

Set 3:

Task 1 and 2 considers many of the examples that are given in the compendium. Crystal structures derived from sphere packing models may be used to describe metals (see task 2), ionic compounds (e.g. alkali-halogenides and earth alkali oxides that adopts the NaCl-type structure), and for atomic and molecular compounds. For these phases, the packing sphere (the largest sphere) will follow the same repulsion pattern as for dense sphere packing. The ideal model refers to spheres of equal size and which are non-compressible and without interactions. In task 3 we will treat a real crystal structure, which with the help of literature data and tables, shall be drawn. The coordination relationships shall be identified and the bond lengths calculated.

Task 1:

We shall first regard the dense sphere packing model.

- 1.1. Draw a two dimensional pattern of dense packing spheres. Identify the two-dimensional unit cell.
- 1.2. Call the axis for the two dimensional unit cell as a and b . What relationship is there between the lengths of these axes? What is the angle between the axes? Determine the coordinates for the sphere(s) that represents the all positions for the spheres in the two dimensional structure. Note this layer of spheres as layer A.
- 1.3. Place a new layer (noted as layer B) of correspondingly packed spheres over the spheres in layer A. There are two possibly positions for creation of a dense sphere packing. What is the coordinates for these two possible situations? Note these as B and C respectively.
- 1.4. Consider then a ABABAB... dense sphere packing. Take as basis the two dimensional unit cell you found under 1.1. and sketch the unit lattice for the three dimensional structure.
- 1.5. The hexagonal unit lattice from 1.4. has the axis $a = b \neq c$. Calculate the relationship c/a for an ideal sphere packing. What fraction of the unit cell vilume is filled with spheres?
- 1.6. What types of holes are there for (a) a dense cubic spherepacking, ABCABC... (b) dense hexagonal spherepacking, ABAB... and (c) open AAA. Hexagonal packing. How many holes are there of the different types pr. packing sphere?
- 1.7. What is the reason that the c/a relationship for real compounds with the AB... spherepacking often deviates from the ideal value?

Task 2

The three usual metal structures are body centered cubic (bcc), hexagonal dense sphere packing (hcp) and cubic dense sphere packing (ccp). The pure metals usually crystallize with this type of structures. The same applies to a number of alloys that are solid solutions with arbitrary distribution of the different atoms on the “sphere” positions. In order to look a bit more carefully on these structures we will take basis in crystallographic data for three usual and industrially rather important metals; aluminum, magnesium and iron.

Al: Cu-type structure (fcc)
 $a = 4.0488 \text{ \AA}$ (at 298 K)
spacegroup $Fm\bar{3}m$; Al in 4(a): 0,0,0 and $1/2, 1/2, 0$ and $1/2, 0, 1/2$.

Mg: Mg-type structure (hcp)
 $a = 3.2089 \text{ \AA}$ (at 298 K)
 $c = 5.2101 \text{ \AA}$ (at 298 K)
spacegroup $P6_3/mmc$; Mg i 2(c): $1/3, 2/3, 1/4$ and $2/3, 1/3, 3/4$.

Iron exist in multiple modifications. At roomtemperature Fe is ferromagnetic ordered with the bcc- structure. The unordered, paramagnetic high temperature phase is fcc. Over ca. 1650 K this goes through at first order phase transition ot bcc-type. At large pressures a hcp modification is obtained.

bcc (ferromagnetic) \rightarrow fcc (paramagnetic) \rightarrow bcc (paramagnetic)

hcp

Fe: W-type structure (bcc) (0 – 1223 K)
 $a = 2.8865 \text{ \AA}$ (at 298 K)
spacegroup $Im\bar{3}m$; Fe i 2(a): 0,0,0 and $1/2, 1/2, 1/2$.

Fe: Cu-type structure (1223 – 1634 K)
 $a = 3.6660 \text{ \AA}$ (at 1440 K)
spacegroup $Fm\bar{3}m$; Fe i 4(a): 0,0,0 and $1/2, 1/2, 0$ and $0, 1/2, 1/2$ and $1/2, 0, 1/2$.

Fe: W-type structure (1663 K \rightarrow)
 $a = 2.9378 \text{ \AA}$ (at 1753 K)
spacegroup $Im\bar{3}m$; Fe i 2(a): 0,0,0 and $1/2, 1/2, 1/2$.

Fe: Mg-type structure (293 K, 183 kbar)
 $a = 2.452 \text{ \AA}$ (293 K, 183 kbar)
 $c = 3.932 \text{ \AA}$ (293 K, 183 kbar)
spacegroup $P6_3/mmc$; Fe i 2(c): $1/3, 2/3, 1/4$ and $2/3, 1/3, 3/4$.

- 2.1. Calculate the unit cell volume for the four modifications of iron.
- 2.2. Compare the different volumes per. formula unit of Fe.
- 2.3. Calculate the density of Al, Mg and Fe at 298 K.
- 2.4. What type of Bravais-lattice adopts Cu-, Mg- and W-type structures?
- 2.5. Describe the three structure types from: structure = lattice + basis, and draw the structures (unit lattice included atoms). Which of the structures are centrosymmetric?
- 2.6. Note what systematical extinction rules one will find for powder x-ray

- diffraction analysis of the different modifications of Fe.
- 2.7. Explain the following symbols that are in the space group symbols: (a) 6_3 , (b) $6_3/m$, (c) m , (d) -3 , (e) c .
 - 2.8. What is the belonging crystallographic point group for the space group $P6_3/mmc$?
 - 2.9. Given the crystallographic point group $6/mmm$. The second symbol (m) notes the symmetry along the axis a and b in the hexagonal unit cell, the third symbol (also m) notes the symmetry normal to the a - and b - axes. Draw a stereographic projection that illustrates how the symmetry elements are placed. Then place a general point and find how many times this is repeated by usage of the symmetry elements. Explain the difference between a general and special position.

Task 3

From general inorganic chemistry we have learned a lot about carbon compounds, about ionic, covalent and metallic carbides. One factor to regard is the electronegativity. With basic cations (specially maingroup 1 and 2) we will get ionic carbides. The ionic carbides hydrolyze under creation of C_nH_m . Compound with C^{-IV} gave methane and was called metanizers. CaC_2 gave ethyne and contains C_2^{2-} dimers. Practical use of carbides is usually connected to covalent (SiC) and metallic carbides (WC, steel Fe-C).

In this task we will regard the crystal structure of Mg_2C_3 . The structure is determined on the basis of powder x-ray diffraction data at UiO. The structural aspects in Mg_2C_3 expands the knowledge on ionic carbides by that this compound is the first example of trimeric C-anions. A selection from the International Tables for Crystallography is appended for the spacegroup Pnnm.

Structuredata (from Inorg. Chem. 31, 1992, 3260-3263).

Unitcell: $a = 6.4108 \text{ \AA}$; $b = 5.2768 \text{ \AA}$ and $c = 3.7283 \text{ \AA}$.

Atomic coordinates:

Mg	4(g)	$x = 0.2903$	$y = 0.3901$
C(1)	2(d)		
C(2)	4(g)	$x = 0.6188$	$y = 0.2070$

- 3.1. State the crystalsystem, Bravais/lattice and corresponding crystallographic spacegroup.
- 3.2. How many formula units are there in a unitcell?
- 3.3. Fill a table of atomic coordinates such that all x_i , y_i and z_i are specified.
- 3.4. What is the point symmetry at Mg, C(1) and C(2)?
- 3.5. Construct mathematical expressions (rotation matrix + translation matrix) for how one can go from the basis (x,y,x) to the transformed positions. (applies to eh 8h positions).
- 3.6. Introduce the starting point $(x,y,0)$ instead of (x,y,x) and operate the matrix you found under 3.5. Compare this with what the table shows for the 4g positions. Do the same for introduction of $(0,1/2,1/2)$ instead of (x,y,z) as basis.
- 3.7. Construct stereographical projections that show the symmetry elements for the

- pointgroup mmm, and how these affect a general point.
- 3.8. How large part of the unit cell must be drawn in order to define all atoms?
 - 3.9. Produce a projection of the structure on the ab-plane.
 - 3.10. Calculate the distances between the C-atoms. What kind of geometry has the carbonanion? What kind of charge is ascribed to the carbon anion if one assumes that the cation has a charge of Mg^{2+} ? What gass molecule is isoelectronic with the carbon anion?
 - 3.11. Evaluate the type of bonding based on that a normal C-C bond is 1.54 Å (diamond); double bond is 1.35 Å and a triple bond (e.g. in CaC_2) is 1.20 Å.

Appended is p. 279 in International Tables. (No. 58, *Pnmm*).

$P n n m$

D_{2h}^{12}

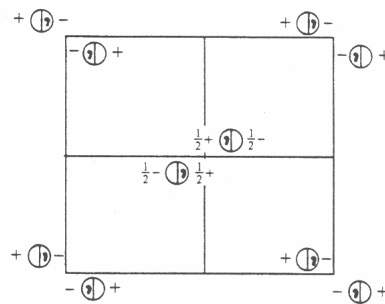
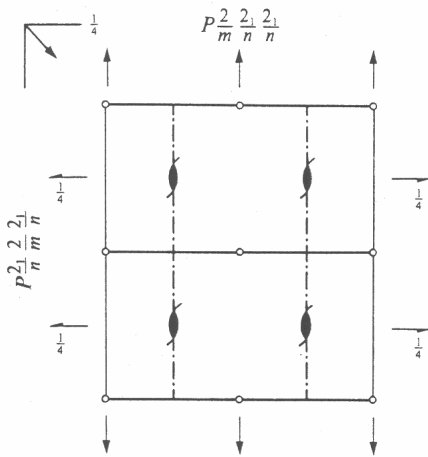
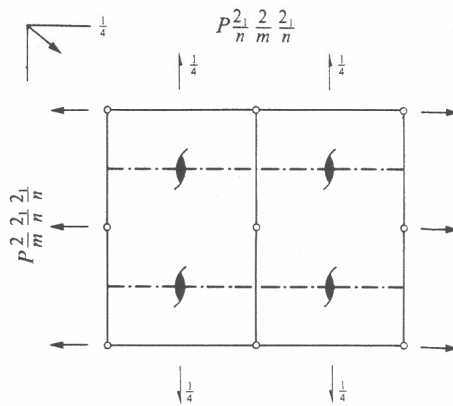
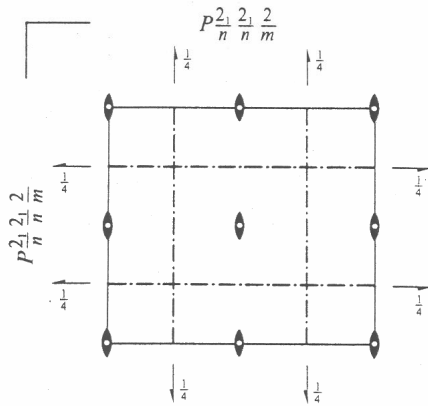
$m m m$

Orthorhombic

No. 58

$P 2_1/n 2_1/n 2/m$

Patterson symmetry $P m m m$



Origin at centre ($2/m$)

Asymmetric unit $0 \leq x \leq \frac{1}{2}$; $0 \leq y \leq \frac{1}{2}$; $0 \leq z \leq \frac{1}{2}$

Symmetry operations

- | | | | |
|-----------------------|-----------------|--|--|
| (1) $\bar{1}$ | (2) $2 \ 0,0,z$ | (3) $2(0,\frac{1}{2},0) \ \frac{1}{4},y,\frac{1}{4}$ | (4) $2(\frac{1}{2},0,0) \ x,\frac{1}{4},\frac{1}{4}$ |
| (5) $\bar{1} \ 0,0,0$ | (6) $m \ x,y,0$ | (7) $n(\frac{1}{2},0,\frac{1}{2}) \ x,\frac{1}{4},z$ | (8) $n(0,\frac{1}{2},\frac{1}{2}) \ \frac{1}{4},y,z$ |

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (3); (5)

Positions

Multiplicity,
Wyckoff letter,
Site symmetry

Coordinates

Reflection conditions

8 *h* 1 (1) x, y, z (2) \bar{x}, \bar{y}, z (3) $\bar{x} + \frac{1}{2}, y + \frac{1}{2}, \bar{z} + \frac{1}{2}$ (4) $x + \frac{1}{2}, \bar{y} + \frac{1}{2}, \bar{z} + \frac{1}{2}$
(5) $\bar{x}, \bar{y}, \bar{z}$ (6) x, y, \bar{z} (7) $x + \frac{1}{2}, \bar{y} + \frac{1}{2}, z + \frac{1}{2}$ (8) $\bar{x} + \frac{1}{2}, y + \frac{1}{2}, z + \frac{1}{2}$

General:

$0kl: k+l=2n$
 $h0l: h+l=2n$
 $h00: h=2n$
 $0k0: k=2n$
 $00l: l=2n$

Special: as above, plus

4 *g* ..*m* $x, y, 0$ $\bar{x}, \bar{y}, 0$ $\bar{x} + \frac{1}{2}, y + \frac{1}{2}, \frac{1}{2}$ $x + \frac{1}{2}, \bar{y} + \frac{1}{2}, \frac{1}{2}$

no extra conditions

4 *f* ..2 $0, \frac{1}{2}, z$ $\frac{1}{2}, 0, \bar{z} + \frac{1}{2}$ $0, \frac{1}{2}, \bar{z}$ $\frac{1}{2}, 0, z + \frac{1}{2}$

 $hkl: h+k+l=2n$

4 *e* ..2 $0, 0, z$ $\frac{1}{2}, \frac{1}{2}, \bar{z} + \frac{1}{2}$ $0, 0, \bar{z}$ $\frac{1}{2}, \frac{1}{2}, z + \frac{1}{2}$

 $hkl: h+k+l=2n$

2 *d* ..2/*m* $0, \frac{1}{2}, \frac{1}{2}$ $\frac{1}{2}, 0, 0$

 $hkl: h+k+l=2n$

2 *c* ..2/*m* $0, \frac{1}{2}, 0$ $\frac{1}{2}, 0, \frac{1}{2}$

 $hkl: h+k+l=2n$

2 *b* ..2/*m* $0, 0, \frac{1}{2}$ $\frac{1}{2}, \frac{1}{2}, 0$

 $hkl: h+k+l=2n$

2 *a* ..2/*m* $0, 0, 0$ $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$

 $hkl: h+k+l=2n$

Symmetry of special projections

Along [001] *p* 2*g* *g* $a' = a$ $b' = b$ Origin at 0,0,*z*Along [100] *c* 2*m* *m* $a' = b$ $b' = c$ Origin at $x, 0, 0$ Along [010] *c* 2*m* *m* $a' = c$ $b' = a$ Origin at 0,*y*,0

Maximal non-isomorphic subgroups

I [2]*P* 2₁ 2₁ 2 1; 2; 3; 4
[2]*P* 1 1 2/*m* (*P* 2/*m*) 1; 2; 5; 6
[2]*P* 1 2₁/*n* 1 (*P* 2₁/*c*) 1; 3; 5; 7
[2]*P* 2₁/*n* 1 1 (*P* 2₁/*c*) 1; 4; 5; 8
[2]*P* *n* *n* 2 1; 2; 7; 8
[2]*P* *n* 2₁ *m* (*P* *m* *n* 2₁) 1; 3; 6; 8
[2]*P* 2₁ *n* *m* (*P* *m* *n* 2₁) 1; 4; 6; 7

IIa none

IIb none

Maximal isomorphic subgroups of lowest index

IIc [3]*P* *n* *n* *m* ($a' = 3a$ or $b' = 3b$); [3]*P* *n* *n* *m* ($c' = 3c$)

Minimal non-isomorphic supergroups

I [2]*P* 4/*m* *n* *c*; [2]*P* 4₂/*m* *n* *m*

II [2]*A* *m* *a* *m* (*C* *m* *c* *m*); [2]*B* *b* *m* *m* (*C* *m* *c* *m*); [2]*C* *c* *c* *m*; [2]*I* *m* *m* *m*; [2]*P* *n* *c* *m* ($2a' = a$) (*P* *m* *n* *a*);
[2]*P* *c* *n* *m* ($2b' = b$) (*P* *m* *n* *a*); [2]*P* *b* *a* *m* ($2c' = c$)