

Ionic Crystals

Basics

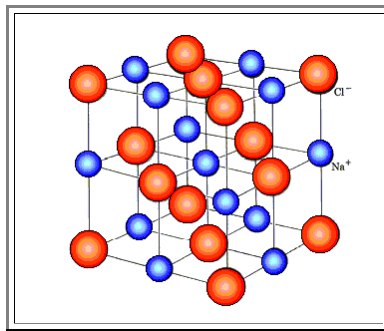
Ionic crystals have at least two atoms in their **base** which are ionized. Charge neutrality demands that the total charge in the base must be zero; so we always need ions with opposing charge.

- The binding between the ions is mostly electrostatic and rather strong (binding energies around **1000 kJ/mol**); it has no directionality.
- Ionic crystals thus can be described as an ensemble of hard spheres which try to occupy a minimum volume while minimizing electrostatic energy at the same time (i.e. having charge neutrality in small volumes, too).
- There are no free electrons, ionic crystals are insulators.

Ionic crystals come in simple and more complicated lattice types; the latter is true in particular for oxides which are often counted among ionic crystals. Some prominent lattice types follow

The NaCl Structure

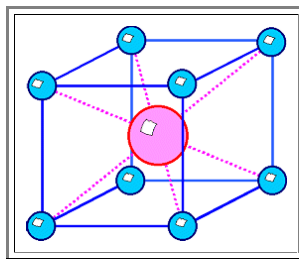
The lattice is **face centered cubic (fcc)**, with **two** atoms in the base: one at **(0, 0, 0)**, the other one at **($\frac{1}{2}$, 0, 0)**



- Many salts and oxides have this structure, e.g. **KCl, AgBr, KBr, PbS, ...**
or
MgO, FeO, ...

The CsCl Structure

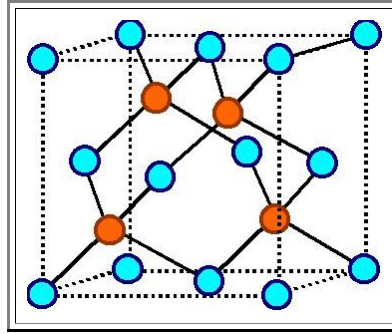
The lattice is **cubic primitive** with **two** atoms in the base at **(0,0,0)** and **($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$)**. It is a common error to mistake it for a bcc lattice.



- Intermetallic compounds (not necessarily ionic crystals), but also common salts assume this structure; e.g. **CsCl, TiJ, ...**,
or **AlNi, CuZn**,

The ZnS (or Diamond, or Sphalerite) Structure

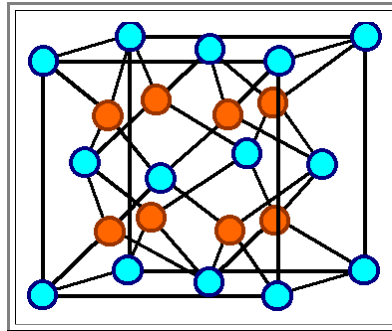
▶ The "zinc blende" lattice is *face centered cubic (fcc)* with two atoms in the base at $(0,0,0)$ and $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$.



- It is not only an important lattice for other ionic crystals like **ZnS**, which gave it its name, but also the typical lattice of *covalently bonded group IV semiconductors* (**C** (diamond form), **Si**, **Ge**) or III-V compounds semiconductors (**GaAs**, **GaP**, **InSb**, **InP**, ...)
- The **ZnS** lattice is easily confused with the **ZrO₂** lattice below.

The CaF₂ or ZrO₂ Structure

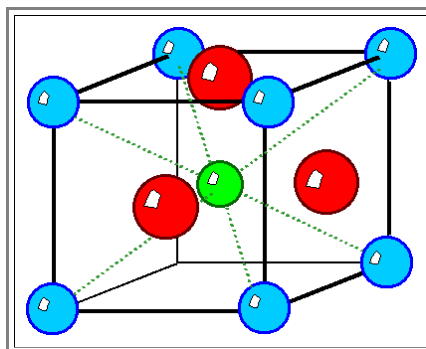
▶ The lattice is *face centered cubic (fcc)* with *three* atoms in the base, one kind (the cations) at $(0,0,0)$, and the other two (anions of the same kind) at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, and $(\frac{1}{4}, \frac{3}{4}, \frac{1}{4})$.



- It is often just called the "fluorite structure".

Perovskite Structure

▶ The lattice is essentially *cubic primitive*, but may be distorted to some extent and then becomes *orthorhombic* or worse. It is also known as the **BaTiO₃** or **CaTiO₃** lattice and has *three* different atoms in the base. In the example it would be **Ba** at $(0,0,0)$, **O** at $(\frac{1}{2}, \frac{1}{2}, 0)$ and **Ti** at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.

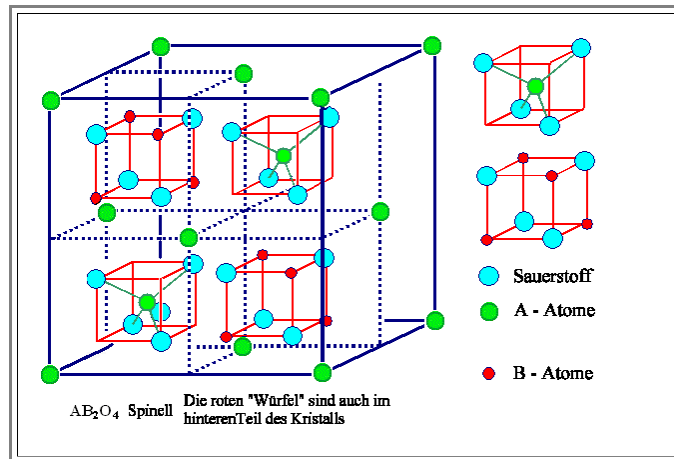


- A particular interesting perovskite (at high pressures) is **MgSiO₃**. It is assumed to form the bulk of the mantle of the earth, so it is the most abundant stuff on this planet, neglecting its Fe/Ni core. The mechanical properties (including the movement of dislocations) of this (and related) minerals are essential for geotectonics - forming the continents, making and quenching volcanoes, earthquakes - quite interesting stuff!

Spinel Structure

The spinel structure (sometimes called **garnet structure**) is named after the mineral *spinel* (MgAl_2O_4); the general composition is AB_2O_4 . It is essentially *cubic*, with the **O** - ions forming a fcc lattice. The cations (usually metals) occupy $\frac{1}{8}$ of the [tetrahedral sites](#) and $\frac{1}{2}$ of the [octahedral sites](#) and there are **32 O**-ions in the unit cell.

This sounds complicated, but it is not as bad as it could be; look at the drawing. We "simply" have two types of cubic building units inside a big **fcc O**-ion lattice, filling all **8** octants.



The spinel structure is very flexible with respect to the cations it can incorporate; there are over **100** known compounds. In particular, the **A** and **B** cations can mix! In other words, the composition with respect to one unit cell can be

- $(\text{A}_8)(\text{B}_{16})\text{O}_{32}$, or
- $\text{A}_8(\text{B}_8\text{A}_8)\text{O}_{32} = \text{A}(\text{AB})\text{O}_4$ in regular chemical spelling, or
- $(\text{A}_{8/3}\text{B}_{16/3})(\text{A}_{16/3}\text{B}_{32/3})\text{O}_{32}$

and so on, with the atoms in the brackets occupying the respective site at random.

A few examples (in regular chemical symbols)

- Magnetite; $\text{Fe}^{3+}(\text{Fe}^{2+}\text{Fe}^{3+})\text{O}_4$
- Spinel; $\text{Mg}^{2+}(\text{Al}_2^{3+})\text{O}_4$
- Chromite; $\text{Fe}^{3+}(\text{Cr}_2^{3+})\text{O}_4$
- Jacobsite; $\text{Fe}^{3+}(\text{Mn}^{2+}\text{Fe}^{3+})\text{O}_4$

The spinel structure is also interesting because it may contain **vacancies as regular part of the crystal**. For example, if magnetite is slowly oxidized by lying around a couple of billion years, or when rocks cool, Fe^{2+} will turn into Fe^{3+} (oxidation, in chemical terms, means you take electrons away). If all Fe^{2+} is converted into Fe^{3+} , charge balance requires a net formula of $\text{Fe}_{21,67}\text{O}_{32}$ per unit cell and this means that 2,33 sites must be vacant - we have what is called a **defect spinel**. In a way, the composition is now $\text{Fe}_{21,67}\text{Vac}_{2,33}\text{O}_3$; having lots of vacancies as an *integral part of the structure*.