KJM-MENA 3120

Structure and properties of functional materials

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1. Introduction and basic concepts

1.1 Bridging KJM1120 and KJM-MENA 3120

In KJM1120 we have learned basic inorganic chemistry with focus on trends in physical and chemical properties, bonding, and electrochemistry. The main aspect has been qualitative inorganic chemistry; with focus on the chemistry of the elements in groups 1-18. Already in the starting course in general chemistry, the molecular structure of small inorganic molecules has been described, in terms of Lewis structures, and the structure directing effect of non-bonding electrons according to the VSEPR theory. In KJM1120 the crystal structure of compounds is given little attention. One touches upon metallic structures of ccp (fcc), hcp and bcc types, and on spinel type oxides $\text{AB}_2\text{O}_4$, otherwise structures are visualized in lectures and seminars, but basically for emphasizing chemical bonding, reactivity, boiling/melting points etc. The structure and electronic properties of complexes receive much attention, primarily octahedral complexes, the effect of certain $d^n$ electron configurations on distortions (Jahn Teller distortions), stabilization of square planar coordination ($d^8$ ions), splitting of $d$-orbitals and the role of crystal fields for color and excitations. A discussion of primary building stones for crystal structures were done for tetrahedral oxoanions, exemplified by $\text{SiO}_4^{4-}$ and various silicate structures with dimeric anions, rings, chains, sheets and 3D-connected networks.

KJM-MENA3120 elaborates on five selected topics; crystal structure and property relations; symmetry, molecules and complexes; reactivity; electrochemistry and thermodynamics. The idea is to provide a more solid insight into these five topics, and provide examples from materials of use in different types of technologies. The coarse becomes thereby able to bridge beginner level chemistry with courses at the master and PhD level currently taught at UiO; in inorganic structure chemistry, defect chemistry, nanochemistry, advanced inorganic chemistry. On the other hand, the content in KJM-MENA3120 will not overlap significantly with the course MENA3000, and we recommend students to follow both courses in the same semester. We believe the course will prove useful for students who plan a master in inorganic chemistry, materials chemistry, catalysis or nanochemistry.

In KJM-MENA 3120 we focus on a few selected structures, describing building principles, becoming able to draw and investigate the atomic arrangement by means of the DIAMOND software, and to understand how the crystal structure will affect the properties of certain
functional materials: primarily electrode materials for Li-ion batteries, solid electrolytes, materials for solid oxide fuel cells, high temperature oxide superconductors, some magnetic materials, and hydrogen storage in metals.

1.2 Coordination number, coordination polyhedron, relative atom/ion size

Coordination number and coordination polyhedron are essential concepts for describing a crystal structure. The coordination number for a cation (metal atom) is typically between 2 and 12, and some guidelines are possible, Table 1:

<table>
<thead>
<tr>
<th>Coordination Nb</th>
<th>Geometry/polyhedron</th>
<th>Examples</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Linear</td>
<td>HgS, Cu₂O, YBa₂Cu₃O₆</td>
<td>d¹⁰ ions; hybridization</td>
</tr>
<tr>
<td>3</td>
<td>Triangular</td>
<td>Bi₂O₃, CO₂⁺, NO₃⁻</td>
<td>Small cat ions; oxoanions</td>
</tr>
<tr>
<td>4</td>
<td>Tetrahedral</td>
<td>ZnO, SiO₂, CrO₃</td>
<td>Small cations</td>
</tr>
<tr>
<td>4</td>
<td>Square planar</td>
<td></td>
<td>d⁶ ions; CFSE e₂ splitting</td>
</tr>
<tr>
<td>5</td>
<td>Square pyramidal</td>
<td>High-Tc cuprates</td>
<td>d⁴, d⁹ Jahn Teller distortion</td>
</tr>
<tr>
<td>5</td>
<td>Trigonal bipyramidal</td>
<td>Ni₂In</td>
<td>Filling of interstices in hcp</td>
</tr>
<tr>
<td>6</td>
<td>Octahedral</td>
<td>MgO, LiAlO₃, LaCoO₃</td>
<td>Rock salt; NiAs-type, perovskite</td>
</tr>
<tr>
<td>6</td>
<td>Trigonal prismatic</td>
<td>Ca₃CoO₆</td>
<td>For 50% of the Co-atoms</td>
</tr>
<tr>
<td>8</td>
<td>Cubic</td>
<td>CaF₂, ZrO₂, CsCl, AuCu, Na</td>
<td>Fluorite structure, CsCl-type, bcc-metals</td>
</tr>
<tr>
<td>12</td>
<td>Cuboctahedron</td>
<td>hcp, ccp</td>
<td>Several metals</td>
</tr>
</tbody>
</table>

In inorganic compounds the bonding situation is more complex than in organic molecules. The structures are frequently periodic (crystalline solids), and less focus is put on molecules in liquid or gaseous states. In some cases studies of the electric properties and reactivity of a compound may provide key data for entangling riddles on how atoms are connected. This is for instance the case for compounds that are semiconducting and are supposed to follow the regular rules for 2e-covalent bonds. One may speculate how it could be that a compound with the surprising composition NaSi can exist. This illustrates the need to think out of the box – there exists more possibilities that the alternating picture of cations and anions. NaSi follows the rules of 2-electron covalent single bonds, fully consistent with our conception of oxidation states. How can that be possible? The compound is a semiconductor, not a metal, and hence there is no metal-metal bonding (at least not percolating throughout the structure). A timely question is: how can the valence electrons from the very electronegative sodium be used by the more electronegative silicon? Each silicon atom can formally acquire one electron from sodium, making Si⁻, which is isoelectronic to P. We know that the white phosphorous
allotrope is molecular and consists of $P_4$ entities. Hence, we may imagine having $Si_4^{4+}$ entities in sea of $Na^+$ cations; with 2e single bonds between Si-atoms, Figure 1. And that is indeed the correct answer. NaSi is unusual; it has nonmetal-nonmetal bonds. (However, this is nothing but the well-known situation with dimeric anions in CaC$_2$ and BaO$_2$). Correspondingly there exist a few cation-anion compounds with metal-metal bonds. They also have unusual stoichiometries at first look when just considering electron configurations (oxidation states). The rest, which is the gross majority of inorganic materials, are normal compounds. Our focus in KJM-MENA 3120 will indeed be on such normal compounds, $A_xB_y$, with no A-A bonds and no B-B bonds.

**Figure 1:** Crystal structure of NaSi. Note the $Si_4^{4+}$ tetrahedra.

The examples of CN in various compounds in Table 1 can mainly be rationalized in terms of the relative size between cations and anions. A stable situation is considered to exist when the cation fits perfectly into the interstice (hole) made up by the anions, or when the cation is slightly larger – pushing towards the anions in contact. Obviously one may calculate the ideal $R_{cation}/R_{anion}$ ratio for perfect size fitting, Figure 2. In these considerations atoms are considered as rigid spheres. Tabulated ionic or metallic radii are used when using the calculated ratios for considering the likely coordination number for a given cation – anion pair. The $R_{cation}/R_{anion}$ ratios for different coordinations are listed in Table 2. Note that linear coordination is not included here. For such examples in Table 1 size is not the decisive parameter since special hybridization schemes apply for the listed d$^{10}$ cations.

**Table 2:** Coordination number (CN), type of preferred coordination polyhedron and values for $R_{cation}/R_{anion}$ calculated for contact between cation and anion.

<table>
<thead>
<tr>
<th>Coordination number</th>
<th>Coordination polyhedron</th>
<th>$R_{cation}/R_{anion}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Trigonal</td>
<td>0.155</td>
</tr>
<tr>
<td>4</td>
<td>Tetrahedral</td>
<td>0.225</td>
</tr>
<tr>
<td>6</td>
<td>Octahedral</td>
<td>0.414</td>
</tr>
<tr>
<td>8</td>
<td>Cubic</td>
<td>0.732</td>
</tr>
</tbody>
</table>
Figure 2: Example on how the $R_{\text{cation}}/R_{\text{anion}}$ ratio can be calculated for cations exactly fitting the void between four anions (as in the central layer of an octahedron).

Note that Table 2 is useful for assessing the lowest likely coordination number, but the CN can be higher than calculated since expanded interstices/holes are acceptable because the cation and anion is then in direct contact. Example: an oxide with $R_{\text{cation}}/R_{\text{anion}} = 0.45$ ought to have octahedral cations, but tetrahedral coordination cannot be fully excluded. On the other hand, the cations cannot be so small that they will rattle inside the interstice. For instance, a cation with $R_{\text{cation}}/R_{\text{anion}} = 0.40$ is not stable in octahedral coordination. However, there exist examples of perovskite type oxides with such small cations in what would ideally be an octahedral interstice. However, in these cases a structural deformation will take place, shifting the cation off-centre from the ideal octahedral position and thereby modify the chemical bonding (typically by gaining some shorter A-O metal oxygen bonds, due to covalency; example BaTiO$_3$). It must be emphasized that size is not the sole parameter determining the CN, but is essential. Covalency, and thereby requirements on directional bonding (i.e. certain hybridizations are more effective than others) may influence and switch the situation.

Once the coordination number for the cation is known, the coordination number for the anion can be calculated – given that the $A_xB_y$ compound in question is a normal inorganic compound (no A-A and no B-B bonds):

$$a \cdot \text{CN}_A = b \cdot \text{CN}_B$$  \hspace{1cm} (Equation 1)

This can be extended to $a \cdot \text{CN}_A + b \cdot \text{CN}_B = c \cdot \text{CN}_C$ for a regular ternary $A_xB_yC_z$ compound.

Example: In MgO with rock salt type structure, Mg$^{2+}$ has octahedral coordination ($CN = 6$). What is then the coordination number for oxygen? $1 \cdot \text{CN}_{\text{Mg}} = 1 \cdot \text{CN}_O \Rightarrow \text{CN}_O = 6$
Example: In TiO$_2$ with rutile type structure, Ti$^{4+}$ has octahedral coordination (CN = 6). What is then the coordination number for oxygen?  

\[ 1 \cdot \text{CN}_{Ti} = 2 \cdot \text{CN}_O \rightarrow \text{CN}_O = 3 \]

Different coordination polyhedra are shown in Figure 3.

Figure 3: Coordination polyhedra for coordination numbers 2 – 12.

1.3 Tetrahedral oxoanions and relevant crystal structures

In KJM1120 several structures based on tetrahedral oxoanions were discussed. We will recapitulate some main aspects. The crystal structures of silicates are conveniently used to describe the diversity of structures based on corner (vertex) sharing of tetrahedra as the primary building unit.

Relevant tetrahedral oxyanions are for instance; SiO$_4^{4-}$, PO$_4^{3-}$, SO$_4^{2-}$, ClO$_4^{-}$ from the p-group elements (note that similar oxoanions frequently exist for period 4 elements like Ge, As, Se, Br and some period 5 elements). Examples from the 3d-transition metals include VO$_4^{3-}$, CrO$_4^{2-}$, MnO$_4^{-}$. There exist compounds like RuO$_4$ and OsO$_4$, also tetrahedral. However, in the latter case the (RuO$_4$) molecule is neutral. No charge compensation is required. For the other oxoanions, charge balance is obtained by either adding cations under formation of a compound, or alternatively, the oxoanions polymerize and end up with charge neutral oxide compounds of the elements. Obviously, monovalent oxoanions become neutral when making a dimer via sharing of a common corner (oxygen atoms). One may of course argue that other principles for condensation/polymerization could be applicable than just corner sharing. However, the dominant principle is corner sharing for tetrahedra (with highly charged cations). This is understandable when considering the interatomic distance between the central cations of two neighbouring tetrahedra. Since these cations have a high oxidation state (IV to VII in the examples above) they will repel and prefer maximum separation. Therefore
corner sharing (= vertex sharing) is favorable, Figures 4 and 5. Edge sharing may occur, but never face sharing.

Figure 4. Schematic drawing of a tetrahedral oxoanion (left) and dimer by vertex sharing (right)

Figure 5. Rings, chains and fragment of 2D-layered structure of tetrahedra sharing vertices (respectively, two, two and three shared vertices between involved tetrahedra); their compositions are SiO$_3^{2-}$, SiO$_3^{2-}$ and Si$_2$O$_5^{2-}$.

The dimers Mn$_2$O$_7$ and Cl$_2$O$_7$ are neutral and these molecules have the form of two connected tetrahedra. CrO$_3$ (and SO$_3$) consists of tetrahedra that share two of their oxygen corners with other identical tetrahedra. Hence, as solids they take chainlike structures (CrO$_3$; chains linked with weak van der Waals interactions) or smaller rings (SO$_3$), see Figure 6.

Figure 6. Six-rings of S$_6$O$_{18}$ (SO$_3$) and 1D-chain structure of CrO$_3$ (right)

In the silicates the O/Si ratio (actually O : tetrahedrally coordinated cation that also could be Al replacing Si etc.) carries information on the connectivity. Only SiO$_2$ is charge neutral. The
latter situation is achieved when all the four oxygen corners of the $\text{SiO}_4^{4-}$ primary units are shared with other tetrahedra. The $\text{SiO}_2$ structure (different polymorphs exist) contains a number of rings of tetrahedra that are connected via their four O-corners. The porous zeolite structures are in principle of the same type, the difference being a much larger size of the rings (and cavities), which typically is achieved during synthesis by means of template molecules that fill part of the (final) voids.

Table 3: $O : \text{Si}$ ratio (corner : number of tetrahedral cation ratio) and key features of the structures

<table>
<thead>
<tr>
<th>$O : \text{Si}$ (T) ratio</th>
<th>Key feature of the structure</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>Single oxoanions $\text{SiO}_4^{4-}$</td>
<td>Orthosilicates</td>
</tr>
<tr>
<td>3.5</td>
<td>Dimeric anions $\text{Si}_2\text{O}_7^{6-}$</td>
<td>Pyrosilicates</td>
</tr>
<tr>
<td>3</td>
<td>Chains or rings $\text{Si}_3\text{O}_6^{5-}$</td>
<td>Metasilicates</td>
</tr>
<tr>
<td>2.5</td>
<td>2D layered anions</td>
<td>Phyllosilicates; clays</td>
</tr>
<tr>
<td>2</td>
<td>3D structures (neutral $\text{SiO}_2$)</td>
<td>Framework structures; zeolites, ...</td>
</tr>
</tbody>
</table>

**Task:** what is the composition of a double chain of corner-shared $\text{SiO}_4^{4-}$ tetrahedra?

Crystal structures with edge sharing of $\text{MO}_4$-tetrahedra can only be expected in the case of lower oxidation states for the $M$-atom. We will below consider $\text{ZnO}$, which takes two polymorphic forms, the wurtzite and the sphalerite type structures, in both cases with edge shared $\text{ZnO}_4$-tetrahedra.

A final remark; in KJM1120 we discussed in length the acidity of oxoacids in water. Many of these have tetrahedral oxoanions; $\text{H}_3\text{PO}_4$, $\text{H}_2\text{PO}_3$ (PO$_3$H tetrahedron), HPO$_3$, H$_2$SO$_4$, HClO$_4$, Si(OH)$_4$. In the solid state pure acids may exist as imagined from their ideal molecular structures, however, influenced by significant hydrogen bonding, in certain cases also through incorporation of crystal water.

### 1.4 Describing crystal structures on the basis of coordination polyhedra

There are several ways to follow when describing the crystal structures of inorganic solids. From a chemical bonding point of view, it is natural to focus on the coordination polyhedra of the involved cations; coordination number (CN) and geometry (including bond distances). Note, that there is no direct connection between the type of coordination polyhedra and the chemical bonding; tetrahedral coordination is favored by e.g. $\text{sp}^3$ hybridization in a covalent picture; by small cations ($R_M/R_X > 0.225$) in an ionic model, and by tetrahedral holes in metallic hcp or ccp. A second approach, which is more limited in its application, is to describe
crystal structures on the basis of dense packing of spheres, for instance by considering the larger anions (oxide, chloride, hydride,…) being densely packed and with cations in interstitial holes. The latter approach is discussed below for some selected structures.

Regarding coordination polyhedra, it is reasonable to assume strong (directional) bonding when the charge density of the cation is substantial. Hence, we will focus on using descriptions based on coordination polyhedra when the oxidation state is III or higher, in some cases also on M(II) cations with strong (polar)covalent bonding, typically 3d-elements. We are less focused on the coordination polyhedra of large alkali and alkaline earth cations. Such atoms may in oxides take coordination numbers between six and twelve, sometimes even higher.

Some examples: LaMnO$_3$; Ca$_3$Co$_2$O$_6$; MgO; Cu$_2$O; La$_2$Ni$_2$O$_5$; CaF$_2$. Some of these will be inspected during the seminars on structure visualization and modelling. Inspect the figures and identify the coordination of the smaller cation in these compounds.

**Task:** What is the coordination number or the two different Ni-atoms in La$_2$Ni$_2$O$_5$? Explain on the basis of their d-electron configuration.

**Task:** What is the coordination number for oxygen in Cu$_2$O with linear O–Cu–O entities?

Above, we considered structures based on linkage of tetrahedra. Exactly the same considerations can be done for octahedra. In this case the interatomic separations between the central atoms are longer than for pairs of tetrahedra. Octahedra are commonly linked via corners (vertices), but frequently also via edges, whereas face-sharing is rare. The stability of structures with different polyhedral linking is: vertex-sharing > edge-sharing > face-sharing. The effect is large for cations with high charge.

Figure 7: ReO$_3$ (left), NaCl (middle) and NiAs (right) type structures with respective corner sharing, edge sharing and face sharing of octahedra. (We will not consider the NiAs type
structure below, however, compounds with this structure type are metallic owing to short M – M distances between the face-shared octahedra.)

One may also here consider how composition change when going from an individual MX$_6$ octahedron to a dimer; if sharing a vertex the dimer has composition M$_2$X$_{11}$; if sharing an edge M$_2$X$_{10}$, and if sharing a face M$_2$X$_9$, Figure 8.

![Figure 8: Dimers of M$_2$X$_{11}$ corner (left) and M$_2$X$_{10}$ edge (right) shared octahedra.](image)

Octahedral coordination is common for halides and oxides. A main difference is the charge of the unit (oxidation number for halogen = -I, oxygen = -II). For instance Bi(V) fluoride forms one-dimensional BiF$_5$ chains in the solid state, Figure 9. SnF$_4$ consists of 2D sheets of corner shared octahedra Figure 9, whereas 3D network with all 6 vertices being shared occurs in ReO$_3$.

![Figure 9: Schematic drawing of 1-D chains and 2-D sheets based on vertex shared octahedra.](image)
Task: what is the composition of a trimer of octahedra; based on (i) sharing of vertices; (ii) sharing of edges; (iii) sharing of faces.

Task: Draw a 180° M–O–M linkage, and illustrate the overlap between eg and p-orbitals on the M (3d) and O atoms, respectively. What will happen with the overlap if the angle M–O–M departs from 180°?

Quite analogously, the BO₆-octahedra in perovskite type oxides share all their vertices with other octahedra, resulting in ABO₃ compounds with oxidation states for A and B summing up to six. For vertex shared octahedra one realizes that the eg orbitals of the B transition metal are directly oriented towards oxygen p-orbitals. This is relevant when it comes to magnetism and electric conductivity.

The rock salt structure (MgO) is based on MgO₆ octahedra sharing edges, Figure 10. The same applies to the 2D-layers in the structures of some hydroxides, e.g. Mg(OH)₂, that can be deduced from sphere packing models with cations in octahedral holes, see below.

Figure 10: Edge shared octahedra (left) in the rock salt type crystal structure right).

1.5 Describing crystal structures on the basis of dense packing of spheres

Metal atoms, noble gas atoms, anions and cations in ideal ionic structures, can be considered as spherical. In many respects nature tends to favor dense structures. In order to achieve dense volume packing of such spherical atoms, we first consider a 1D-line of atoms, then extend to 2D by merging adjacent chains, and finally stack the 2D dense layers along the [001] stacking direction, again by displacing the layers with respect to each other to benefit from the cavities between the spheres. This can be achieved in numerous ways. However, there are just two main, simple close packed stacking sequences; the hcp with ABAB… stacking, and ccp with ABCABC… stacking (underlined sequence repeating). But notably any other sequence that does not include two succeeding layers of the same type (no AA, no BB, no CC) are closest
packed. In these, 74% of the volume is occupied by the atoms, here considered as rigid spheres. However, this implies as much as 26% of voids, i.e. interstitial holes that potentially can be filled by smaller atoms (cations; or small atoms H, B, C, N,…).

The ccp stacking in Figure 11 is visualized in a hexagonal setting, with c-axis perpendicular to the paper plane. The ccp stacking can easily be shown to be identical to the fcc unit cell. The latter fcc unit cell is preferred when drawing structures based on ccp stacked anion substructures. In this case the packing atoms have relative coordinates (0,0,0), (1/2,1/2,0), (1/2,0,1/2) and (0,1/2,1/2); see Figure 11.

Figure 11: Closest packing of spheres (hcp left, ccp middle) and fcc unit cell (right) identical to ccp.

In addition to ccp (=fcc) and hcp, the body centered cubic structure (bcc) occurs frequently. The bcc is dense, but not closest packed, Figure 12. Interstitial holes are differently sized and shaped between bcc and ccp/hcp, see below. Many metallic elements and noble gases take these structures, see Figure 13.

Figure 12: The more open bcc stacking of spheres; CN = 8.

The ABAB… stacking in hcp gives rise to the so-called trigonal bipyramidal hole (tbp), with CN = 5. The tbp is located in close vicinity to the two different tetrahedral holes in hcp, and in reality only one of these three holes can be filled by reasonable sized atoms simultaneously.
A considerable number of simple structures can be derived from ccp and hcp stacking of anions, with cations filling some of the different categories of interstices. We will not discuss this in any larger extent, and refer to Table 4 for an overview and MENA3000 or further details.

Table 4: Structures types and degree of filling of various interstices (T+, T- tetrahedral interstices; O octahedral interstice). In ccp there are: 2 tetrahedral holes and 1 octahedral hole per packing sphere; in hcp similarly, but in addition on trigonal bipyramidal holes situated at the midpoint between two close tetrahedral holes.

<table>
<thead>
<tr>
<th>Stacking</th>
<th>T+</th>
<th>T-</th>
<th>O</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>ccp</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>NaCl</td>
</tr>
<tr>
<td></td>
<td>1/8</td>
<td>1/8</td>
<td>1/2</td>
<td>MgAl₂O₄ spinel</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>1/2</td>
<td>CdCl₂</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>1/3</td>
<td>CrCl₃</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1</td>
<td>-</td>
<td>Na₂O antifluorite</td>
</tr>
<tr>
<td>hcp</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>NiAs</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>ZnS wurtzite</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>1/2</td>
<td>CdI₂</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>1/2</td>
<td>Rutile</td>
</tr>
<tr>
<td></td>
<td>1/8</td>
<td>1/8</td>
<td>1/2</td>
<td>Mg₂SiO₄ olivine</td>
</tr>
</tbody>
</table>

Task: Identify the close packed planes of spheres in the fcc unit cell.

Task: What is the difference between CaF₂ and antifluorite type structure?

Task: CdI₂ and TiO₂ rutile have the same degree of filling of sites in the hcp of anions. Yet CdI₂ Is layered and TiO₂ is a 3D-network structure with strong bonding. Explain.
Task: Calculate the percentage of empty voids in bcc, and in ccp (hint: consider the fcc unit cell)

2. Eleven selected examples; structure – property relations

The atomic arrangement combined with the properties of the involved ions (electron configuration, oxidation state, size, polarizability, electronegativity) is decisive for resulting chemical bonding (ionic, polar covalent, covalent, metallic) and chemical (stoichiometry, reactivity, stability) and physical (optical, electric, magnetic, mechanical) properties.

In KJM-MENA 3120 we will look into the atomic arrangement of around ten different compounds that are all of interest for applications within energy technologies. The idea is to get a solid understanding for their atomic arrangements, and how the crystal structure in combination with the specific elements give rise to compounds that can act as TCO (transparency and electronic conductivity), electrodes in Li-ion batteries, solid electrolytes for batteries and fuel cells, superconductors and hydrogen storage in solid state. The structures/compounds to be considered are:

- ZnO wurtzite as TCO
- CuAlO₂ delafossite as p-type TCO
- Ca₃Co₂O₆ one-dimensional metal oxide chain
- LiFePO₄ olivine type cathode material
- LiCoO₂ layered cathode material
- Li₂Mn₃NiO₈ spinel type cathode material
- BaZrO₃ proton conductor
- ZrO₂, YSZ and oxygen conductors
- LiₓC and anode materials; graphene
- YBa₂Cu₃O₇ and high Tc cuprates
- fcc/ccp, hcp, bcc alloys; hydrogen storage and steel

Details as well as qualitative description of these structures, coordination, vacancies, channels and dimensionality of structural features; chemical bonding, interatomic distances, and structure – property relationship will be practiced during seminars and modelling/simulation sessions.

Before entering into the examples, a minimum introduction to crystallography is required.
A crystal structure is described on basis of a repeating box, the unit cell. The unit cell is defined by three unit vectors $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$ with length $a$, $b$ and $c$, and angles $\alpha$ between $\mathbf{b}$ and $\mathbf{c}$, $\beta$ between $\mathbf{a}$ and $\mathbf{c}$, and $\gamma$ between $\mathbf{a}$ and $\mathbf{b}$. The length of the unit cell dimensions $a$, $b$ and $c$, are for most inorganic compounds in the range 3 - 30 Å. The unit cell vectors start at the origin with its relative coordinates $(0,0,0)$. The unit cell is constrained by three sets of parallel planes. All x,y,z coordinates inside the unit cell are limited between zero and one (note, these are relative coordinates). The unit cell (“box”) repeats along all the three directions, [100], [010] and [001]. Frequently one will draw more than just one unit cell in order to gain the best possible overview on how atoms are positioned with respect to each other, recognize the structural building bricks, and discuss chemical bonding.

The atoms (of relevant types and numbers) are situated inside the unit cell, i.e. their atomic x,y,z coordinates are in the range $0 \leq x \leq 1$, $0 \leq y \leq 1$, $0 \leq z \leq 1$. They repeat in neighbouring cells via unit translations.

When drawing a structure (using the DIAMOND program in the simulation seminar) you upload the required information from a data file; extension cif. This minimum information is:

- Space group (provides information on crystal system, Bravais lattice, symmetry operation)
- Unit cell dimensions
- Relative atomic coordinates for all involved atoms

**Task:** Consider a xxx.cif file and familiarize yourself with how structural (crystallographic) information is coded.

**Task:** Consider the cubic NaCl-type structure; $a = b = c$; all angles 90°; $a = 5.20Å$ Cations (M) in $(0,0,0)$, $(1/2,1/2,0)$, $(1/2,0,1/2)$, $(0,1/2,1/2)$ and anion (X) in $(1/2,0,0)$, $(0,1/2,0)$, $(0,0,1/2)$, $(1/2,1/2,1/2)$. Draw on paper a projection of the structure on the ab-plane (use open and filled symbols for atoms in different heights, i.e. different z-coordinates). Calculate the M-X bond distance, and the X-X separation for close X neighbour atoms.
2.1 ZnO wurtzite - a TCO material

ZnO crystallizes in two polymorphic forms; the hexagonal wurtzite and the cubic sphalerite types. Both are described on the basis of a close packed oxygen substructure with zinc cations in tetrahedral holes, Table 4. In wurtzite the oxygen substructure is hcp, while ccp in sphalerite (zinc blende). In hcp, trigonal bipyramidal holes are available in addition to those listed in Table 4.

Figure 14: Three closed packed spheres (left) with a hole that corresponds to the tbp interstice. Note T_+ and T_- tetrahedral holes are positioned in close vicinity to the tbp hole.

The space group of ZnO is P6_3mc and the corresponding crystallographic point group is 6mm (topic is covered in MENA3000). 6mm is among the 10 polar point groups which may give rise to crystals with special properties. One such property of ZnO is pyroelectricity. We will here limit ourselves to take a close look at the crystal structure for identifying the structural

Figure 15: Wurtzite type structure of ZnO; black spheres oxygen, white spheres zinc. Unit cell outlined by thick lines. Note; the ZnO_4-tetrahedra are all oriented the same way (only one shown). The structure also contains OZn_4-tetrahedra.

Since the a- and c-axes are independent in the hexagonal crystal system, ZnO may exhibit different thermal expansion within the basal ab-plane and along the c-axis (stacking direction of close packed anions). Since there is no mirror plane perpendicular to the c-axis, any dipole between positive and negative charge will not be cancelled by its mirror image [cf. molecules;
dipole moment in H$_2$O, whereas no dipole moment in CO$_2$ since the O-C and C-O dipoles cancel by inversion/mirroring). Therefore the total electric polarization of ZnO will be temperature dependent; i.e. ZnO will exhibit pyroelectric behaviour. By considering the structure, we realize that the surfaces perpendicular to the c-axis are polar in nature, Figure 15. They either contain just Zn-cations (with O-atoms below) or oppositely; O-anions with Zn-atoms below. Hence, surface absorption properties will be different on the different categories of external surfaces on ZnO crystals/particles, the amount of which can possibly be controlled during wet chemical materials synthesis.

Pure and perfect w-ZnO (w = wurtzite) is charge neutral; Zn(II) and O(-II) give a complete charge balance. On this basis, noting that Zn(II) has d$^{10}$ electron configuration, we expect ZnO to be colourless and quite ionic, though with some covalency (Zn$^{2+}$ polarizing the large e-cloud of O$^{2-}$, cf Fajans rules). The band gap is expected to be large. Measurements give 3.3 eV (direct). The perfect crystal structure can be used as input into quantum mechanical calculations of the electronic band structure. Modern codes gives a calculated band gap in excellent correspondence with observations.

How can the conductivity of ZnO be modified? The band gap for the pure ZnO semiconductor is substantial. We may suggest substitutions and/or introduction of impurity atoms that influence the size of the band gap, or gives rise to additional levels in the band gap, and/or adds more charge carriers in terms of electrons (e) or holes (h). We inspect the crystal structure to search ideas on how to proceed.

At this point we need to stress a very important difference between inorganic solids and molecules of organic or inorganic nature. Molecules have a well-defined composition; methane is CH$_4$ and nothing but that, tetrachloromethane is CCl$_4$, ethanol C$_2$H$_5$OH and so on, from simple to very complex molecules, including biomolecules. If a small chemical change is done, i.e. exchanging just one atom, the molecule is no longer the same – it is different; e.g. CHCl$_3$ is different from CH$_4$ and CCl$_4$, C$_2$H$_5$SH is different from C$_2$H$_5$OH. This reflects the strong (polar) covalent interactions within the molecules and the weaker dispersion forces between the molecules. ZnO is not molecular. It is a compound where Zn$^{2+}$ and O$^{2-}$ ions are distributed systematically (periodically) in space according to what depicted for the unit cell in Figure 15. In a crystallite of ZnO with mass of some mg there is roughly $N_A$/1000 atoms. They are ideally correlated in space as described by the wurtzite crystal structure. We may now imagine that we exchange a few Zn-atoms by other divalent cations, i.e. making a
solution in the solid state (= a solid solution). This resembles mixing of organic liquids with different molecules. If they are similar in size, shape, polarity – one may obtain fully miscible liquids. If the divalent cation is sufficiently similar to zinc in size (and charge), one may exchange a lot, if not all zinc atoms by the divalent substituent. Thermodynamically there is one obvious driving force for a small amount of such substitutions. The mixing process creates disorder. Hence, the entropy will increase upon mixing. On the other hand, it might well be the case that the chemical binding is no longer optimum, hence there may be a penalty to pay with respect to bonding enthalpy. Finally, the balance is set by Gibbs free energy; \( \Delta G = \Delta H - T \Delta S \).

The mechanism described will also govern situations where the substitution process is more complex. This is where periodic inorganic materials (solids) become very different from small molecules. Let us consider some of the more complex options. All these are based on the assumption that we maintain charge balance for the compound in question: (i) one may replace Zn(II) by another M(II) but due to size aspects it is no longer accommodated in a tetrahedral hole in the hcp packing of oxygen atoms, but in an octahedral hole (see Table 4; there are always 2 tetrahedral, 1 tbp, and 1 octahedral hole per packing sphere in hcp). The introduced impurity atom (dopant; substituent) is shifted in location from a regular Zn-site to a vacant interstitial position; (ii) one may replace Zn(II) by two monovalent cations M(I) that occupy either the regular position and/or interstitial positions; (iii) one may replace two Zn(II) atoms by one M(III) and one M(I) cation – again on either regular Zn-site or interstitial positions; (iv) the M(I) could be a proton and bind strongly to oxygen atoms, forming OH-groups; (v) the oxygen anion can be replaced by S(-II) or possibly also by X(-I) anions like H\(^-\), F\(^-\), Cl\(^-\). We remind that the “substitution” process for all these mechanisms is governed by the thermodynamic considerations above. Hence, some situations can be favorable and dominant (small \( \Delta H \) of formation); others do not take place to any significant extent. In reality the situation is frequently even more complex since energy minimalization will involve a larger number of atoms around a given substituent/defect. This will in turn give rise to so-called defect clusters or defect complexes (which mean the same), i.e. small assemblies where a few atoms (up to 10-25) acquire a local arrangement that minimize energy. Such cluster will be randomly distributed throughout the crystallites.

Task: Use the DIAMOND program to construct the ZnO structure (several unit cells), identify octahedral sites, and visualize furthermore also the scenarios (i) – (v).
One may ask where do all the M(I), M(II), M(III), X(-II), X(-I) substituents come from? How are they introduced to the ZnO crystallite? It is essential first to consider purity of reactants and environments. When making a compound, one needs starting reactants. Those can be the elements. However, even the elements (zinc and oxygen in this case) must be produced from natural sources. Oxygen can easily be received with high purity (at least with impurities of little concern for the current reaction), however, zinc is produced from mineral ores of sulfides according to a process with rosting and carbothermal reduction. A large number of other metallic elements will coexist with zinc in the sulfide ore. After reduction and purification we have a material of say 99.99% purity, but that is far from 100% when it is compared with e.g. the purity of semiconductor grade silicon. Furthermore, we use various chemical reaction pathways, frequently solvent/water based; sometimes with precursors like nitrates and acetates as cation sources; sometimes organic acids/alcohols like citric acid is used as chelating agent, etc. All these chemicals have a given level of purity, often limited to 99.5%. Hence, any inorganic compound tends in the as-synthesized state to include impurity atoms. They may be distributed in the crystal structure as indicated for ZnO above, as solid solutions, or via mechanisms (i) – (v). For some chemical and physical properties such small levels of impurity is of no concern. For ZnO as a TCO, the transparency and electric conductivity are two key properties. Hence, we ask: how do various impurities possibly influence ZnO as a TCO? Technologically, ZnO is achieved as single crystals or thin film coatings. The obtained products can be purified, but extrinsic (impurity) atoms are an issue which one never can neglect totally. It is important to be aware of the synthesis history of a sample before embarking on complex studies of physical properties.

The substitution of Zn(II) by M(II) does not change the concentration of charge carriers. However, since the electronegativities of these elements will be different, their nuclear effective charge is different, which will affect the positioning of orbitals (bands). Hence, substitutions may modify the size of the band gap, normally to moderate extents. Mg(II) and Cd(II) are two likely substituents used in so-called band gap engineering.

During synthesis one may achieve incorporation of Al(III) at zinc sites with one additional electron ideally to provide charge balance. Likewise incorporation of lithium cations can take place at octahedral sites with one electron acting as charge compensation. In both these cases one obtains additional electrons that occupy new donor levels in the band gap. These are efficient charge carriers, with lower activation barriers for excitation into the conduction band owing to the position of the levels within the band gap. Thereby Al-substitution provides
a conductive and transparent material, i.e. an n-type TCO with conductivity by electrons. The substitution levels for achieving good n-type ZnO are moderate, say 1-2 atomic %. If one could be able synthetically to position a Li\(^+\) at a Zn-site with an electron hole acting as charge compensation, one would have achieved a p-type TCO where conductivity is provided by holes (lacking electrons) in the valence band and acceptor levels close to the valence band.

Introduction of heterovalent substituents or impurity atoms (at regular sites of atoms in the crystal structure or at interstitial sites provided by the specific atomic arrangement of the compound in question) can have profound effect on electronic properties of semiconductors, change conduction pathways and magnetic interactions in complex oxides, provide defects of key importance for transport of ions in proton or oxygen conductors, etc.

![Figure 16: Acceptor (left) and donor (right) doping of elemental silicon, Si.](image)

In semiconductor physics a dopant atom is termed an acceptor in the case when the added atom provide a p-type region, and hence p-type conductivity. In the simple case of elemental silicon (Si), boron is an acceptor dopant providing p-type Si. Boron is short of valence electrons (group 13; 2s\(^2\)2p\(^1\)), likewise other elements in group 13 (Al, Ga,...). Boron will form covalent bonds with the surrounding Si-atoms, see Figure 16. However, boron can not achieve four 2e bonds in the sp\(^3\)-hybridized diamond type structure of silicon. This results in an electron hole; p. The unsatisfied B – Si bond attracts electrons from the neighbouring bonds. An electron from a neighbouring bond will jump to repair the unsatisfied bond thus leaving another hole (a place where an electron is deficient). The hole will again attract an electron from the neighbouring bond to repair this unsatisfied bond. This chain-like process results in the hole moving around the crystal and able to carry a current thus acting as a charge carrier.

Correspondingly, a donor is a dopant that when added to a semiconductor forms an n-type region. This occurs when the dopant (substituent) has more valence electrons than silicon. This is the case for group 15 elements like phosphorus and arsenic. Four of the valence
electrons of phosphorus will form covalent bonds with the neighbouring Si atoms. The fifth electron will remain weakly bonded and can move around the Si crystal and can carry a current and provide so-called n-type conductivity.

2.2 CuAlO\textsubscript{2} delafossite - a p-type TCO material

A number of oxides with late transition metals show p-type conductivity. This applies for instance to Cu(I) and Ag(I) compounds. Since transparency is an additional issue, d\textsuperscript{10} cations are attractive since they do not possess any d-d electronic transitions (all five d-orbitals being completely filled). Tiny amounts of Cu(I) vacancies are proposed as mechanism for the p-type conductivity in e.g. Cu\textsubscript{2}O. In some high oxidation state Fe-, Co-, Ni-, Cu-compounds, the electronic band structure (calculations, observations) contain both d-levels and band with strong O-character at the fermi level (highest occupied energy level). In some cases one rather say that one does not have Fe(IV) and O(-II) but rather Fe(III) and O(-I); in this sense one has a hole in the band dominated by oxygen.

Figure 17: 3D perspective of the delafossite type crystal structure; ABO\textsubscript{2}. The 2D-slabs with connected octahedra are seen in middle section of the figures; the linearly coordinated M(I) atoms are shown in red (left) and black (right).

The delafossite type structure has interesting features and belongs to a family of ternary oxides with general formula A(I)B(III)O\textsubscript{2}. The A-atoms are linearly coordinated by two O-atoms. The d\textsuperscript{10} ions Cu(I) and Ag(I) have indeed preference for linear coordination (CN = 2; special hybridization being responsible, not size or charge). The B(III) ions obtain octahedral coordination CN = 6, and form 2D layers of edge-shared octahedra, Figures 16 and 17. The interatomic distance between the A-cations is quite small, around 3.0 Å. The B-cations can be either p-block cations Ga, In, and Al; transition metal cations Fe, Co, and Y; or rare earth elements La, Nd, and Eu.
The delafossite structure can schematically be described in terms of two types of alternating layers: a layer with two-coordinated A(I) cations (in a triangular pattern) and a layer of edge-sharing BO₆ octahedra. Depending on the relative orientation of these layers, two stacking variants of the delafossite structure are formed; see Figure 17. These variants have the exact same composition. All key bonding environments are identical. Hence, differences occur at longer separations and bonding enthalpies are expected to be close to identical. Such stacking variants of a given structure are termed polytypes. Synthetically it is hard, sometimes impossible, to obtain a phase pure material with respect to just one of the polytypes. X-ray diffraction is used as characterization method since the observed diffraction pattern is a fingerprint of the crystal structures. The structures are different for the two polytypes along the c-axis, see Figure 17, hence their XRD patterns (fingerprints) are different. By stacking the octahedral layers with alternating A(I) layers oriented 180° relative to each other, the 2H polytype is obtained (P6₃/mmc space group). If the octahedral B(III) layers are stacked with the A layers offset from each other in a three layer ABC sequence, the 3R type is obtained (R-3m).

Figure 17: Two polymorphs of the delafossite type crystal structure; 2H (left) and 3R (right), with difference in the stacking sequence of layers, and hence different repetition lengths along [001].

The monovalent A(I) atoms, in particular copper, can be partly oxidized to A(II), giving a mixture of cations in oxidation states I and II. From inspection of the crystal structure there is obviously a lot of empty space in the layers of the A(I) atoms. Additional oxygen atoms can take interstitial positions located in these layers. Thereby the oxidized A(II) atoms obtain a higher coordination by oxygen atoms. On the average, these oxygen atoms will appear as
randomly distributed over possible interstitial sites. However, given that one were able to watch directly the coordination environment of an oxidized A(II) ion, it is most likely that the ion will have CN = 4, 5 or 6. Considering the M(II) cation to be Cu(II) with $d^9$ configuration and therefore normally a Jahn Teller distortion (which emerge when there is an odd number of electrons in $e_g$ orbitals for “octahedral” coordination), it is likely that the local coordinations of Cu(II) is either square planar (CN = 4) or square pyramidal (CN = 5) or deformed octahedral (2 + 4). It turns feasible to almost oxidize all Cu(I) to Cu(II) in delafossites. However, when everything has become Cu(II) the delafossite type compound is no longer stable, and other structures are formed ($A_2B_2O_5$). Upon oxidation of Cu(I) into Cu(II) one has an interesting balance; are the holes (= the additional charge) located on the copper atoms (and hence what chemists will describe as $Cu^{2+}$) or will be holes be associated with electron bands of predominant oxygen character? In the latter case one will say that the oxygen has a character of $O^-$ (rather than $O^{2-}$, equally to express that there exists a ligand hole (= lack of electrons in orbitals connected with the O-ligands). The mixed A(I)/A(II) situation will increase conductivity, which will be of p-type, however, the materials may for higher A(II) concentrations lose transparency and appear as black compounds.

Task: Calculate the separation between A(I) atoms in the relevant layers of the delafossite structure.

Task: Consider the layer with A(I) cations. Is there space to include more O-anions in this layer? What would the resulting A-O bond distance be?

2.3 $Ca_3Co_2O_6$ – an example of a one-dimensional metal oxide

Crystal structures are frequently described as molecular, one-dimensional, layered or two-dimensional, network or three-dimensional. These descriptions point at key features of the atomic arrangements.

In a one-dimensional structure, like $Ca_3Co_2O_6$, there would normally be certain key structural features that are chain-like. That could be for instance 1D chains of vertex shared tetrahedra in CrO$_3$ or MnSiO$_3$; 1D chains of vertex shared octahedra in BiF$_3$; or edge or face shared polyhedra as is the case for $Ca_3Co_2O_6$. However, in $Ca_3Co_2O_6$ the prominent chain has composition $CoO_3^{3-}$ and is charge balanced by $Ca^{2+}$ cations in between the chains, Figure 18. This is fully in parallel to $Mn^{2+}$ cations between $SiO_3^{2-}$ chains in MnSiO$_3$. Other 1D-compounds to mention are CsCuCl$_3$ and BaNiO$_3$. 
Figure 18: Crystal structure of \( \text{Ca}_3\text{Co}_2\text{O}_6 \). Left; chains along the \( c \)-axis [001] of composition \( \text{CoO}_3^3^- \) separated by \( \text{Ca}^{2+} \) cations; middle; single chain; right, projection of the chains on the \( ab \)-plane.

In these 1D-compounds the \( \text{MO}_6 \)-coordination polyhedra share faces. A careful look into \( \text{Ca}_3\text{Co}_2\text{O}_6 \) reveals two different polyhedra; i.e. an alternating sequence of octahedra and trigonal prisms, Figures 18 and 19. In both cases the central cation is cobalt. However, the symmetry of the electrical fields set up by the O-ligands is different, which imply different splittings of the d–orbitals.

Figure 19: Alternating sequence of octahedra and trigonal prisms.

Task: Draw the \( \text{Ca}_3\text{Co}_2\text{O}_6 \) structure with DIAMOND, and identify the \( \text{MO}_6 \)-coordination polyhedra. Look up in literature how the d–orbitals split in octahedral and trigonal prismatic electric fields.

Task: Draw the structure of \( \text{CsCuCl}_3 \) in two forms; high temperature (symmetric form) n low temperature form (with deformation due to spin-peierls distortion of the \( d^9 \) chain structure).

The octahedral site is smaller in size than the trigonal prismatic site. This becomes of importance when making solid solution compounds, i.e. when Co is substituted by other M(III) in small (moderate) amounts. For instance scandium enters the \( \text{tp} \)-site, whereas manganese enters the \( \text{o} \)-site, Figure 20.
Selective substitution by manganese of one of the two Co-sites in Ca$_3$Co$_2$O$_6$

It is possible also to substitute the divalent Ca-atoms by cations of similar size (ionic radius). If these atoms are trivalent like Y(III), one will have a so-called heterovalent substitution. In this case we will replace a lower valent cation, here Ca(II), with a higher valent cation, here Y(III). We need to consider which types of mechanisms will provide a charge neutral compound. There are a few options:

- cation vacancies occur so that the total positive charge is fully balanced by the O-anions
- interstitial anions are inserted to counterbalance the additional positive charge of Y(III)
- the oxidation state of the redox active cobalt is changed

Experiments are required to specify which of these options that are in operation. However, normally when redox active transition metal cations involved, the heterovalent substitution will be compensated by change in oxidation state of the metal component. For instance, in Ca$_3$Co$_2$O$_6$ the average Co-oxidation state is 3.00. For the substituted compound (Ca$_{0.90}$Y$_{0.10}$)$_3$Co$_2$O$_6$, the average Co-oxidation state will be \((12 - 3*2*0.90 - 3*3*0.10)/2 = 2.85\). A follow-up question will be; are both Co-atoms equally affected; is just one of them reduced, and if so, which of them? Here experiments will be helpful: if the oxidation state is lowered, the cation will be larger in size, and hence the Co – O interatomic distances will expand. X-ray diffraction will here provide an answer.

In physics the properties of 1-D magnetic/electronic systems attract a lot of interest. Many times it is of interest to have an idea about the degree of the 1D-character. One possibility is to calculate the Co-Co separations within the chain and compare with the Co-Co separations between chains. The larger the separation between chains, the larger is the 1D-character.
Task: Calculate Co-Co separations within the 1D-chain of Ca$_3$Co$_2$O$_6$, calculate furthermore the closest Co-Co separation between chains, and calculate the ratio (a measure of the 1D character).

2.4 LiFePO$_4$ - an olivine type cathode material for Li-ion batteries

LiFePO$_4$ (LFP) is an important cathode material for Li-ion batteries. The material is of low cost, is non-toxic, there is a high natural abundance of iron, and the material shows excellent thermal stability and safety characteristics, excellent electrochemical performance, and has a specific capacity (170 mA·h/g). Because of the nominal 3.2 V output from LiFePO$_4$ batteries, four cells can be placed in series for a nominal voltage of 12.8 V. This comes close to the nominal voltage of six-cell lead-acid batteries. And along with the good safety characteristics of LFP batteries, this makes LFP a good potential replacement for lead-acid batteries in applications such as automotive and solar. One important advantage over other lithium-ion chemistries is thermal and chemical stability, which improves battery safety. LiFePO$_4$ is an intrinsically safer cathode material than LiCoO$_2$ and manganese spinel (see below). The Fe-P-O bond is stronger than the Co-O bond, so that when abused, (short-circuited, overheated, etc.) the oxygen atoms are much harder to remove.

In LiFePO$_4$, iron takes oxidation state +II. However, it is feasible to remove lithium electrochemically and finally achieve FePO$_4$ with iron in oxidation state +III. The redox potential of the cathode material is hence defined by the Fe(II)/Fe(III) redox couple. Interestingly, the removal of lithium can take place continuously. Such a process where the basic crystal structure is retained during a chemical reaction is said to be topotactic. The crystal structure of is shown in Figure 21. It is of the olivine type, named after the silicate (Mg,Fe)$_2$SiO$_4$. Since the ratio O : Si = 4, we now that this is an orthosilicate with separate SiO$_4^{4-}$ anions. Hence, we can easily identify separate phosphate anions in Figure 21, left. The phosphorous atoms therefore occupy tetrahedral sites, while the iron and lithium atoms occupy octahedral sites. The FeO$_6$ octahedra are linked through common corners in the bc-plane, and the LiO$_6$-octahedra form edge-sharing chains along the b-axis. One FeO$_6$-octahedron has common edges with two LiO$_6$ octahedra and a PO$_4$ tetrahedron. PO$_4$-groups share one edge with a FeO$_6$-octahedron and two edges with LiO$_6$-octahedra.
The ionic conductivity is a critical parameter when it comes to rapid diffusion of Li-ions in electrodes and electrolytes, which relates directly to the applicable charging/discharging rate of the LIB battery. The crystal structure, Figure 21, has an apparent quasi-two dimensional nature; the Fe-octahedra form layers in the bc-plane. This might suggest inplane Li-diffusion (along b and c). However, measurements of Li-ion conductivities on single crystals reveal that the diffusion in LiFePO$_4$ is, to a large extent, confined to one dimension. Oriented powders of LiFePO$_4$ have been suggested as a means to improve the performance of this material in rechargeable batteries. Numerous attempts to enhance the ionic conductivity by introducing divalent and trivalent substitutions that produce vacancies in the Li sheets, appears rather to impede the diffusion in the tunnels than to be helpful.

When considering potential inorganic compounds for high capacity cathodes in Li-ion batteries, the involved redox couple is defining the potential (vs Li$^+/\text{Li}$), which will be in the range 2.5 – 5 V; typically around 4 V. Usually the jump in oxidation state is just one, which limits the capacity per mole material. If one could have cations that allowed jumps of two or even more in oxidation state, the capacity will multiply accordingly. A different aspect is the charging/discharging rates. Here Li-ion diffusion enters as a critical parameter. From a structural point of view, channels in more directions, or 2D-conductivity would be favourable, compared with 1D-conductivity in certain materials such as LFP. In addition to these topological features, the strength of the bonding of Li-ion is of relevance. Conductivity depends on activation enthalpies connected with bond breaking and with ion mobility. A strongly bonded lithium cation implies higher activation energies and reduced conductivities at operational temperatures.
The migration of Li-ions from one site to the next site can be modeled by so-called nudgel elastic band calculations. These show that the activation barriers are far less for ion transport along the [010] direction; Table 5. This direction is indicated by yellow arrow in Figure 22. The calculations provide furthermore insight into the details of the pathway. Two different pathways are considered in Figure 23; a straight line pathway between two Li-sites along the b-axis [010]; and the minimum energy pathway which is curved. The curved pathway is drawn in Figure 23 (left). The energy cost of being displaced from the ideal site (i.e. the position of resting Li-atoms as shown by the crystal structure picture) is shown in Figure 23 (right). It is evident that the barrier is lower for the curved than for the straight line pathway. The calculated activation energy of 0.55 eV is in excellent agreement with experiments that give values in the range 0.54 – 0.63 eV. LiFePO$_4$ is a semiconductor, and not a particular good electric conductor. Essential points in making LiFePO$_4$ a well-working electrode material are two-fold; nanostructuring is important (reducing transport length for ions and electrons); good electric conductivity between particles and current collector (metallic plate) is critical and is achieved by proper mixing with conducting and flexible carbon/polymer materials.

<table>
<thead>
<tr>
<th>mechanism</th>
<th>path</th>
<th>Li-Li separation (Å)</th>
<th>$E_{\text{mig}}$ (eV)</th>
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<tr>
<td>B: Li$^{\text{ii}}<em>{\text{Li}}$ $\rightarrow$ V$^{\text{i}}</em>{\text{Li}}$</td>
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<td>[101]</td>
<td>5.69</td>
<td>3.36</td>
</tr>
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</table>

Table 5: Li-Li separations and activation energies for Li-ion migration along the three directions in the unit cell.

Figure 22: Direction for possible Li-ion diffusion in LiFePO$_4$. Calculated activation energies for migration by DFT (density functional theory).
2.5 LiCoO₂—a layered cathode material for Li-ion batteries

LiCoO₂ is a commercial cathode material for Li-ion batteries. In a sense LiCoO₂ is a complex material since it can be obtained in many crystallographic forms, dependent on synthesis conditions. LiCoO₂ exhibits two basic forms, a hexagonal structure (high temperature HT-LiCoO₂), and a cubic structure (low temperature LT-LiCoO₂). The hexagonal and cubic structures are based on the same oxide substructure, and are distinguished only by the spatial arrangement of cations. We will here discuss one idealized layered form of LiCoO₂, the ideal hexagonal high temperature form, HT-LiCoO₂ (space group R₃₃m). The layered structure is of the so-called NaFeO₂ type. Here Co and Li planes alternate in the ABCABC oxygen stacking, see Figure 24.

Figure 23: Calculated curved migration pathway for Li-ions along [010] (left), the direction with lowest energy activation barriers. Energy plotted as function of ∆y migration coordinate (note Li-atoms are separated by 0.5 in y); data shown for linear and curved pathways (right).

Figure 24: Crystal structure of LiCoO₂; (left) one layer showing AB stacking of oxygen atoms (red spheres) with Co in octahedral voids; (middle) AB… stacking of CoO₂ layers with Li cations in interlayer regions; note that the O-atoms are stacked ABCABC… along the c-axis; (right) perspective of the layered stacking.

Batteries produced with LiCoO₂ as cathodes became available in the 1980ies after the discovery of LiCoO₂ in 1970, and has been extensively used in handheld electronics. LiCoO₂ provides high energy capacity, however, the compound is more reactive and have less thermal stability than many other cathode chemistries (like LFP). A major step towards improved stability was provided by structurally related compounds of lithium-nickel-cobalt-aluminum-oxide (NMC materials). The problem with LiCoO₂ batteries is thermal runaway in cases of abuse, which can be high temperature operation (>130 °C) or overcharging. In such situations...
LiCoO$_2$ may decompose and generates oxygen, which reacts with the organic electrolyte of the battery cell. This reaction is highly exothermic and can spread to adjacent cells and ignite combustible material. In the Boing 787 dreamliner aeroplanes some incidents occurred, probably for related reasons. At the ordering of batteries back in 2005 LiCoO$_2$ were the only type of lithium aerospace battery available. This has now changed and today newer and safer types [LiFePO$_4$ (see above) and spinline type LiMn$_2$O$_4$ (see below)], are available. The structurally related lithium nickel manganese cobalt oxide (NMC) has lower energy density, but longer lifetime and inherent safety. In NMC most of the cobalt in the 2D-layers (see Figure 24) is replaced by nickel and manganese.

**Figure 25: Deintercalation of Li-cations upon charging of the LiCoO$_2$ cathode material. Complete charging to unstable CoO$_2$ is shown.**

During charging the Li-atoms are continuously removed from LiCoO$_2$. Normally the process is limited to provide just Li$_{0.5}$CoO$_2$ (i.e. exchange of 0.5 electrons). Thereby the oxidation state of cobalt is increased. The positive electrode half reaction is:

$$\text{LiCoO}_2 \leftrightarrow \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^-$$

Extreme overcharging to 5.2 V may give CoO$_2$; however, this compound is not stable, see above.

$$\text{LiCoO}_2 \rightarrow \text{CoO}_2 + \text{Li}^+ + e^-$$

The complete charging of LiCoO$_2$ to unstable CoO$_2$ is illustrated in Figure 25.
2.6 \( \text{Li}_2\text{Mn}_3\text{NiO}_8 \) – a spinel type cathode material for Li-ion batteries

The spinel type structure is based on ccp of O-anions. Let us first repeat the simple situation with just filling of one type of interstice (hole). In the rock salt type structure (NaCl-type), the anion forms a ccp, Figure 26 (left). The cations fill 100% of the octahedral holes (note that the cations in this special case also form a ccp). From Figure 26 we note that the small spheres of the cations are positioned in the (111) plane of the cubic unit cell of NaCl. This holds in general. Owing to the identity between ccp and fcc, the (111) planes in the fcc unit cell are identical to the close packed planes in the conventional presentation of the ccp stacking. If 100% of the tetrahedral holes in the ccp are filled (and all octahedral sites remain empty) one obtains the fluorite, \( \text{CaF}_2 \) type structure, Figure 26 right. In this figure the Ca-atoms form the ccp, and F-atoms take tetrahedral holes. Note, \( \text{Na}_2\text{O} \) takes the identical structure, however, now termed anti-fluorite structure since the cation and anions are oppositely distributed with respect to being packing sphere and interstitial atom.

![Figure 26: NaCl-type structure (left); note the close packed layers of cations in the (111) plane (identical for the anions. Right; the \( \text{CaF}_2 \) type structure (or \( \text{Na}_2\text{O} \)).](image)

In the spinel type structure both octahedral and tetrahedral holes are filled in the ccp of O-atoms. The unit cell dimension of the cubic spinel unit cell is around 8.1 Å, which is twice that of the fcc unit cell of the rock salt structure (consider e.g. MgO as example).

If we count the number of atoms in the repeating unit cell of MgO (Figure 26 left) we arrive at \( Z = 4 \), i.e. four formula units MgO per unit cell. When counting atoms, note that

- an atom inside the unit cell counts 1
- an atom at the face of the unit cell counts 1/2
- an atom at the edge of the unit cell counts 1/4
- an atom at the corner of the unit cell counts 1/8
The spinel unit cell contains hence $2 \times 2 \times 2 \times 4$ packing spheres = 32 packing spheres (oxygen atoms). This large cubic unit cell contains 32 octahedral and 64 tetrahedral holes. Just a fraction of these are filled with cations. The normal spinels take the formula $A_tB_o^2O_4$, where $t$ and $o$ denotes tetrahedral and octahedral sites, respectively. The A-atom is always considered as the divalent species, the B-atoms as trivalent. We note that the unit cell has $Z = 8$ for the formula $A_tB_o^2O_4$.

Dependent on the distribution of the di- and trivalent cations with respect to tetrahedral and octahedral sites, one distinguishes between the following three types of spinels:

- Normal spinels $A_tB_o^2O_4$
- Inverse spinels $B'(A^6B^8)O_4$
- Random spinels $(A,B)^t(A,B)^o_2O_4$

Normal spinel structures are cubic close-packed oxides with one octahedral and two tetrahedral sites per formula unit. $B^{3+}$ ions occupy half of the available octahedral holes, while $A^{2+}$ ions occupy one-eighth of the tetrahedral holes. The mineral termed spinel, $\text{MgAl}_2O_4$, has a normal spinel structure.

Inverse spinel structures have a different cation distribution. All A-cations and half of the B-cations occupy now the octahedral sites, while the second half of the B cations occupies the tetrahedral sites. An example of an inverse spinel is $\text{Fe}_3O_4$, with $\text{Fe}^{2+}$ ($A^{2+}$) ions being d$^6$ high-spin and $\text{Fe}^{3+}$ ($B^{3+}$) ions d$^5$ high-spin.

There exist materials with random distribution of the A and B cations over the two interstices; random spinels $(A,B)^t(A,B)^o_2O_4$. In addition, there are intermediate cases where the distribution can be described as $(A_{1-x}B_x)^t[A_{x/2}B_{1-x/2}]^o_2O_4$. The degree of inversion (x) adopts a value between 0 (normal) and 1 (inverse), and is equal to 2/3 for a completely random cation distribution.

In KJM1120 we explained the particular cation distribution in a spinel structure by considering crystal field stabilization energies (CFSE) of the transition metals being present. In these calculations both tetrahedral and octahedral sites are taken into account (remember than $\Delta_{\text{tetrahedron}} \approx 4/9 \Delta_{\text{octahedron}}$). Some ions may have a distinct preference for the octahedral site depending on the d-electron count. If the $A^{2+}$ ions have a strong preference for the octahedral site (i.e. by having a large number of electrons in t$_{2g}$ orbitals and hence a high
CFSE), they will displace half of the B\(^{3+}\) ions from the octahedral sites into tetrahedral sites. Similarly, if the B\(^{3+}\) ions have a low or zero octahedral site stabilization energy, then they will occupy tetrahedral sites, leaving octahedral sites for the A\(^{2+}\) ions.

**Task (repetition): Calculate CFSE for NiFe\(_2\)O\(_4\) and evaluate whether it is a normal or inverse spinel.**

The simple model with CFSE as the main governing factor for the cation distribution is working surprisingly well; however, there are exceptions. For instance, Al\(^{3+}\) cations have a marked preference for octahedral sites and Zn\(^{2+}\) for tetrahedral sites. Since both are d\(^0\) ions, they ought according to the CFSE concept to have no particular preference. It has been proposed that the relative size of the s- and p-orbitals of the two types of involved cations determine the site preference owing to σ-bond interactions between the cations and the oxide anions.

Various spinel structured materials are of interest as cathode material for Li-ion batteries. The first successful reversible Li\(^{+}\) intercalation was achieved for the LiMn\(_2\)O\(_4\) spinel. The theoretical capacities of Li\(_{1-x}\)Mn\(_2\)O\(_4\) and Li\(_{1+x}\)Mn\(_2\)O\(_4\) spinels are limited to 0.5 Li per Mn (~147 mAh/g), however, this is in the range of the practical capacity of LiCoO\(_2\) (~140 mAh/g). The spinels are interesting alternative cathodes, since they are based on inexpensive and environmentally benign elements. The spinel cathode LiMn\(_{1.5}\)Ni\(_{0.5}\)O\(_4\) is derived from LiMn\(_2\)O\(_4\) by substitution, and has gained attention due to higher gravimetric energy density and lower cost compared to LiCoO\(_2\). For LiMn\(_{1.5}\)Ni\(_{0.5}\)O\(_4\), the electrochemically active red-ox couple is Ni\(^{2+/4+}\), leading to a higher potential of ~ 4.7 V versus Li/Li\(^+\). The gravimetric energy density is as high as ~700 Wh/kg.

The LiMn\(_{1.5}\)Ni\(_{0.5}\)O\(_4\) spinel exhibits one more feature when it comes to cation distribution. Dependent on the synthesis conditions, the Mn- and Ni-cations cat be randomly distributed over the octahedral B-substructure, or they can take an ordered distribution. The disordered variant is governed by entropy, and is obtained by high temperature annealings, followed by rapid cooling. The ordered variant is obtained by heat treatments at intermediate temperatures. Completely ordered variants can only be achieved for certain compositions. In the space group \(P4_332\) complete ordering is possible for a Mn : Ni ratio of 3 : 1, i.e. the ratio for the sample in question. The size of the unit cell is unchanged, around \(a = 8.1\ \text{Å}\). However, the most relevant chemical formula for the ordered variant would no longer be LiMn\(_{1.5}\)Ni\(_{0.5}\)O\(_4\).
(which indicates disorder by the non-integer compositions), but rather Li$_2$Mn$_3$NiO$_8$ ($Z = 16$). The differences in the structures are attempted visualized in Figure 27.

The spinel structure is an O-ccp based structure, and Li-ion diffusion will follow the many pathways that connect tetrahedral and octahedral interstices, in all directions of the structure. Hence, Li-conductivity takes place in 3D, however, there are no open channels in any directions which means that activation energies are not as low as desirable for an optimum material. Still, diffusivity does not create major problems. The spinel materials tend to remain crystalline after charge/discharge. This can be understood on the basis of the O-packing substructure with (Mn,Ni) atoms in octahedral holes.

![Figure 27: Li$_2$Mn$_3$NiO$_8$ (left; ordered) and LiMn$_{1.5}$Ni$_{0.5}$O$_4$ (right, disordered). Green atoms oxygen packing spheres, small red spheres lithium, whereas multicolored intermediately sized spheres are Mn/Ni randomly mixed (right), while grey atoms with orange circle represents the ordered distribution of Ni-atoms.](image)

2.7 Perovskites and BaZrO$_3$ as proton conductor

BaZrO$_3$ takes the perovskite type structure, a structure type taken by a large number of technologically interesting compounds. It occurs in many variants, from simple structural distortions of the ideal cubic atomic arrangement, to modified compositions (oxygen vacancies; ordered or disordered), intergrowth with other structure elements to form more complicated crystal structures (e.g. intergrowth with a thin slab of NaCl-type structure to generate the class of Ruddlesden-Popper type oxides), etc.

The ABO$_3$ perovskite type crystal structure can easily be described according to both the sphere packing model and coordination polyhedra, see below. The ideal compositions can be fulfilled by various combinations of cation oxidation states for A and B. The following combinations are common
- A(I) and B(V); example NaNbO$_3$
- A(II) and B(IV); example CaTiO$_3$
- A(III) and B(III); example LaCrO$_3$

There are size restrictions on the relative sizes between the larger A-cations and the smaller B-cations. The ideal cubic-symmetry structure has the B cation in 6-fold coordination, surrounded by an octahedron of anions, and the A cation is in 12-fold cuboctahedral coordination. The relative ion size requirements for stability of the cubic structure are quite strict. A slight buckling and distortion of the structure can produce several lower-symmetry variants, in which the coordination numbers of the A cations, (or the B cations or both) are lowered. The Goldschmidt tolerance factor ($t$) is a dimensionless number that is calculated from the ratio of the ionic radii; here $r_A$ is the radius of the A-cation; $r_B$ is the radius of the B-cation, and $r_0$ is the radius of the anion (in our case oxygen). The $t$-factor is given as

$$t = \frac{r_A + r_0}{\sqrt{2}(r_B + r_0)}$$

The $t$-factor ought to be > 0.71 for the perovskite type structure to be stable. For values of $t$ between 0.71 and 0.9, the symmetry is typically rhombohedral or orthorombic (i.e. deformed with respect to the perfect cubic structure), whereas for $t > 0.9$ the structure is normally cubic. Outside the 0.71 - 1.00 stability window for the perovskite type structure, other ABO$_3$ structure types will form for the candidate compounds. For $t < 0.7$, the ABO$_3$ ilmenite type structure is typically formed (e.g. FeTiO$_3$), whereas for $t > 1$ chain like structures may form as in the case of BaNiO$_3$.

Figure 28: The (cubic) perovskite type unit cell; left: A atom at origin; middle: B-atom at origin; right tilted octahedra thereby modifying the O-surrounding for the large (blue) A-atom.

Task: use the extended version of formula 1.2. and calculate the coordination number for the large A cation when knowing that the structure is built of 3D net of corner shared BO$_6$ octahedra and that the O-atoms bond to 2 B-atoms and 4 A-atoms.
We consider now the perovskite unit cell. In the idealized cubic unit cell of such an ABO$_3$ compound, the A-atom sits at cube corner positions (0, 0, 0), the B atom sits at a body centred position (1/2, 1/2, 1/2) and oxygen atoms sit at face centred positions (1/2, 1/2, 0), see Figure 28 (left). However, frequently the origin is shifted so that (0,0,0) corresponds to the position of the B-cation in the center of the BO$_6$-octahedron, Figure 28 middle. In that case the coordinates are: A in (1/2,1/2,1/2), B in (0,0,0) and oxygen in (1/2,0,0), (0,1/2,0), (0,0,1/2).

Let us consider the second choice of origin and draw projections of the structure, Figure 29.

![Figure 29: The perovskite type structure in the ab-plane for values z = 0.00 (left) and 0.50 (right)](image)

In the cubic structure, $a = b = c$ with respect to length of the unit cell axes (dimensions). From Figure 29 we see that $a = 2r_B + 2r_O$ under the assumption of ionic bonding and cation and anion spheres in physical contact. From Figure 29 (right), we note that the diagonal $a\sqrt{2} = 2r_A + 2r_O$. Combining these two expressions for $a$, we obtain $2r_B + 2r_O = (2r_A + 2r_O)/\sqrt{2}$. We see immediately the connection to Goldschmidt's t-factor; $t = (2r_A + 2r_O)/(\sqrt{2}(2r_B + 2r_O))$. So when $t = 1$, the relative size of all atoms fits perfectly a model of rigid spheres in contact and with cubic symmetry. Any larger size-mismatch will lead to structural deformations. If for instance the A atom is too small, it is undersized, the octahedra will tilt in order to reduce the void of the A-site, Figure 28 (right). Such tilting of the BO$_6$ octahedra can reduce the coordination number of an undersized A cation from 12 to as low as 8. If the B atom is too small, it will not fill entirely the octahedral hole in the ccp of O-atoms. Such a situation is not stable, and hence off-centering of an undersized B cation within its octahedron allows it to attain a stable bonding pattern. Such off-centering is for instance a mechanism for piezoelectricity in BaTiO$_3$. 
The perovskite type structure can be derived from sphere packing models. The way forward is as follows; A and O spheres form a 2D-layer described by the unit cell \(a = b; \gamma = 120^\circ\), with A in \((0,0)\) and O in \((0,1/2), (1/2,0), (1/2,1/2)\). Such layers are then stacked (along the \(c\)-axis of this hexagonal cell; [001]), however, in such a way that any A sphere is situated in the cavity between three O-spheres, see Figure 30. For the perovskite type structure, such layers follow an **ABC** stacking sequence.

**Figure 30:** 2D-model of \(\text{AO}_3\)-layers in ccp packing that provides basis for the perovskite type structure. Suitable octahedral hole is shown in middle. ccp of \(\text{AO}_3\) shown for the perovskite unit cell.

Since this is a ccp stacking of \(\text{AO}_3\) layers, we should be able to recognize these ccp layers in the cubic unit cell of the perovskite, Figure 30. We know from earlier that in the fcc description (which corresponds to our unit cell; though we do not have all identical spheres since we have one A-atom and 3 O-atoms in the unit cell; rather than 4 of the same type for an ideal fcc) the ccp layers are forming the \(\{111\}\) planes; actually \(\{111\}\).

The perovskite structure is more frequently described on the basis on coordination polyhedra, and then with emphasis on the connectivity of octahedra. As shown in Figure 28 the \(\text{MO}_6\) octahedra share common vertices along the \(\mathbf{a}, \mathbf{b}, \mathbf{c}\)-directions. A structure that consists solely of vertex shared \(\text{MO}_6\) octahedra will have bulk composition \(\text{MO}_3\). Such a structure does exist. An example is \(\text{ReO}_3\). The perovskite type structure is hence related to the \(\text{ReO}_3\) type by having large cations occupying the large void between eight octahedra; consider Figure 28 in this respect.

Since the octahedra share vertices, the \(\text{O} - \text{M} - \text{O}\) bond angle will ideally be \(180^\circ\). This has important consequences on magnetism and electronic conductivity. Ferromagnetism, antiferromagnetism, high Tc-superconductivity, colossal magnetoresistance, etc may occur in perovskite related oxides. This represents a large research topic in itself and will not be
covered in more detail in this course. Let us just add that the interesting compounds typically contain 3d-elements. In KJM1120 we learned how the local electric field of ligands does split d-orbitals with consequences on magnetism (unpaired electrons; low- versus high-spin) and optical properties (color; electron excitations). Certain $d^n$ electron configurations gave rise to Jahn Teller deformations (singly occupied $e_g$ orbitals; $d^4$ HS, $d^7$ LS, $d^9$), whereas $d^8$ could stabilize either paramagnetic octahedral coordination or diamagnetic square planar configurations. All these types of features are actually coming into play also in perovskite related oxides, and are responsible for many exotic features.

Before turning to BaZrO$_3$, an excellent material for proton conductivity, we will discuss some other aspects of chemical modification and defects. The physical properties of perovskites are frequently modified by incorporating homovalent or heterovalent substitutents on the A-site. The usual response of the material in question is to adjust the oxidation state of the B-cation which normally is redox active. If for instance Sr(II) is substituted for La(III) in LaFeO$_3$, the following solid solution is formed:

$$La_{(1-x)}Sr_xFe^{III+x}O_3 \text{ or } La_{(1-x)}Sr_xFe(III)_{1-x}Fe(IV)_xO_3$$

Since the substituted phase now contains iron in a higher oxidation state it appears reasonable that it could be possible to reduce iron back into Fe(III), however, that will at the same time imply formation of oxygen vacancies in order to keep charge neutrality:

$$La_{(1-x)}Sr_xFe(III)_{1-x}Fe(IV)_xO_3(s) \rightarrow La_{(1-x)}Sr_xFe(III)O_3-x/2(s) + x/2 \text{ O}_2(g) \quad \text{Equation 3}$$

The latter situation is an example of oxygen-nonstoichiometry. The concentration of oxygen vacancies can vary a lot. In some compounds it is close to zero, in others the oxygen composition can be as low as 2.70 compared with 3.00 for the perfect situation. Actually even larger vacancy concentrations are known. In such oxides with mixed oxidation state (mixed valence) of the transition metal, one expects and observes quite good electronic conductivity (good semiconductor, metal). At the same time there are available vacancies (sites) to which an oxygen atom may jump into – from filled oxygen sites. Hence, vacancies can promote oxygen diffusion (ion transport). Certain perovskite type oxides are hence good electrode and electrolyte materials for use in solid oxide fuel cells, catalysis, etc.

The thermodynamics of oxygen stoichiometry can be considered on the basis of Equation 3, noting that the equilibrium will depend on oxygen partial pressure as well on temperature. In
a first approximation Equation 3 corresponds to the stability conditions discussed in Ellingham diagrams in KJM1120.

BaZrO₃ is an excellent material for proton conductivity. Considering the involved elements, Ba(II), Zr(IV) and O(-II), it is quite obvious that BaZrO₃ is an insulator or a wide band gap semiconductor. Heterovalent substitutions appear possible. But introducing A(III) on Ba(II) site (donor doping) is not likely since it must be charge balanced by reduction of Zr(IV) to Zr(III), which we know from basic chemistry is hard to achieve. On the other hand, acceptor doing is possible, either by introducing M(I) on the A(II) site, or by introducing a trivalent substituent on the Zr(IV) site. However, introduction of M(I) is synthetically difficult owing to the high vapor pressure of the M₂O compounds. Y-doped BaZrO₃ (BYZ) has been widely used as a proton conducting electrolyte in protonic ceramic fuel cells (PCFC) due to its advantages in terms of high bulk proton conductivity and high chemical stability in fuel cell atmosphere. By introducing Y(III) on Zr(IV) site, an oxide vacancy is created according to the defect reaction in Equation 4

\[ \text{Y}_2\text{O}_3 \rightarrow 2\text{Y}^{\text{Zr}} + \text{V}^{\text{O}} + 3\text{O}^{\text{X}} \]  

Equation 4

This is read in the following way: two Y(III) are introduced on Zr(IV) site which formally is then negatively charged Y$^{\text{Zr}}$; one vacancy is formed on an O-site and is doubly positively charged and three neutral oxygen atoms are added to the crystallites at O-sites. The nomenclature used is termed Kröger-Vink defect chemistry notation. Protons are added to the material in a next step, by treating the sample in humid atmosphere. Thereby O-atoms from the H₂O molecules fill the vacant O-sites, whereas protons are dissolved in the structure by being affiliated with O-atoms forming OH-groups. This is written as:

\[ \text{H}_2\text{O}(g) + \text{V}^{\text{O}} + \text{O}^{\text{X}} \rightarrow 2\text{OH}_0 \]  

Equation 5

The conductivity of BYZ will be dominated by the protons. The electronic conductivity is negligible. Note, the proton conductivity is a result of an intended heterovalent acceptor doping. In order to be successful it is required that the intended substitution really occurs. That means, characterization must be carried out that proves that the yttrium has been dissolved into barium zirconate, instead of being precipitated as an impurity phase in the sample specimen. The proton mobility is temperature dependent, again ruled by activation energies and concentration of mobile species. The concentration depends on the doping level
(amount of heterovalent substituent and water incorporation subsequently), the mobility depends on the strength of the O – H bonding and is material and structure specific.

Explanation of Kröger-Vink symbols:

\[
\begin{align*}
\text{Al}^{\text{Al}}_\text{Al} & = \text{an aluminum atom sitting on an aluminum site, with neutral charge.} \\
\text{Ni}^{\text{Cu}}_\text{Cu} & = \text{a nickel atom sitting on a copper site, with neutral charge.} \\
\text{V}^{\text{Cl}}_\text{Cl} & = \text{a vacancy at a chlorine site, with singular positive charge.} \\
\text{Ca}^{\text{Ca}}_i & = \text{a calcium interstitial ion, with double positive charge.} \\
\text{O}^{\text{O}}_j & = \text{an oxygen anion on an interstitial site, with double negative charge.} \\
\text{e} & = \text{an electron. No site is specified.}
\end{align*}
\]

2.8 ZrO₂, YSZ and oxygen ion conductors

Zirconia, ZrO₂, takes a deformed structure at room temperature. We are here, however, interested in one high-temperature polymorph; cubic zirconia which is stable above 2370°C. An interesting aspect is that this cubic structure can be stabilized to room temperature by introducing yttrium at the Zr-sites, making so-called yttrium stabilized zirconia YSZ.

The cubic structure is of the fluorite type, CaF₂-type. In this structure the cations form (formally) a ccp substructure, and anions fill 100% of the tetrahedral voids. The fcc setting of the unit cell is shown in Figure 31 (right); a projection is shown in Figure 31 (left). The Ca₄F tetrahedra are evident from Figures 31 and 32. We can use the relationship described above to calculate that calcium will be eight-coordinated, given that CaF₂ is a regular structure without F-F and Ca-Ca bonding. The coordination polyhedra are CaF₈-cubes as shown in Figure 32. Interestingly, the CaF₂ can be described on the basis of tetrahedra sharing edges and equally on the basis of cubes sharing vertices, Figure 32. Importantly, in Figure 32 empty and filled cubes [CaF₈-cubes and F₈-cubes] alternate in the a- and b-directions, and actually also along the c-direction. When we analyse the surroundings of the Ca-atoms in even more detail it becomes clear that the center position of the empty cubes has six rather close calcium neighbour atoms; hence the coordination of the central spot of the empty cubes can be described as Ca₆F₈. Therefore this empty site is indeed the octahedral site of the ccp packing of Ca-atoms.
In YSZ, with some 4-8 atomic % of the Zr-atoms are replaced by yttrium cations. This stabilization of the cubic polymorph of zirconia over wider range of temperatures is caused by better size matching of the involved anions and cations. The Zr\(^{4+}\) ions (ionic radius 0.82 Å) are too small to fit into the ideal fluorite structure, and hence deformations of the structure
occurs (symmetry lowering to tetragonal and monoclinic, and also shift in atomic coordinates). A better fit for the crystal structure is achieved for slightly larger ions, e.g., those of $Y^{3+}$ (ionic radius of 0.96 Å). In addition the introduction of Y(III) for Zr(IV) needs to the charge balanced. In principle there are two options; introduction of interstitial cations (into the empty Ca$_6$F$_8$ interstices); or random anion vacancies. The latter situation is realized.

The CaF$_2$-type structure is also taken by the compound PbF$_2$. Lead as a group 16 element can take oxidation states +II and +IV (cf. the oxides PbO, PbO$_2$ and the mixed valence oxide Pb$_3$O$_4$). Interestingly, it is possible partly to oxidize PbF$_2$, making PbF$_{2+x}$. The latter compound is an excellent fluoride ion conductor. How can that be understood? The additional fluroide anions (concentration $x$) occupy the Ca$_6$F$_8$ interstices, and from Figure 32 we realize a possibility that fluoride ions can move by jumping from filled into empty boxes and so onwards.

YSZ is a good oxygen ion conductor, of use in technology for oxygen permeable membranes and electrolytes, e.g. in solid oxide fuel cells. The oxygen vacancies along with the available Zr$_6$O$_8$ interstitial sites permit YSZ to conduct O$_{2^-}$ ions and thereby conduct an electrical current by means of ions. The conductivity depends on the oxygen ion/vacancy site mobility, which increases with increasing temperature. The ionic conductivity of YSZ increases with increasing concentration of the lower-valent substituent (Ca, Y,...), first quite linearly at low substituent concentrations, then saturating, before starting to decrease. Maximum conductivity is obtained when some 8% Y$_2$O$_3$ is substituted into ZrO$_2$.

### 2.9 Li$_x$C and carbon based anode materials; graphene

Graphite is a layered material. Figure 33 shows a larger selection of layered compounds. The chemical bonding is strong within the layers (polar covalent), but weak between layers; normally just dispersion forces (van der Waals forces), in some case the bonding is substantial yet weaker than in the layers. This is the case for the double hydroxides in Figure 33 where the layers are bonded along the stacking direction by means of hydrogen bonding and coulomb interactions. In some cases a structure is describes as layered since that is apparent from the drawing of the crystal structure. This is the case for the perovskite related materials in Figure 33 (Ruddlesden Popper and Dion Jacobsen oxides), however, the structure contains two different structural fragments, and the bonding in the thinner slab is not drastically weaker than inside the perovskite blocks.
Graphite consists of 2D sheets of hexagons, see Figure 34 (middle). In these layers carbon use three of its valence electrons (C s^2p^2) in sp^2 hybridized orbitals giving 120° angles between C-atoms. The fourth electron (p_z) give rise to delocalized π-orbitals perpendicular to the plane of the carbon atoms. The layers are displaced along the c-axis (stacking direction), see the guiding fully drawn lines in Figure 34 (left). The ideal 2D sheet is shown schematically in Figure 34 (middle).

The physical properties of graphite can be understood on the basis of the atomic arrangement and electron structure. First, there is weak bonding between the layers while strong bonds within the layers. Therefore mechanical properties are highly anisotropic and carbon sheets can easily slide with respect to each other thereby making graphite an excellent solid lubricant.
Second, the delocalized \( \pi \)-electrons give rise to good in-plane electronic conductivity. The conductivity is poor in the c-direction [001]. The material we have described so far is perfect graphite. In reality graphitic carbon contains some impurities which can occupy positions between the sheets, and thereby make the layers poorly oriented with respect to each other.

In recent years graphene has attracted focus. Graphene consists of just one single layer of graphite. Technically seen, graphene can be considered a crystalline allotrope of carbon with 2-dimensional properties. Graphene is the basic structural element of other allotropes and carbon materials, including graphite, charcoal, carbon nanotubes and fullerenes. Graphene can be considered as an indefinitely large aromatic molecule, the limiting case of the family of flat polycyclic aromatic hydrocarbons.

A related material is graphite oxide (GO), earlier termed graphitic oxide or graphitic acid. GO is obtained by treating graphite with strong oxidizers. The oxidized bulk product is a yellow solid with C : O ratio between 2.1 and 2.9, that retains the layer structure of graphite but with a much larger interlayer spacing (and with irregularly stacked layers). Graphite oxide is an insulator. Bulk GO disperses in basic solutions to yield monomolecular sheets, known as graphene oxide. These layers are about 1.1 ± 0.2 nm thick. The structure and properties of graphite oxide depend on the applied synthesis method and the degree of oxidation. Strictly speaking "oxide" is an incorrect name. Besides oxygen epoxide groups (bridging oxygen atoms), other functional groups experimentally found are: carbonyl (C=O), hydroxyl (-OH), and phenol. Graphite oxide is hydrophilic and is easily hydrated when exposed to water.

The p-orbitals of graphite are half occupied. This gives graphite the option to act as an electron donor (\( \pi \) electrons) or as an electron acceptor (filling empty states in the \( \pi \)-orbitals). Such types of derivative materials are prepared by treating graphite with a strong oxidant or a strong reducing agent:

\[
\text{C + m } X \rightarrow \text{CX}_m
\]

Equation 6

Graphite is here acting as host and the X reactant is termed guest. This reaction is reversible and involves charge transfer. We will look more into such processes in connection with Li-ion batteries where graphite is used as anode (the negative material).

During the intercalation reaction, the guest species enters inbetween graphene layers, however, not necessarily between every layer. Staging may occur; i.e. there are distinct phases
with a specific sequence of layers and intercalates. In the so-called stage-1 compounds, empty and intercalated layers alternate, see Figure 35. In stage-2 compounds two layers of graphite structure alternate with one intercalated layer, Figure 35. Intermediate situations can occur in a given material; parts of the material may be of stage-1 type, other parts of stage-2 type. This may even occur with one and same crystallite that has a large number of graphite layers along the stacking direction. In this way the stoichiometry becomes variable. However, the properties are typically analysed in terms of the well-defined stage-1 or stage-2 situations. Even higher stagings are possible. During the intercalation, the layers are pushed apart and the intercalated species is chemically bonded to the graphene layers.

The well-defined stage-1 and stage-2 structures can be identified by their chemical compositions. In the case of reduction of graphite by potassium, stage-1 and stage-2 materials are formed. Their arrangements are shown in Figure 35. Potassium provides one electron to the half-filled π-orbitals of 8 or 16 carbon atoms in graphite. The resultant material shows increased electronic conductivity.

![Graphite and intercalated potassium products](image)

**Figure 35:** Structure of graphite and stage-1 and stage-2 intercalated potassium products.

Natural graphite can be reduced electrochemically upon Li-insertion between the layers. The interlayer distance increases from 3.35 Å for graphite to 3.70 Å for stage-1 LiC₆ (golden yellow in color). A number of higher stage compounds have been reported; LiC₁₂ (7.06 Å / 2 = 3.53 Å), stage-3 LiC₂₇ (10.4 Å/3 = 3.46 Å), stage-4 LiC₃₆ (13.8 Å/4 = 3.45 Å). Graphite is today the most common anode material in Li-ion batteries, and is attractive due to low cost and good energy density. The charging rate is governed by the shape of the thin graphene sheets. While charging, the lithium ions must travel to the outer edges of the graphene sheet before coming to rest (intercalating) between the sheets.
2.10 YBa$_2$Cu$_3$O$_7$ as an example of superconducting high Tc cuprates

The high temperature YBa$_2$Cu$_3$O$_7$ superconductor (YBCO) was first time synthesized in 1987. Its crystal structure is related to the perovskite type structure discussed above. During the following years a number of Cu-based high-Tc superconductors were synthesized and characterized. Today the highest known Tc is 133 K (confirmed by multiple independent research groups for mercury barium calcium copper oxide HgBa$_2$Ca$_2$Cu$_3$O$_8$), compared with 93 K for YBCO. We will here consider the YBCO structure in more detail, and focus on common structural denominators for cuprate based high-Tc oxides, and discuss the possibility to tune electronic properties via heterovalent substitutions. The YBCO unit cell consists of three perovskite-type cells stacked on top of each other along the c-direction [001], see Figure 36.

![Figure 36: Unit cell of YBa$_2$Cu$_3$O$_7$ with positioning of the atoms (left); coordination polyhedra around Cu-atoms indicated (right).](image)

YBCO represents an ordered superstucture of the simple perovskite type; the relationship to the perovskite is evident from Figure 36 and from the rewritten formula of YBCO: ABO$_{3-\delta}$ = (Y$_{0.33}$Ba$_{0.67}$)CuO$_{3-0.67}$. The superstructure is caused by: i) ordered distribution of Y and two Ba atoms; ii) oxygen vacancies in the center of the YBCO unit cell (at z = ½) and in the basal plane (1/2,0,0). These O-vacancies have consequences on the Cu-coordination polyhedra; they are no longer octahedra, and one notices two types of copper atoms; Cu1 in square planar coordination forming chains along the b-axis [010]; Cu2 in square pyramidal coordination forming two sets of 2D-planes in the unit cell, Figure 36 (right). Presence of O-vacancies reduces the coordination number for the A-cations (Y and Ba). From Figure 36, we see that yttrium is 8-coordinated (cube), whereas barium is 10-coordinated.
YBCO is fully oxidized at the YBa$_2$Cu$_3$O$_7$ composition. The average oxidation state for copper is 2.33. One may ask whether one of the non-equivalent Cu-atoms have a higher oxidation state, and the second a lower oxidation state. In this case the concept of bond valence can be adopted. An estimate is then made based on the Cu-O interatomic distances according to a parameterized equation; however, for YBa$_2$Cu$_3$O$_7$ the differences between the two Cu-sites are negligible. The coordination polyhedra of copper, square pyramids and square planar, are fully consistent with our expectations for d$^9$ [Cu(II)] or d$^8$ [Cu(III)] ions.

As evident from the formula (Y$_{0.33}$Ba$_{0.67}$)CuO$_{3-0.67}$ there are oxygen vacancies connected with the O-substructure. In the case of YBCO these vacancies are ordered. The YBCO structure does never have any O-atoms in the positions described as vacancies. In a sense they are not defect sites (vacancies) that could be occupied; they are always empty and that is an integrated part of the crystal structure. Such vacancies are termed structural vacancies, in contrast to vacancies form by the earlier mentioned defect processes governed by thermodynamics. Copper is in a high oxidation state in YBCO. Normally we do have Cu(I) and Cu(II) compounds; Cu(III) only occurs in connection with highly electropositive elements (group 1 and 2). Hence, one may ask whether YBCO can be reduced by removing some O-atoms from some of the O-sites. This is indeed possible, with YBa$_2$Cu$_3$O$_6$ being the limiting composition. So, where are the new (and real) vacancies located; how does the Cu-coordination polyhedra change; and what happens with the electronic properties (superconductivity)? In YBa$_2$Cu$_3$O$_6$ the average Cu-oxidation state is 1.67. This stoichiometry is consistent with the formal description YBa$_2$Cu(I)Cu(II)$_2$O$_6$.

![Diagram of YBa$_2$Cu$_3$O$_7$ and YBa$_2$Cu$_3$O$_6$](image)

Figure 37: Comparison of superconducting YBa$_2$Cu$_3$O$_7$ (left) and metallic YBa$_2$Cu$_3$O$_6$ (right).
From Figure 37 (right) we notice that O-atoms are systematically removed from the (0,1/2,0) site, thereby breaking the connectivity of chains of connected square planar CuO$_4$ units along [010], Figure 36 (right). Instead we obtain a number of linear O-Cu-O units along [001]. Theoretical calculations show that the density of states (DOS; electronic structure) at the pyramidal coordiated Cu2-site is not substantially modified on turning to the reduced phase. However, the loss of the CuO$_4$-connected chain and the appearance of linear O-Cu1-O entities typically of Cu(I) induces a major change in the electronic structure for those Cu1-atoms in the structure, and the DOS is vanishingly small at the Fermi level. On this basis one conclude that the oxidation state as well as the CuO$_4$-chains plays a major role for the appearance of superconductivity in YBCO.

There are some common structural motifs in high-Tc cuprates. The Cu-planes are believed to be responsible for the superconductivity and are given special attention. The CuO$_4$-chains are on the other hand non-conducting. The more layers of “CuO$_2$” the higher the $T_c$. The layered structure causes a large anisotropy in normal conducting and in superconducting properties. The electrical currents are carried by holes induced in the oxygen sites of the CuO$_2$ sheets. The conduction is much higher parallel to the CuO$_2$ planes than in the perpendicular direction.

![Figure 38. Critical temperature $T_c$ for various inorganic compounds in a historical perspective.](image)

<table>
<thead>
<tr>
<th>Formula</th>
<th>Notation</th>
<th>$T_c$ (K)</th>
<th>Nb. of Cu-O planes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_6$</td>
<td>Bi-2223</td>
<td>110</td>
<td>3</td>
</tr>
<tr>
<td>Bi$_2$Sr$_2$CaCu$_2$O$_8$</td>
<td>Bi-2212</td>
<td>85</td>
<td>2</td>
</tr>
<tr>
<td>Bi$_2$Sr$_2$CuO$_6$</td>
<td>Bi-2201</td>
<td>20</td>
<td>1</td>
</tr>
<tr>
<td>HgBa$_2$Ca$_2$Cu$_3$O$_8$</td>
<td>Hg-1223</td>
<td>134</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 6. High-Tc cuprates with chemical formula, short hand notation, $T_c$ and number of conducting Cu-O planes.
There exists a nomenclature for the complex structures of the cuprates. This is as follows: $M^{abcd}$, where $M$ is the atom situated in the insulating layers between the conducting blocks, and $(a)$ denotes the number of layers in this insulating block. The second $(b)$ represents the number of spacing layers between identical CuO$_2$ blocks. The third $(c)$ gives the number of layers that separate adjacent CuO$_2$ planes within the conducting block. And, the fourth $(d)$ is the number of CuO$_2$ planes within a conducting block.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Symbol</th>
<th>$a$</th>
<th>$b$</th>
<th>$c$</th>
<th>$d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HgBa$_2$CaCu$_2$O$_6$</td>
<td>Hg-1212</td>
<td>128</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HgBa$_2$CuO$_4$</td>
<td>Hg-1201</td>
<td>94</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tl$_2$Ba$_2$Ca$_2$Cu$<em>3$O$</em>{10}$</td>
<td>Tl-2223</td>
<td>125</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tl$_2$Ba$_2$CaCu$_2$O$_8$</td>
<td>Tl-2212</td>
<td>108</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tl$_2$Ba$_2$CuO$_6$</td>
<td>Tl-2201</td>
<td>80</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TlBa$_2$Ca$_3$Cu$<em>4$O$</em>{11}$</td>
<td>Tl-1234</td>
<td>122</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>YBa$_2$Cu$_3$O$_7$</td>
<td>123</td>
<td>92</td>
<td>2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 39:** Bi$_2$Sr$_2$CaCu$_2$O$_8$ crystal structure and explanations for the short hand notation Bi-2212.

An example is given in Figure 39. As seen, the involved cations are Bi, Sr, Ca and Cu; Bi is the key cation of the insulating layer; there is a double Bi-O layer in the insulating block; there are two layers between the apical O-of the CuO$_5$ pyramide in the Cu-O layers; there is one layer of Ca atoms between the CuO$_2$-planes; there are two CuO$_2$ planes in the conducting
unit. On this basis the short hand notation for the compound will be Bi-2212. Table 6 includes some important high-Tc cuprates and lists chemical formula, short hand notation, Tc and number of conducting Cu-O planes. Figure 38 shows critical temperature Tc for various inorganic compounds in a historical perspective.

In most cuprates, the interactions are so powerful that the Fermi level is situated in band of O-character (one may speak of O\(^-\) rather than Cu\(^{3+}\); i.e. putting the last charge on oxygen rather than on copper) and the charge carriers are holes. When the number of oxygen ions in the crystal structure or the nature of the other atoms (their oxidation state; note fixed charges for alkaline earth, rare earth elements of +2 and +3) is changed, the number of holes in CuO\(_2\) layers is modified. This change in number of additional holes is termed “doping”. The effect of doping is quite universal for all cuprates. Above 0.05 additional holes by copper atom, the material stops being insulating and antiferromagnetic and rather becomes superconducting. Above Tc the oxides behave as a metal, in the sense that the resistivity decreases with decreasing temperature. On increasing doping level, T\(_c\) increases up to an optimal value at a doping level of 0.2 for the so-called “underdoped” phase, and thereafter it decreases for the “overdoped” phase. A schematic phase diagram is shown in Figure 40.

![Figure 40 - Schematic phase diagram showing how antiferromagnetic ground state can switch into a superconducting ground state at low temperatures upon increasing the doping level of holes.](image)

2.11 fcc/ccp, hcp, bcc alloys; examples connected with hydrogen storage and steel

The three important crystal structures for metals; hcp, ccp and bcc, have already been discussed above. We will here focus on a few important aspects:
- Mechanical properties related to close packing of metal atoms
- Filling up of interstitial sites by small atoms (H, B, C, N)
- Ordered variants, intermetallic compounds

The mechanical properties of metals are related to the number of close packed planes and close packed directions in their crystal structures. The more close packed planes, the more ductile is the material. These properties represent actually the genuine properties of the pure metals. Certain (impurity, alloying) mechanisms are responsible for brittleness and hardening observed in various cases.

In the ccp there are 4 identical planes (by symmetry) with closest packing of atoms; i.e. the family of (111) planes, termed \(\{111\}\). In each of the cp-layers there are 3 close packed directions, Figure 41. In bcc there are no closest packed planes, but 4 close packed directions.

![Figure 41: Close packed directions within a 2D plane of closest packed metal atoms.](image)

In the hcp structure, the stacking sequence is ABAB... with tetrahedral and octahedral voids (interstices) as indicated, Figure 42.

![Figure 42: AB... (hcp) stacked layers of close packed spheres. Positions of tetrahedral and octahedral voids (interstices) are indicated.](image)
Above we discussed interstices in hcp and ccp layers of spheres (metal atoms). From size considerations we know that smaller atoms may enter into the tetrahedral sites, whereas somewhat larger atoms prefer octahedral interstices ($r_{\text{interstitial}}/r_{\text{packing}} > 0.414$). Small atoms like H, B, C and N may donate/accept electrons to the delocalized electrons of the relevant metal. The amounts of absorbed interstitial atoms can be low, below 0.1% or much higher – even up to 10% or more. These phases are termed interstitial hydrides (interstitial metal hydrides) and similarly for B, C and N. In these phases, the small interstitial atoms are randomly distributed over a larger number of possible sites (note there is as much a 1 octahedral and 2 tetrahedral holes per packing sphere). Examples of some important intermetallic hydrides are given in Figure 43, right panel.

Figure 43: Schematic process of hydrogen incorporation into a metal under first formation of an interstitial metal hydride phase $\alpha$ and thereafter a metal hydride phase with some variation in M/H stoichiometry. Right panel: some important intermetallic hydrides and their structure types.

At higher H, B, C, N-contents, distinct phases are formed with an atomic arrangement either similar or quite different from the interstitial phase. In Figure 43 this is indicated by the metal hydride phase $\text{MH}_n$. In some cases $n$ is a fixed number (1, 2, 3 typically; e.g. NaH, MgH$_2$, YH$_3$), in other cases it spans a certain compositional interval (i.e. the phase has a homogeniety region). In Figure 43 the equilibrium pressure $p(\text{H}_2)$ is shown on the vertical axis. This pressure varies with the composition of the interstitial metal hydride or the metal hydride phase as indicated within the blue regions of Figure 43. In the intermediate region, the equilibrium pressure is defined by the two-phase mixture of $\alpha$ and $\beta$ ($\text{MH}_n$) – note the pressure is fixed for a two-phase mixture at equilibrium:

$$\text{MH}_n \rightarrow \text{MH}_\alpha + (n-x)/2\text{H}_2(\text{g}) \quad \text{Equation 7}$$
\[ K_t = \frac{[\text{MH}_x(s)]pH_2^{(n-x)/2}}{[\text{MH}_n(s)]} = pH_2^{(n-x)/2} \]

Figure 44: PCT diagram for hypothetical MH\(_x\) system (left). Van’t Hoff plot (left) along with van’t Hoff equation relating equilibrium pressure and enthalpy and entropy.

The pressure – composition situations depicted in Figures 43 are temperature dependent. Hence we can construct a P, C, T (pressure – composition - temperature) diagram as shown in Figure 44. For such a system, hydrogen will be released at ambient pressure for temperatures where \( P_{eq} > 1 \) bar.

Absorption and desorption of hydrogen are key aspects when developing a metal that can act as solid reservoir for hydrogen (hydrogen storage). Other key parameters are gravimetric density, reversibility, costs. Volumetric density is normally no issue for the dense metal hydrides. Absorption of hydrogen is exothermic, desorption endothermic. The latter provides additional security to a solid hydrogen storage system – heating up will be counteracted by endothermic H\(_2\)-release.

The absorption reaction between hydrogen gas and the pure metal involves more steps:

- Hydrogen splitting \( H_2 = 2H; \) 218 kJ/mole H
- Physisorption of hydrogen on the metal surface; -10 kJ/mole H
- Chemisorption of hydrogen on the metal surface; -50 kJ/mole H
- Absorption (migration) of hydrogen into interstices of the metal structure

The formation energies of the hydrides vary strongly; formation of some are highly favored, while other imagined MH\(_n\) compounds are not stable at standard conditions, Figure 45. Based on the affinity to form stable hydride phases, the elements of the periodic table are conveniently divided into two groups, one of which is termed hydride forming elements. These are required components for an alloy capable to store significant amounts of hydrogen.
Addition of elements from the second category (non-forming hydride elements) will destabilize the metal hydride. This represents a means to tune the PCT behavior of an alloy to fit technological windows for applications.

![Figure 45: Schematics of reaction between gas phase hydrogen and metal surface (right). Energies of formation at 273 K for some binary hydrides (left).](image)

The best metallic materials for solid state storage of hydrogen are two- or three component alloys, some having a random distribution of the metallic elements in the crystal structure, some taking a well-defined ordered (intermetallic) crystal structure. We will briefly consider two metal hydrides of practical interest.

The first example is bcc based alloys. They have intrinsically a large hydrogen storage capacity, examples being Ti-V-Mn, Ti-V-Cr and Ti-Cr-(Mo, Ru) that can store up to 3.0 wt% hydrogen. These hydrides are very stable, with their first plateau in the pressure-temperature isotherms far below atmospheric pressure at 295 K. Hence, efforts are required to raise the equilibrium pressure. This can be done by alloying with an element that does not form very stable hydrides. Interestingly, the crystal structure changes from bcc to fcc or pseudo-fcc structures upon hydrogenation.

Socaled AB$_2$ intermetallic compounds are good candidates as hydrogen storage materials; in particular compounds of the cubic C15 Laves type (Cu$_2$Mg type structure, space group $Fd-3m$) or the hexagonal C14 Laves type (MgZn$_2$ type structure, space group $P6_3/mmc$). These are based on strong hydride-forming elements A (e.g. Ti, Zr, Hf) along with weaker hydride forming elements B (V, Mn, Cr, Fe, Co, Ni,….). In the cubic Cu$_2$Mg type structure one can identify three possible interstitial sites for hydrogen absorption, Figure 46. These are all tetrahedral, but with different local surroundings; one has 4B, another has 1A3B and the last have 2A2B atoms in the first coordination sphere, see Figure 46.
Figure 46: Cubic Cu$_2$Mg type crystal structure (Laves phase C15); local coordination around possible interstitial sites indicated.

The way of filling up some of the vacant sites in intermetallic hydrides follows certain guide lines. First, there is a minimum H – H atom separation of 2.1 Å. This means that no interstitial sites closer than 2.1 Å can simultaneously be filled with hydrogen atoms (there exists a few exceptions, but they are really rare). This is referred to as “the rule of 2Å”, or the Westlake criterion. Secondly, the relative stability of the sites with respect to hydrogen incorporation follow some simple guide lines; the most stable site has the higher number of hydride forming elements in its first coordination sphere (when evaluating/comparing a number of different interstices). The size of the interstice (void/ hole) should be in the range 0.4 – 0.5 Å for being candidate for hydrogen uptake.

On heating a metal hydride (in inert atmosphere), hydrogen will eventually be released. This process may involve distinct steps or can be rather continuous. In all cases the least stable interstices (see above) are emptied first, and the most stable interstice remains (partly) filled up to the thermal stability limit.

Quite in parallel with the situation for metal hydrides, there exist interstitial metal carbides and well-defined metal carbide compounds. This is illustrated in the phase diagrams below, Figure 47; in the Cr – C system there are three stoichiometric carbides Cr$_2$C$_3$, Cr$_7$C$_3$ and Cr$_{23}$C$_6$; in the Fe – C phase diagram interstitial carbon can be dissolved in iron, both in the low-temperature α ferrite polytype, and in the high temperature γ austenite polytype..
Figure 47: Cr – C (left) and Fe – C (right) phase diagrams (temperature vs composition).

From Figure 47 (right) it is evident that the carbon dissolution in iron is polytype dependent. Just small amounts of carbon can be incorporated into the interstitial sites of bcc $\alpha$-Fe, whereas 2.14wt% C can be dissolved into the interstices of ccp (fcc) $\gamma$-Fe. The reason for this large difference in solubility can be found by considering the interstitial sites in more detail. In ccp/fcc iron, there are ideal tetrahedral and octahedral sites, of which the octahedral sites fit well to the expected relative size ratio between carbon and iron. In bcc-Fe the octahedral sites are highly deformed, Figure 48.

![Octahedral site](image)

**Figure 48:** Projection of the bcc-unit cell on the ab-plane; z-coordinates given. Octahedral site indicated by hexagon.

The position of one deformed octahedral site in the bcc-structure is indicated in Figure 48. Say that the site is located in $z = 0.50$; i.e. in $(1/2,0,1/2)$. Then the distance to the two atoms in $z = 0.50$ [at $(1/2,-1/2,1/2)$ and $(1/2,1/2,1/2)$] equals $a/2$ in length (2.00 Å if $a = 4.00$ Å); whereas the distance to the four red atoms $[(0,0,0), (0,0,1),(1,0,0),(1,0,1)]$ equals $a/\sqrt{2}$ (2.82
Å if \( a = 4.00 \text{ Å} \). Obviously carbon can not achieve a symmetrical octahedral coordination in this interstitial site. Experiments show that when carbon enters into such sites, it is rather displaced from the center, trying to optimize binding to five of the six surrounding metal atoms. Anyhow this is less attractive than filling the ideal octahedral sites of a ccp/fcc. In \( \gamma \)-Fe there are other parameters that restrict the amount of dissolved carbon than the size/geometry factor, however, these come first into play at concentrations above 2.1at\% C.