystals and between organic molecules.
- For a correct description of the experimental data, an additional weak-repulsive potential of the hard-core type $\sim r^{-12}$ is needed.

The **Lennard-Jones potential** results from combining the hard-core repulsion with the Van der Waals potential

Lennard-Jones potential			ML^2T^{-2}
$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$ $C = 4\epsilon\sigma^6$	Symbol	Unit	Quantity
	$U(r)$	J	binding potential
	r	m	distance
	ϵ	J	parameter
	σ	m	parameter

with new parameters ϵ and σ , where $C = 4\epsilon\sigma^6$.

Table of ϵ , σ and C for the noble gases:

Noble gas	He	Ne	Ar	Kr	Xe
$\epsilon/10^{-23} \text{ J}$	14	50	167	225	320
$\sigma/10^{-10} \text{ m}$	2.56	2.74	3.40	3.65	3.98
$C = 4\epsilon\sigma^6/(10^{-77} \text{ J m}^6)$	0.016	0.085	1.032	2.128	5.088

28.2 Lattice defects

Lattice defect, deviation from the ideal structure of strict spatial periodicity by construction faults (vacancies, dislocations, stacking disorders, etc.).

- ▲ Type and abundance of lattice defects modify the mechanical, electric, magnetic and optical properties of solids in a characteristic manner.

28.2.1 Point defects

1. Vacancies

Vacancies, atoms missing on regular lattice sites.

Divacancies, neighboring vacancies.

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