

Script for the Solid States Physics lecture
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Crystal structures

Symmetries and lattice types

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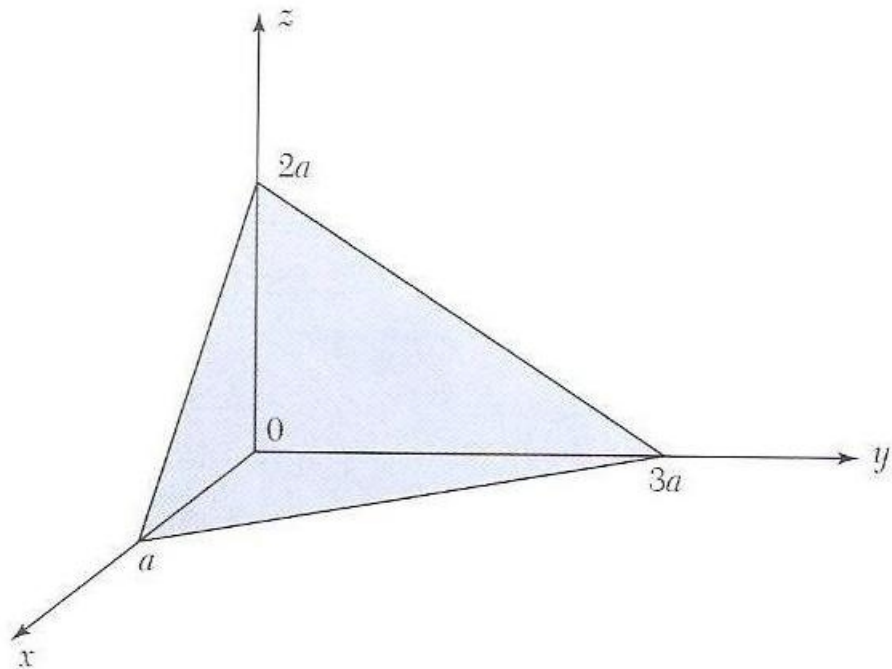
The hkl plane

To construct the hkl-plane the intercepts, where the plane crosses the axis, have to be considered. A plane with the intercepts h,k,l is the $(1/h,1/k,1/l)$ plane. When h, k and l are known, the plane is determined by the following steps:

1. take the reciprocal values of h, k and l $\Rightarrow 1/h, 1/k, 1/l$
2. multiply the reciprocal values with the lowest integer, that gives integers again \Rightarrow intercepts in terms of a

Example: (623)-plane

- 1.) reciprocal values: $(1/6, 1/2, 1/3)$
- 2.) multiply with 6 $\Rightarrow (1,3,2)$



A (623)-crystal plane.

Figure 1: The (623)-plane

Example: (562)-plane

- 1.) reciprocal values: $(1/5, 1/6, 1/2)$
- 2.) multiply with 30 $\Rightarrow (6,5,15)$

Symmetries

The Bravais lattice could be used to classify crystals, but a more common method is to use the symmetries of the crystals for the classification. There are some kinds of symmetries, such as:

- translational symmetry
- rotational symmetry
- reflection symmetry
- inversion symmetry

If there is a **rotational symmetry**, it is possible to turn the crystal among a certain angle, so that all atoms fall back onto equivalent atoms. For instance, a cubic crystal can be turned by 90 degrees along the x-, y- or z-axis.

Reflection symmetry means, that it is possible to reflect the atoms of the crystal through a plane.

On **inversion symmetry** the points of a crystal can be inverted through the origin. That means (in Cartesian coordinates): $x \rightarrow -x$, $y \rightarrow -y$ and $z \rightarrow -z$.

Space groups

For every crystal a list of all the symmetries can be made. So the crystals can be classified by putting all crystals with the same list of symmetries together in a group.

It turns out, that a Bravais lattice is uniquely determined by the symmetries of a crystal. For instance, if you can turn a lattice by 90 degrees over the x-, y- and z-axis, the lattice can't be orthorhombic or tetragonal. For this lattice types the unit cell is not the same in the x- and y-direction (so they have a different set of symmetries). The Bravais lattice itself is also a symmetry.

Symmetries are mathematically described in the **group theory**. A group is specified by a set of symmetries. Overall there are 230 possible sets of symmetries, the so called **space groups**.

Point groups

A set of symmetries, where at least one point does not move is called **point group**. For instance, at a rotation around an axis (the points on this axis don't move), at a reflection through a plane or on inversion (the points, through that inversion is done, don't move). Because at least one point remains fixed during the transformation, this symmetries can be represented by 3x3 matrices. For instance, the following matrix represents the rotation around the x-axis by the angle α :

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos(\alpha) & \sin(\alpha) \\ 0 & -\sin(\alpha) & \cos(\alpha) \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \quad (1)$$

An example for a not point-symmetric transformation is the combination of a rotation and a translation.

A symmetry multiplied by itself, or with another symmetry, produces a symmetry again. For instance, a cubic structure has a rotational symmetry by 90 degrees, 180 degrees and

270 degrees. Multiplication of the 90-degrees-rotation matrix with itself results in the 180-degrees-rotation matrix and so on.

Generally for point groups this means, that every 3x3-symmetry-matrix multiplied with another 3x3-symmetry-matrix produces another 3x3-symmetry-matrix which is an element of the same point group:

$$\mathbf{AB} \in \mathbf{G} \text{ for } \mathbf{A}, \mathbf{B} \in \mathbf{G} \quad (2)$$

All over there are 32 point groups (this is determined by the group theory). So more of one of the 230 space groups can correspond to a single point group.

A list of crystal lattices and their point groups can be found at the following site:

<http://lamp.tu-graz.ac.at/hadley/ss2/crystalphysics/crystalclasses/crystalclasses.html>

At the top of the list there is the group with the lowest symmetry and at the bottom is the group with the highest symmetry. At the right side of the list is the column with group elements. For instance, for the first group it is just the identity matrix (ones down the diagonal). This means that this group has no rotation, no inversion and no reflection symmetry. The group elements are produced by multiplications of the generating matrices with themselves and with the other generating matrices.

In this table there are also informations about the number of symmetry elements per group and about what space groups correspond to a specific point group.

More information about space groups can be found on <http://it.iucr.org> (you have only access to the database from computers of the TU Graz) but for the exam it is not necessary to know details about specific space groups.

Asymmetric unit

The **asymmetric unit** is the smallest unit (even smaller than the unit cell) that can be used to specify the crystal structure. Therefore the symmetries (space groups) are needed.

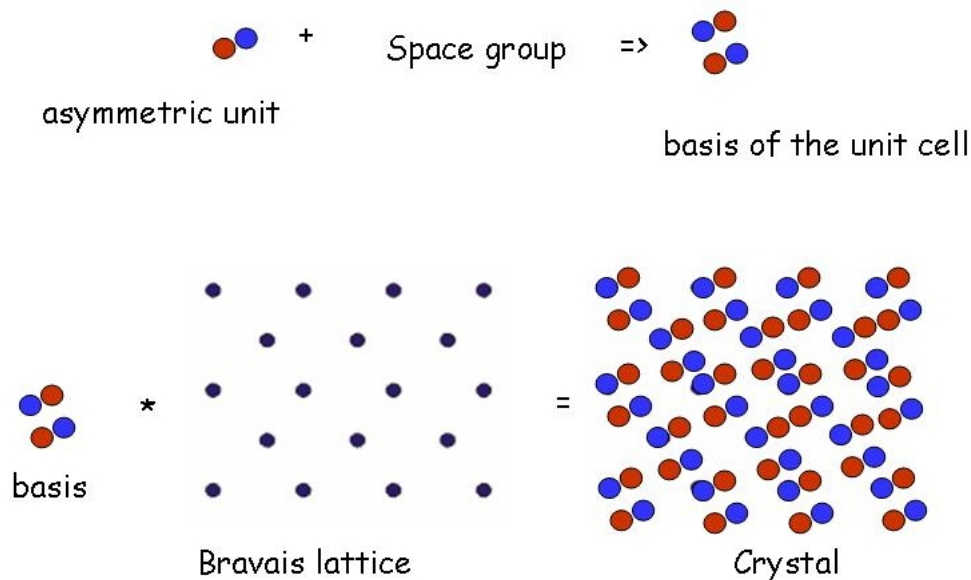


Figure 2: From the asymmetric unit to the crystal structure

Figure 2 shows, how to construct the crystal structure beginning with the asymmetric unit. This is done by the following two steps:

1. apply all transformations of the space group on the asymmetric unit, this results in the basis of the unit cell
2. perform a convolution (Faltung) of the basis with the Bravais lattice \Rightarrow crystal structure

The basis of the unit cell specifies where and which atoms are in the unit cell.

Example: Cementite Fe_3C

Cementite can be found in the production of steel. Figure 3 shows the asymmetric unit and the unit cell, produced by the program powder cell, and some descriptions from a crystallography database. The first line describes the unit cell, first 3 numbers are the length in Å, the other 3 numbers are the angles \Rightarrow orthorhombic structure. The second line gives the number of atoms in the asymmetric unit and the next three lines give the positions of the atoms in the asymmetric unit. The line "rgnr" gives the number of the space group (german: Raumgruppe), in this case it is 62.

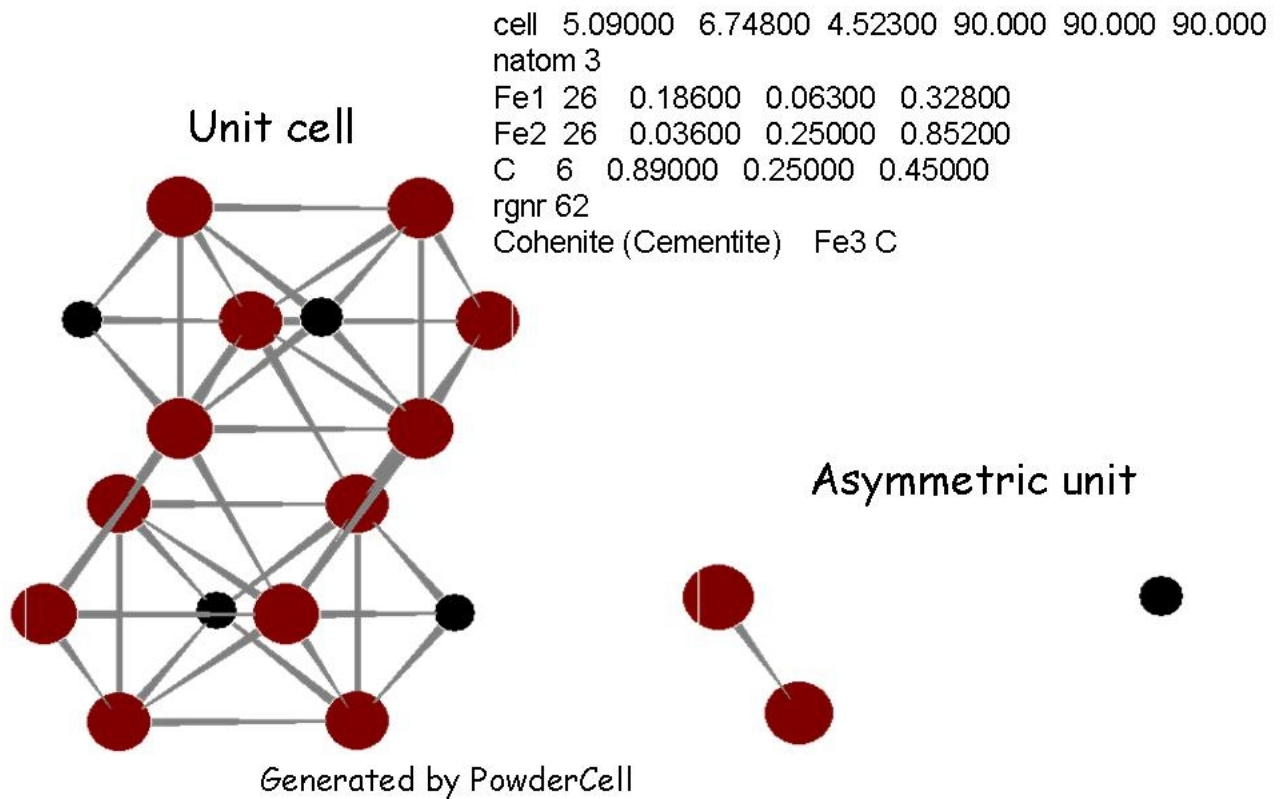


Figure 3: Cementite

Program: powder cell

As mentioned, the unit cell in figure 3 is generated by the program **powder cell**. This is a free software which is mainly used for the calculation of x-ray-diffraction. It is from the BAM (Bundesanstalt fuer Materialforschung und -pruefung, http://www.bam.de/de/service/publikationen/powder_cell.htm).

Lattice types

Simple cubic

For a simple cubic crystal structure the conventional and the primitive unit cell are the same. It is a not very common crystal structure, there is only one element with a simple cubic structure (Po). The corresponding space group has the number 221. Some details about simple cubic (with "a" as the lattice constant):

- number of nearest neighbours: 6
- distance between nearest neighbours: a
- volume of the primitive unit cell: a^3
- number of atoms in the primitive unit cell: 1
- number of atoms in the conventional unit cell: 1
- atomic packaging factor: $AFP \approx 0.52$

The primitive vectors are:

$$\vec{a}_1 = a * \vec{X}$$

$$\vec{a}_2 = a * \vec{Y}$$

$$\vec{a}_3 = a * \vec{Z}$$

The basis vector is: $\vec{B}_1 = 0$

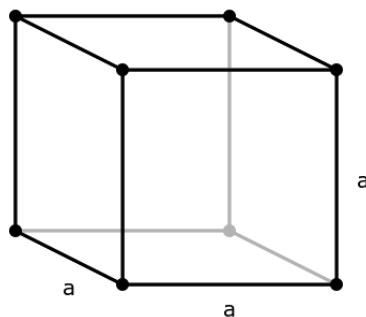


Figure 4: Conventional unit cell of simple cubic

Face centered cubic - FCC

In the fcc crystal structure there is one atom at each corner and one atom at each face of a cube. There are many elements with a fcc-structure, most of them are metals. Metals often form fcc-structures because their bonds are not very directional. One consequence of this is, that it is possible to bend metals because the atoms don't care in which directions their bond partners are. Bending causes a rearrangement of the partners and the number of bonds of the atoms. Some details about fcc:

- number of nearest neighbours: 12
- distance between nearest neighbours: $\frac{a}{\sqrt{2}}$
- volume of the primitive unit cell: $\frac{a^3}{4}$
- number of atoms in the primitive unit cell: 1
- number of atoms in the conventional unit cell: 4
- APF ≈ 0.74
- corresponding space group: 225
- elements with fcc-structure: Al, Cu, Ni, Sr, Rh, Pd, Ag, Ce, Ir, Pt, Au, Pb, Th

Primitive vectors:

$$\vec{a}_1 = 1/2 * a * \vec{Y} + 1/2 * a * \vec{Z}$$

$$\vec{a}_2 = 1/2 * a * \vec{X} + 1/2 * a * \vec{Z}$$

$$\vec{a}_3 = 1/2 * a * \vec{X} + 1/2 * a * \vec{Y}$$

The basis vector is: $\vec{B}_1 = 0$

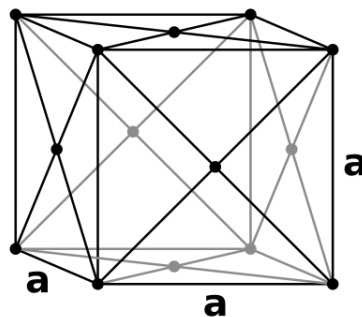


Figure 5: Conventional unit cell of face centered cubic

Hexagonal close pack - HCP

Hcp has the same coordination number (=number of nearest neighbours) as fcc. A lot of metals have hcp-structure. Some details about hcp:

- number of nearest neighbours: 12
- distance between nearest neighbours: a
- volume of the primitive unit cell: $a^3 * \sqrt{2}$
- number of atoms in the primitive unit cell: 2
- APF \approx 0.74
- corresponding space group: 194
- elements with hcp-structure: Mg, Be, Sc, Ti, Co, Zn, Y, Zr, Tc, Ru, Cd, Gd, Tb, Dy, Ho, Er, Tm, Lu, Hf, Re, Os, Tl

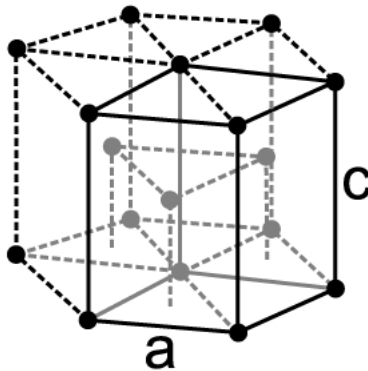


Figure 6: Conventional unit cell of hexagonal close pack

Body centered cubic - BCC

In the bcc-structure there is one atom at each corner and one atom in the middle of a cube. It has the same point group as fcc but a different space group. Many metals form bcc crystal structure. Some details about bcc:

- number of nearest neighbours: 8
- distance between nearest neighbours: $\frac{a}{2} * \sqrt{3}$
- volume of the primitive unit cell: $\frac{a^3}{2}$
- number of atoms in the primitive unit cell: 1
- number of atoms in the conventional unit cell: 2
- APF \approx 0.68
- corresponding space group: 229
- elements with bcc-structure: W, Na, K, V, Cr, Fe, Rb, Nb, Mo, Cs, Ba, Eu, Ta

Primitive vectors:

$$\vec{a}_1 = -1/2 * a * \vec{X} + 1/2 * a * \vec{Y} + 1/2 * a * \vec{Z}$$

$$\vec{a}_2 = 1/2 * a * \vec{X} - 1/2 * a * \vec{Y} + 1/2 * a * \vec{Z}$$

$$\vec{a}_3 = 1/2 * a * \vec{X} + 1/2 * a * \vec{Y} - 1/2 * a * \vec{Z}$$

The basis vector is: $\vec{B}_1 = 0$

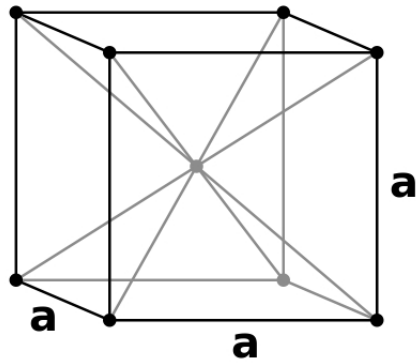


Figure 7: Conventional unit cell of body centered cubic

Crystals with 2 or more atoms

NaCl

This crystal is primarily held together by ionic forces. The sodium (Na) is positively charged and the chloride is negatively charged. Because of the arrangement of the atoms in the crystal every Cl-atom is surrounded by 6 Na-atoms.

A **possible exam question** could be: What is the Bravais lattice of NaCl?

To answer this question, one should focus on one kind of atoms and ignore the other ones. This can be done because the basis, consisting of both kinds of atoms, is copied on the Bravais lattice. The correct answer is FCC.

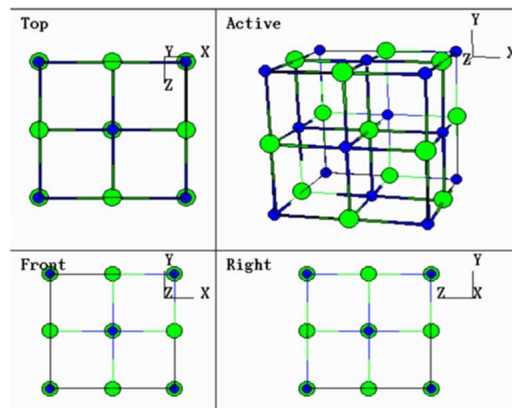


Figure 8: Conventional unit cell of NaCl

CsCl

In CsCl the bonds are also primarily ionic. The Cs has a positive and the Cl a negative charge.

Possible exam question: What is the Bravais lattice of CsCl?

Answer: It is simple cubic.

Attention: It looks a little bit like bcc because of the atom in the center, but that is a different atom than the ones in the corners.

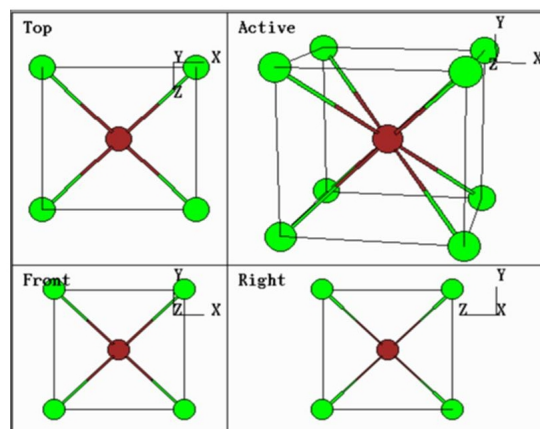


Figure 9: Conventional unit cell of CsCl

Perovskite crystal structure

The Bravais lattice of perovskite is simple cubic. Perovskite is mentioned here because the materials with this structure have some interesting properties and applications. In this structure the center atom of the conventional unit cell is always titanium or niobium. The atoms at the faces are oxygen atoms. At the corners are atoms from other elements (for instance Sr or Li). The following material have perovskite structure:

- **LiNbO₃**: It is used in non-linear optics for the 2nd harmonic generation. When shining red laser light into this material, blue light comes out (frequency doubling).
- **BaTiO₃**: This is a famous ferroelectric material (equivalent to ferromagnetic materials, which have a spontaneous magnetization, ferroelectric materials have a spontaneous electric polarization).
- **Pb_xZr_{1-x}TiO₃**: This is a piezoelectric material (apply voltage \iff change length of crystal). It is used in inject printers, fuel injects and scanning tunnelling microscopes (STM).
- **SrTiO₃**

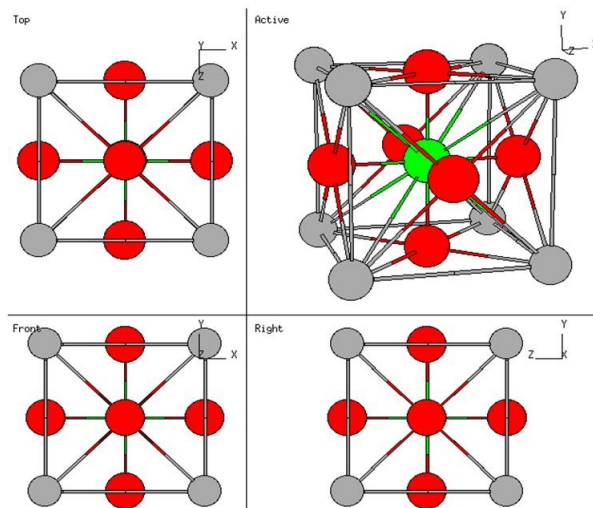


Figure 10: Conventional unit cell of perovskite

Some things, that are important for the exam:

- be able to identify the Bravais lattice
- count atoms in unit cell
- determine the number of nearest neighbours of an atom
- know SC, FCC, BCC (for others: a sketch would be given)
- calculate the distance between nearest neighbours
- calculate density of a material