

Defects in solid state

Different kinds of **defects** are possible in **crystalline solids**. There exist three main groups with additional subgroups. The main groups are point defects, extended defects and dislocations.

Point defects:

- **Schottky defect:** This means, that an equal number of cations and anions have left their normal lattice sites and therefore positive charged anion- and negative charged cation vacancies remain. They occur mainly in alkali halides and structures with high coordination numbers.

- **Frenkel defect:** This defect involves atoms/ions which are displaced from their normal lattice sites into interstitial sites. In the interstitial sites the displaced atoms/ions are tetrahedrally or octahedrally surrounded by other atoms/ions and the interactions between them stabilize the defect.

Frenkel/ Schottky: Both defects lead with their opposite charged vacancies and interstitials to the formation of dipoles. These dipoles attract each other and larger defect structures like clusters and aggregations can occur. Schottky and Frenkel defects are always present in pure materials. The number depends on the thermodynamics. ($G = H - TS$). S increases with increasing number of defects.

- **colour centres:** The F-centre: Empty anion vacancies are traps for electrons. An electron that enters a vacant lattice site, is like a particle in a box. It can reach different energy levels. The energy required for the transfer might be in the range of visible light. This leads to a certain colour for the solid. E.g. $\text{NaCl} + e \rightarrow$ greenish yellow, $\text{KCl} + e \rightarrow$ violet.

- **Interchanged atoms:** Pairs of atoms/ions have exchanged their places. With increasing temperature this can lead to the order-disorder phenomena, where atoms/ions show no longer preferences for particular sites. This can be found in alloys or spinell structures.

Extended defects:

- **Crystallographic shear structures:** Mainly observed in transition metal oxides which are non-stoichiometric. E.g. WO_3 or TiO_2 . They occur by the reduction of the cations and the formation of vacant oxygen sites in order to ensure the electrical equilibrium. The vacancies lead to an unstable structure. To eliminate this, the formation of crystallographic shear planes occur. E.g. in WO_3 corner sharing octahedrons partly convert into edge sharing octahedrons.

- **Stacking faults:** Polytypism materials show frequently this kind of defect. E.g. graphite exists mostly in hcp but sometimes in ccp too. A hcp-layer shows stacking disorder when a C-layer in the normal AB layer is inserted: ABABCABAB...

- **Subgrain boundaries, antiphase boundaries:** Both defects can be found in single crystals. They consist of nearly perfect domains. Between these domains small mismatches like angular orientations $< 1^\circ$ can occur (\rightarrow subgrain boundaries). If the same kind of atoms in adjacent domains are orientated face to face (repulsion!) antiphase boundaries are formed.

Dislocations:

- **dislocation edge:** In an array of parallel atom/ion planes one plane ends. This leads to disorder. The adjacent planes deform and take up the empty space in the crystal. It looks like a stair. (dislocation edge)

- **dislocation screw:** A part of the crystal has undergone a slip until a invisible line in the crystal. Behind this line the lattice layers have not undergone this slip. The dislocation looks like a screw on two sides of a crystal.

- **dislocation loop:** This is the combination of a dislocation screw and a dislocation edge. The dislocation screw makes a quarter rotation in the crystal and ends up as an dislocation edge.

Dislocations are responsible for the malleability, ductility and hardness of metals.

Properties which result from defects:

Defects in the crystals influence properties like mechanical hardness, electrical conductivity, colour and ionic conductivity. Especially the last area (ionic conductivity) is an important part of solid state technology. Defects decrease the barrier for diffusion of ions. This is desirable in semiconductor manufacture, synthesis of new solids, fuel cells, sensors, metallurgy and heterogeneous catalysts. A well known cationic conductor is yttrium stabilized zirconium $\text{Y}_x\text{Zr}_{1-x}\text{O}_{2-x/2}$ (λ -sensor in cars).

Source: Basic solid state chemistry; Anthony R. West; chapter 5. **UQA 2113**