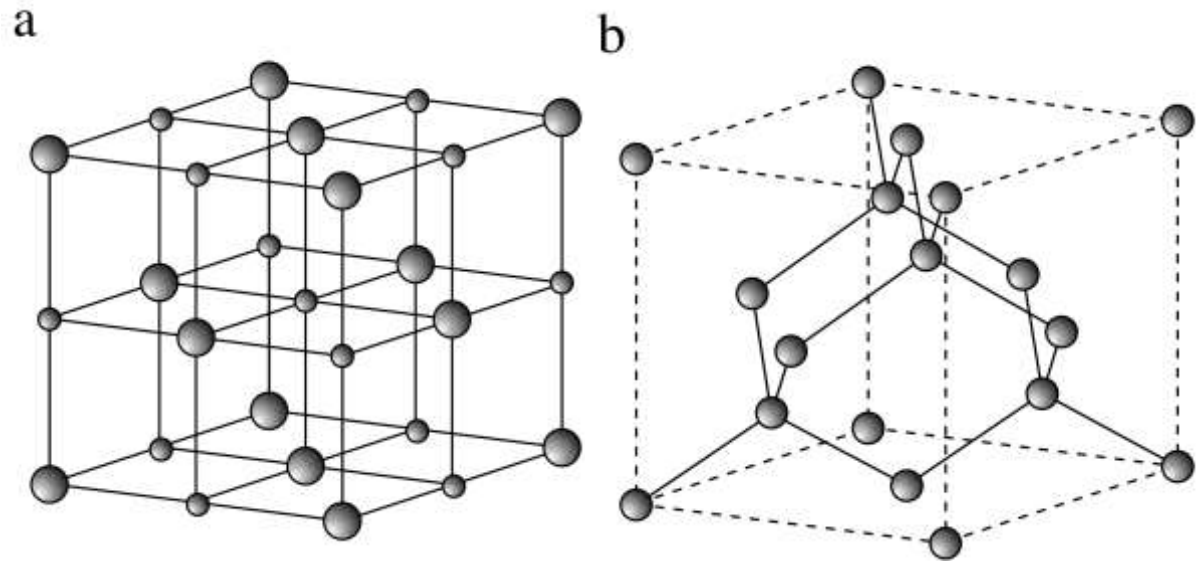
# Solid State Materials

## Crystalline States

most important property is **large-scale periodic order** (highest level of order)

**Ideal crystals are an infinite periodic spatial sequence of identical structural elements**. The geometric properties and the symmetry of the crystal is **defined by the lattice** (the crystal structure is made by putting the right ‘building blocks’ into the lattice at each vertex). The lattice consists of basic units called **elementary cells**.




Elementary cells of NaCl (a) and Si (b) crystals.

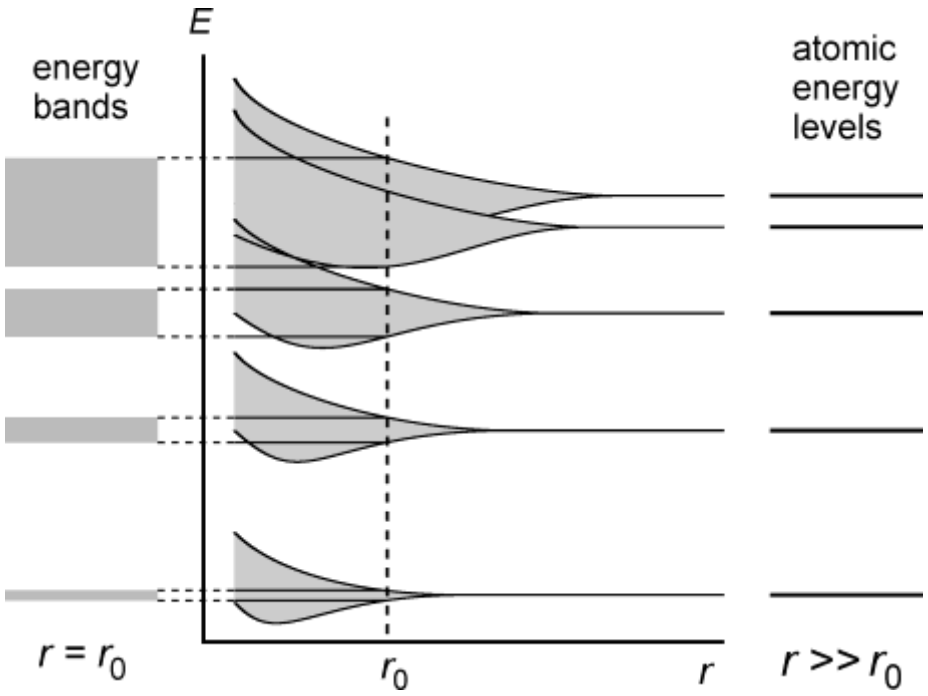
Classification:
**atomic, ionic, metallic, molecular lattice**

**crystalline order** in reality **usually only extends to microscopic scales: microcrystals, monocrystals**

**Crystals** are **anisotropic** substances, i.e. **they have distinguishable directions**. This can manifest, for instance, in the fact that within the crystal, light propagates with different velocities in different directions.

## Energy Bands

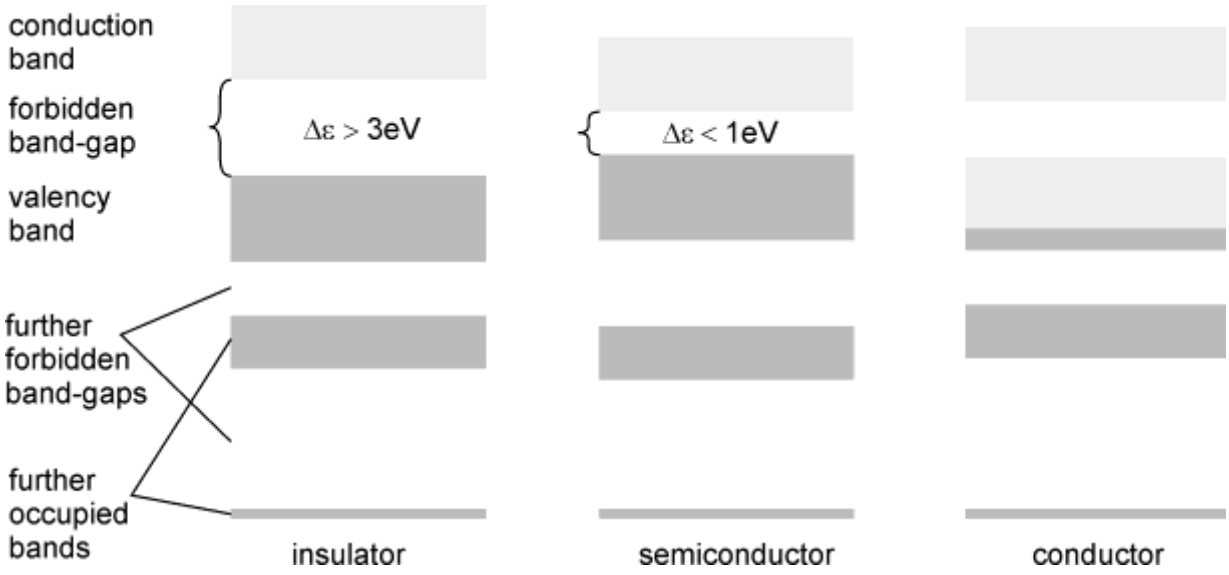
As soon as the atoms get closer to form a crystal, and the state functions of atomic electrons start to overlap, **the Pauli principle comes into effect**. The tendency of the system to avoid identical quantum states is realized through **the 'splitting up' of the equal energies of interacting electrons into *N* close levels.**
As ***N*** **is very large**, the **multitude of close split levels forms in practice a continuous energy band.**




The formation of energy bands in crystals. Due to the decrease of atomic distances ($r$), the atomic energy levels are split up, and energy bands will form ($r_0$ denotes the equilibrium distance).

As the interaction is most significant for the outmost, valence electrons, splitting happens to the greatest extent here as well. This band is called the **valence band.**
The gaps without possible energies between consecutive bands are called **forbidden band-gaps.**
Two bands may broaden to such an extent that the forbidden band-gap between them disappears completely.

If there are electrons in each energy state within the valence band, i.e. the band is ‘completely occupied’, then energy can only be absorbed if a minimum amount of energy corresponding to the width of the next forbidden band-gap is available.
The empty band of allowed states is called **the conduction band.**




The band structure of insulators, semiconductors and conductors. Occupied bands, their occupied sections are shown with darker gray and unoccupied sections with lighter gray. The blank parts in between depict the forbidden band-gaps

## Properties Determined by the Width of the Forbidden Band-Gap

If $\Delta\varepsilon$ is of the order of a few eV, then the substance is an **insulator** at room temperature; if it is only a few tenths of eV, then it is a pure **semiconductor**.

**Conductivity**, however, is not only **affected** by the number of mobile electrons in the conduction band, but **also by** that of the electron vacancies, i.e. **holes** in the valence band.

Holes are also commonly called ***p*-type** (positive) **charge carriers**, as the counterpart of **electrons**, being ***n*-type** (negative) charge carriers.

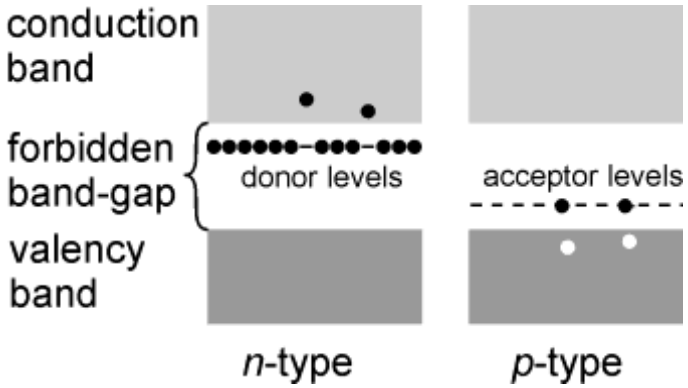
**Conductivity may also appear in the valence band, if it is not completely occupied.**
These materials are **proper conductors**.

**Partial occupancy** may be realized in several ways: one possibility is that **the outermost electrons of the interacting atoms did not have completely occupied electron orbits originally** (as is the case with Li); another would be **an overlap of a saturated and an empty band** during the broadening of energy levels (such is the case with Na).

**Optical properties:**
Insulators with a forbidden band-gap wider that 3 eV are **transparent.**

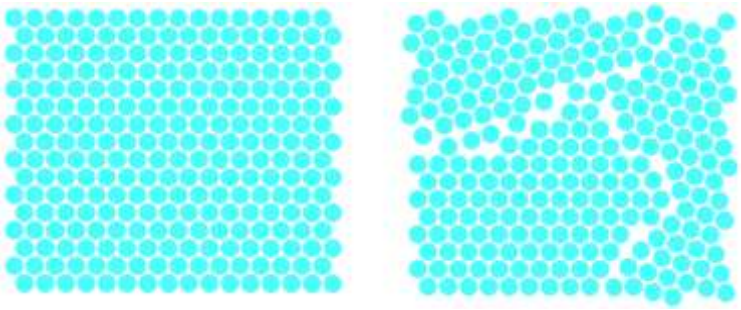
## Creating ‘Semiconductor Properties’ by Doping

From a practical point of view (**electronics,** transistor), so-called doped or extrinsic semiconductors have major importance.
**Adding small amounts** of certain foreign substances (a process known as **doping**) into a pure semi-conductor crystal lattice with a completely occupied valence band results **in the creation of new electron states** that provide the material with properties of a **semiconductor with a very narrow forbidden band-gap**.
The crystal structure of Si is shown in the figure (above).
If a doping atom has a valence of five (such as P), then after forming four covalent bonds, the remaining fifth electron will occupy a loosely bound electron state in the forbidden band-gap called **donor level**.
If the doping atoms have a valence of three (such as Al), then an unpaired valence electron of one of the surrounding Si atoms can form a state capable of taking an electron, called **acceptor level.**

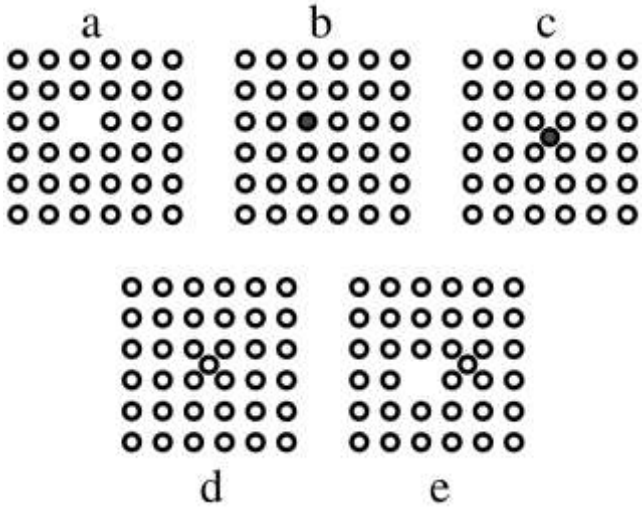



Band structure of doped semiconductors.
Black dots are electrons, white dots are electron vacancies, i.e. holes. The thin dashed line denotes the multitude of donor and acceptor levels.

# Lattice Defects



Perfect crystal and lattice defects along granular borders




**Point defects:**

a) empty vertex, *vacancy* or *Schottky-defect*
b) foreign particle in the lattice (at a vertex), *doping*
c) foreign particle in the interstitial space,
d) lattice particle in the interstitial space (*interstitia***)**
a) and d) together, *Frenkel-defect*

From the law of Boltzmann distribution we also expect that perfect crystal structures could only be formed at zero temperature (0 K).