Colloquium tasks for MEF 3000 / MEF 4000

Sphere packing

Crystal structures derived from sphere packing models may be used to describe metals, 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 repetition pattern as for dense sphere packing. The ideal model refers to spheres of equal size and which are non-compressible and without interactions.

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 volume is filled with spheres?
1.6. What types of holes are there for (a) a dense cubic sphere packing, ABCABC… (b) dense hexagonal sphere packing, ABAB… and (c) open AAA. Hexagonal packing. How many holes are there of the different types pr. packing sphere?

Task 2:

In this task we shall consider what holes that appears in dense packing of spheres, and consider simple structure types derived from the sphere packing model.
Consider first a hcp sphere packing (…AB…) of identical spheres (X).

2.1.   What types of holes occur for hexagonal sphere packing? Sketch the corresponding coordination polyhedra. Which holes can be filled at the same time?

2.2.   What structure types have (a) all octahedral holes filled, (b) half of the tetrahedral holes filled?

2.3.   Which structure type do you get if each second layer (along the c-axis) of octahedral holes between A and B packing layers are filled with atoms?
What composition will a compound with this structure type have? Describe the bonding relations for this structure type.

2.4.   The structure of $ScCl_3$ is related to the $CdCl_2$ type structure. This is made by that within each layer of filled octahedral holes in the $CdCl_2$ type structure, 1/3 of the holes are systematically empty. Sketch such a layer with 1/3 empty and 2/3 full octahedral holes.

2.5.   Describe the Cs_2O structure with basis in the CdI_2 type structure.

2.6.   Consider the NiAs-type structure. What will the composition be altered to if all trigonal bipyramidal holes are filled in addition to the octahedral holes?

2.8.   For hcp based structure types a deviation from the ideal c/a ratio ($\sqrt{8/3} = 1.631$) is often observed. Why are these deviations larger for NiAs-type phases than for pure metals and würtsitt-type phases which all have hcp packing?

Task 3:

The description of the symmetry of dense packed structures is given in the compendium. This should be revised by going through the examples of the compendium. By this, one will obtain an understanding of terms such as dense packed directions, dense packed planes, unit cells, atom coordinates, Bravais lattice, point symmetry operations, screw axis and space group (symbol). For metal structures, the metal atoms form the packing sphere. There are some cases of phases where small atoms fill holes between dense packed layers, e.g. the Ti-group (Ti, Zr, Hf) is known to dissolve relatively large amounts of hydrogen, carbon, nitrogen and oxygen by interstitial positions. Viz. statistically distributed over a large number of tetrahedra and/or octahedra holes. These holes are largest for the big d-elements and occur for hcp and ccp phases (not to the same extent for bcc!). From hcp and ccp packing of anion spheres (which will form the packing spheres) one can derive the simple NaCl-, NiAs-, würtsitt-, zinkblende-, and antifluorit type structures by that the cations fill 100% if the octahedral holes or 50% of the tetrahedral holes. For CdI_2 and $CdCl_2$ type structures, 50% of the octahedral holes are filled – in a systematically way.

The simplest structures derived from the sphere packing model is based on that all the packing spheres are of the <u>same</u> kind (ideally of same size, non-compressible and without interactions). In this task we shall consider a more complicated structure type. It is noted as perovskite type and is derived by the sphere packing model by that one applies two different types of packing spheres (X and Y).

3.1.   The ratio of the X and Y spheres are 1:3. The spheres are of equal size and together form dense sphere packing within a two dimensional layer. The distribution of X and Y spheres are systematic. The two-dimensional unit cell has the relations $a = b$, $\gamma = 120°$. The coordinates for the X-sphere are (0,0), for Y (0,1/2) and (1/2,0) and (1/2,1/2). Draw a XY_3 layer and mark the unit cell.

3.2.   You shall now make a three-dimensional dense sphere packing from the XY_3 layers. When XY_3 layers are stacked on top of each other, either in the form of …AB… or …ABC… packing, holes are formed, among others octahedral holes. How many octahedral holes are there in a three dimensional structure of XY_3 units? (Hint: consider a …AB… packing of identical spheres.)

3.3.   Since the 2D-layers do not contain identical spheres, one must make a choice when the layers are stacked. Place the next layer such that an X-sphere goes in the depression between three Y-spheres in the layer below. Consider then what kind of environments (with respect to X and Y) the octahedral holes have (consider all of the octahedra holes for XY_3, confer 1.2.)

3.4.   Let the X spheres be cations and the Y spheres be anions. In the octahedral holes one shall now place other cations, M. However, only some of the octahedral holes are suitable (of electronically reasons). Which holes are filled and how many are there pr. Y (anion) sphere?

3.6.   Assume that the X and Y atoms has a diameter of 2.70 Å. Calculate the size of the octahedrahole. What is the ratio between the diameter of the octahedrehole and a packing sphere?

3.7.   Consider the ions Na^+, Nb^{5+} and O^{2-} with ionic radii's of respectively 1.30, 0.78 and 1.40 Å. How would you ascribe these ions to the spheres X, Y and M?

3.8.   The structure type you have reached is noted as Perovskite type. You have considered the unit cell from a hexagonal cell. The structure can however be described with the cubic system by setting M in (1/2,1/2,1/2), X in (0,0,0) and Y in (1/2,1/2,0), (0,1/2,1/2) and (1/2,0,1/2). Draw the unit cell. How many formula units does the cell contain? Is the belonging Bravais lattice primitive or centered?

3.9.   The ReO_3 type structure is closely related to the perovskite type, however it lack the X atoms. Describe the ReO_3 structure from connection of coordination polyhedra (Hint: draw many unit cells in projection of the e.g. ab-plane).

3.10. Based on the knowledge of the coordination relationships for the cations in the perovskite type structure (X is included in dense packed layers of anions, M in octahedral holes), calculate the coordination numbers for oxygen.

The perovskite type phase has got important physical and chemical properties. They can be ion conducting, ferroelastic, permanent magnets, superconductors, take part in fuel cells or be heterogeneous catalysts.

Task 4: Connecting polyhedra. Factors that affect choice of structure type.

As description of structures, one can take basis in sphere packing or in connection of coordination polyhedras. We will first consider tetrahedra and octahedra as building blocks for isolated units and three-dimensional structures. Coordinationpolyhedra have got corners, edges, and faces that can be shared with adjoining polyhedra. Considerations of the distances involved shows which forms of connections that are undesirable due to repulsion between central atoms of the different polyhedra. The Principe for connections is often reflected in the chemical formula of the compound.

4.1. Consider the isolated units of connected octahedra in figure 1. What stoichiometry has the units (a) – (e)?

4.2. Al_2Cl_6, $Cr_2O_7^{2-}$, Mn_2O_7, SO_3 and CrO_3 are all constructed from tetrahedral units. Sketch the structure for the units/compounds and note how these are connected.

4.3. First consider an isolated octahedra, and then construct a continuously longer one-dimensional chain by letting the octahedra polymerize through shearing of two corners with neighboring octahedra. (Viz. edge sharing). What is the limiting value with respect to stoichiometry of such a connection of octahedra?

4.4. What type of connections of tetrahedra do you expect for the silicates (a) Ca_2SiO_4, (b) $KAlSiO_4$ (both Al and Si have tetrahedral surroundings of oxygen), (c) $Sc_2Si_2O_7$, (d) $MnSiO_3$ (e) $CaMgSi_2O_6$, (f) $CaAl_2(OH)_2(Si_2Al_2)O_{10}$?

4.5. The silicate minerals are classified according to their structural elements. Construct general formulas for silicate structures that are based on (a) groups of separate tetrahedras (single-, neosilicates), (b) tetrahedral dimmers (double-, sorosilicates), (c) ring formed structures (ring-, cyclosilicates), (d) monochains of tetrahedras (chain-, inosilicates), (e) two-dimensional network of tetrahedra that share three corners (layered-, fyllosilicates), (f) three-dimensional network of tetrahedra that share four corners (network-, tektosilikates).

4.6. How would you describe the CdI_2-type structure from a basis of connection of polyhedra? (Hint: consider an AB-layer in projection on the ab-plane and draw the coordination polyhedra.)

Fig. 1.
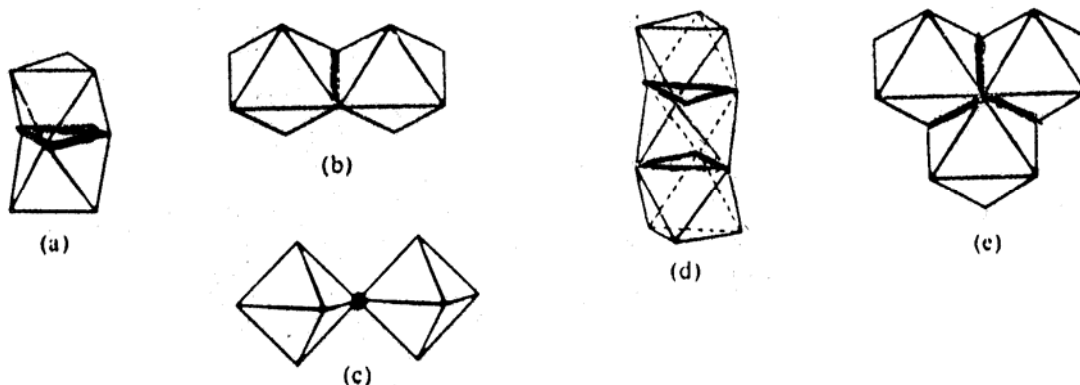
Task 5:

Use the tables in the West compendium (1.8 (NaCl), 1.9 (Zink blende), 1.10 (fluorite), 1.12 (würtsitt), 1.13 (NiAs) and 1.14 (CsCl)), which gives an overview on what compounds that crystallize with the NaCl-, NiAs-, CsCl-, and würtsite-type structures.

5.1.   Discuss for which of these structural types you find compounds that typically represent respectively ionic, covalent, metallic or van der Waals bondings.
5.2.   Why can NH_4Cl adopt the CsCl-type structure?

Task 6:

6.1.   What types of coordination are expected for BeO, CaO and BeO from the basis of relative size of anion and cation?
Be^{2+} r = 0.41 Å O^{2-} r = 1.24 Å
Ca^{2+} r = 1.14 Å
Ba^{2+} r = 1.50 Å
6.2.   Consider an octahedra hole in a ccp anion structure. Calculate the ratio between the anion and a cation (in the octahedra hole) on the assumption that they can be described as spheres that is in contact with each other. Would it be beneficial if the cation was larger or smaller than the case that the ions are in touch? Do the same considerations for CN=8 and cubic as coordination polyhedra. (Hint: the anion spheres are in touch. Find the direction that the anion spheres and cation spheres are touching each other as pearls on a line.
6.5.   LiF, MgO, ScN and TiC have all NaCl-type structure. Consider the degree of ionic vs. covalent character of the bonds in these compounds.
6.6.   Sketch a Moser-Pearson diagram. Note where in the diagram that BeO, CaO, LiF and TiC occur. Note in the diagram where ionic bodings dominate and where directional bonds dominate.
6.7.   The monoxides of 3d-elements have as a rule normal NaCl-type structure. Explain why the structure for CuO is deformed. Compare this to the following structural data for CuO:
$a = 4.95$, $b = 3.41$, $c = 5.11$ Å $\beta = 99.5°$
Spacegroup $C2/c$ [C lattice has as equivalent points (0,0,0) and (1/2,1/2,0)]. Center of symmetry is present.
Cu in (1/4,1/4,0) and (3/4,1/4,1/2); O in (0,y,1/4) with y = 0.416.
Draw the structure in form of projection on the ac-plane. Calculate Cu-O distances. Draw the coordination polyhedra.
6.8.   NiO has normal NaCl-type structure. For PtO (in same bigroup), the structure is deformed and Pt has almost plane quadratic surroundings of oxygen. Explain.
6.9.   Give a possible reason to why the SnS structure deviates from the ideal NaCl-type structure.

Task 7:

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)
        $a = 4.0488$ Å (at 298 K)
        spacegroup $Fm3m$; Al in 4(a): 0,0,0 and 1/2,1/2,0 and 1/2,0,1/2.

Mg: Mg-type structure (hcp)
        $a = 3.2089$ Å (at 298 K)
        $c = 5.2101$ Å (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 room temperature 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)
        $a = 2.8865$ Å (at 298 K)
        spacegroup $Im3m$; Fe i 2(a): 0,0,0 and 1/2,1/2,1/2.
Fe: Cu-type structure (1223 – 1634 K)
        $a = 3.6660$ Å (at 1440 K)
        spacegroup $Fm3m$; Fe i 4(a): 0,0,0 and 1/2,1/2,0 and 0,1/2,1/2 and ½,0,1/2.
Fe: W-type structure (1663 K ->)
        $a = 2.9378$ Å (at 1753 K)
        spacegroup $Im3m$; Fe i 2(a): 0,0,0 and 1/2,1/2,1/2.
Fe: Mg-type structure (293 K, 183 kbar)
        $a = 2.452$ Å (293 K, 183 kbar)
        $c = 3.932$ Å (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.

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

7.7. Explain the following symbols that are in the space group symbols: (a) 6_3, (b) $6_3/m$, (c) m, (d) -3, (e) c.

7.8. What crystallographic point group belongs to the space group $P6_3/mmc$?

7.9. 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 8:

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 Intenational Tables for Crystallography is appended for the space group Pnnm.

Structure data (from Inorg. Chem. 31, 1992, 3260-3263).
Unit-cell: $a = 6.4108$ Å; $b = 5.2768$ Å and $c = 3.7283$ Å.
Atomic coordinates:

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

8.1. State the crystal system, Bravais/lattice and corresponding crystallographic space group.

8.2. How many formula units are there in a unit-cell?

8.3. Fill a table of atomic coordinates such that all x_i, y_i and z_i are specified.

8.4. What is the point symmetry at Mg, C(1) and C(2)?

8.7. Construct stereographical projections that show the symmetry elements for the point group mmm, and how these affect a general point.

8.8. How large part of the unit cell must be drawn in order to define all atoms?

8.9. Produce a projection of the structure on the ab-plane.

8.10. 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 gas molecule is isoelectronic with the carbon anion?

8.11. 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.
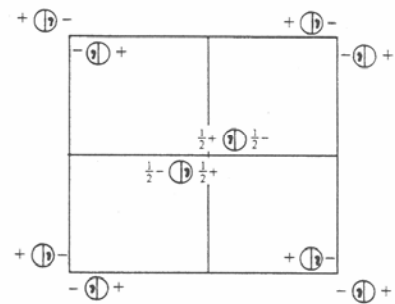
Appended is p. 279 in International Tables. (No. 58, *Pnnm*).
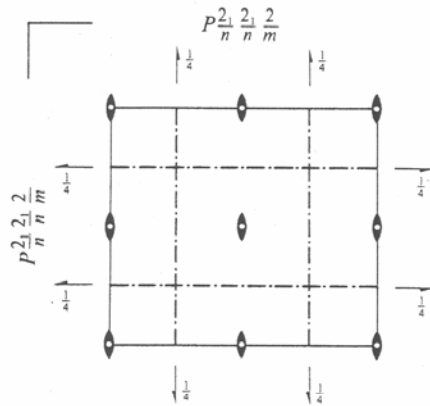
Origin at centre ($2/m$)
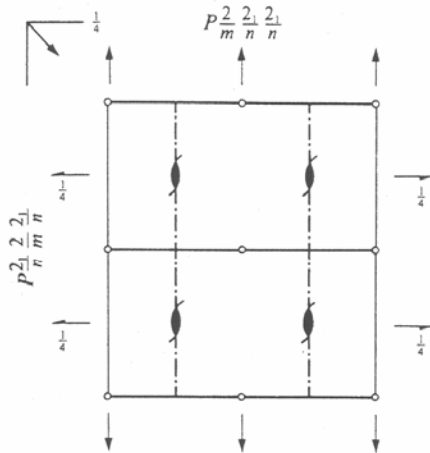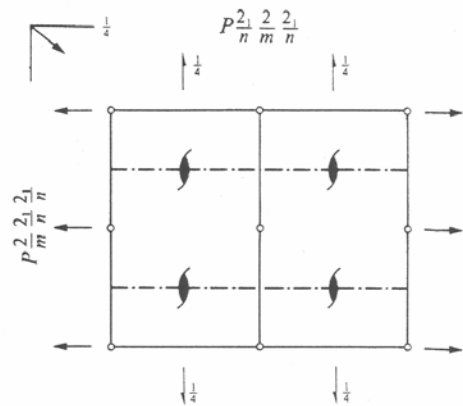
Asymmetric unit $0 \le x \le \frac{1}{2}$; $0 \le y \le \frac{1}{2}$; $0 \le z \le \frac{1}{2}$

Symmetry operations

(1) 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,   Coordinates   Reflection conditions
Site symmetry

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

Maximal non-isomorphic subgroups

I $[2]P\,2_1\,2_1\,2$ $1;2;3;4$
        $[2]P\,1\,1\,2/m\,(P\,2/m)$ $1;2;5;6$
        $[2]P\,1\,2_1/n\,1\,(P\,2_1/c)$ $1;3;5;7$
        $[2]P\,2_1/n\,1\,1\,(P\,2_1/c)$ $1;4;5;8$
        $[2]P\,n\,n\,2$ $1;2;7;8$
        $[2]P\,n\,2_1m\,(P\,m\,n\,2_1)$ $1;3;6;8$
        $[2]P\,2_1n\,m\,(P\,m\,n\,2_1)$ $1;4;6;7$

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 $[2]P\,4/m\,n\,c$; $[2]P\,4_2/m\,n\,m$

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

Task 9: *Defects and solid solubility.*

Defects are classified according to their dimensionality, how they affect the composition and if they originate from impurities. In this respect, terms as point-, line- and plane defects, stoichiometric and non-stoichiometric defects, and intrinsic and extrinsic defects. It is difficult to produce materials that are so pure that the defect situation at all temperatures is dominated by intrinsic defects, controlled by the thermodynamics of that compound. The dominating defect-type is structure specific.

Consider a sample of NaBr (with NaCl type structure) that is very pure. By measuring the defect related properties (here with origin in intrinsic defects) one finds that the dominating defect type is Schottky defects.

9.1. Sketch the Schottky-defects in NaBr. What effective charges are ascribed to the defects?

9.2. The formation enthalpy for Schottky defects are determined to be 200 kJ/mol. Calculate relative ratio of the defect concentrations at room temperature and at 1300 K.

9.3. If the defect concentration is 10^{10} defects/mol NaBr, give an estimate over how many unit cells one on average must cross on going from one Schottky defect to another.

9.4. Is it reasonable to note the situation under 9.2. and 9.3. as point defects?

9.5. Consider then an impurity dominated/extrinsic defect situation. Imagine that an aliovalent substitution is taking place, viz. a solid solubility phase where Na^+ in this case is partly substituted with Mn^{2+}. Let 1% of Na^+ be exchanged with half as much Mn^{2+}. Write an illustrating formula for the phase (inclusive the number of vacancies or interstitials that are crated due to the substitution.)

9.6. Draw a sketch that shows how the defect concentration varies with the inverse of temperature for impure NaBr (viz. assume extrinsic situation at low temperatures and intrinsic at high temperatures).

9.7. Assume that the conduction in NaBr is solely ionic, viz. it is ions that transport the charge, not electrons. It is Na^+ that is the cause of ion transport. The conduction is therefore directly dependant on the concentrations on Na+ positions (viz. octahedra positions in a ccp of Br-anions). How will the conduction be affected by the presence of Mn^{2+} as described under 9.5?

Task 10:

10.1.   Imagine that Na^+ is completely changed with Ag^+, viz. we now consider the compound AgBr. Do you expect this to alter the defect situation?

10.2.   Draw possible paths for moving the ions (assume that it is the cations that are most mobile) in respectively NaBr and AgBr. How many possible interstitial positions are there per. Na^+ (in the perfect structure)?

10.4.   On basis of the considerations ahead, do you believe NaBr or AgBr will be best at transporting ions the solid state (viz. show ionic conduction)?

Task 11:
The following problems are taken from the book *Understanding Solids…*

11.7   The enthalpy of formation of vacancies in pure nickel is $\Delta H = 97.3$ kJ mol^{-1}. What is the fraction of sites vacant at 1100 °C?

11.10   The enthalpy of formation of vacancies in pure aluminium is $\Delta H = 72.4$ kJ mol^{-1}. The density of aluminium is 2698 kg m^{-3}. What number of atom positions is vacant at 600 °C?

11.11   Calculate how the fraction of Schottky defects in a crystal of KCl varies with temperature if the value of ΔH_s is 244 kJ mol^{-1}.

11.14   Silver bromide, AgBr, has cubic unit cell with an edge of 0.576 nm. There are four silver atoms in the unit cell; assume that there are four interstitial positions available for silver atoms. Calculate the absolute number of interstitial defects present per cubic metre at 300K.

11.20   The fraction of Schottky defects in nickel oxide, NiO, at 1000°C is 1.25 x 10^{-4}. The cubic unit cell contains four nickel atoms and has a cell edge of 0.417 nm. Calculate the number of nickel vacancies present.

11.23   A total of 9 mol% of Y_2O_3 is mixed with 91 mol% ZrO_2 and heated until a uniform product with high oxygen ion conductivity is obtained. The resulting crystal is stabilized zirconia with the formula $Y_xZr_yO_z$. Determine x, y and z, explaining your answer.

11.24   CaO forms a solid solution with Bi_2O_3 to give a material with a high anionic conductivity. If 10 mol% CaO is reacted with 90 mol% Bi_2O_3, what is the formula of the final solid and what are the numbers and types of vacancies created?

11.25   What defects will form in the crystals made by adding small amounts of compound A to compound B:

(a) A = LiBr, B = $CaBr_2$?

(b) A = $CaBr_2$, B = LiBr?

(c) A = MgO, B = Fe_2O_3?

(d) A = MgO, B = NiO?

11.26 What defects will form in the crystals made by adding small amounts of compound A to compound B:

(a) A = $CdCl_2$, B = NaCl?

(b) A = NaCl, B = $CdCl_2$?

(c) A = Sc_2O_3, B = ZrO_2?

(d) A = ZrO_2, B = HfO_2?

Task 12:

What type of defects will dominate in the following compounds?

12.1. UO_{2+x} with CaF_2 type structure as starting point.

12.2. W_nO_{3n-1} with ReO_3 type structure for WO_3

12.3. AgCl with NaCl type structure

12.4. RbBr with NaCl type structure

12.5. $ZrC_{0.1}$ with hcp type structure as starting point

12.6. $Ni_{1-x}O$ as analog to $Fe_{1-x}O$ but with less non-stoichiometry.

12.7. $Mn_{1.1}Sb$ with partially filled NiAs-type structure

12.8. α-Fe with some dissolved carbon

12.9. $LaCoO_{2.98}$ with perovskite type structure

12.10. Pure Cu

Task 13:

13.1. Give representative formulas for solid-solubility phases between (i) Al_2O_3 and Cr_2O_3, (ii) NaCl and NaBr, (iii) Fe and Co, (iv) $LaCrO_3$ and $LaCoO_3$.

13.2. Explain how the volume will vary in these solid solubility phases under assumption that Vegards law applies. Sketch how positive deviations will appear. What can a positive deviation indicate?

13.3. Consider the solid solubility phase between MnAs and FeAs. MnAs have unit cell dimensions a = 570 pm, b = 360 pm and c = 630 pm. FeAs have unit cell dimensions a = 540 pm, b = 338 pm and c = 610 pm. A two phase area exists for the interval 20-50 mol% MnAs. Draw how the unit cell dimensions vary according to Vegards law.

Task 14:

14.1. What is meant by defect creating solid solubility?

14.2. Make examples for systems where (i) the concentration of cation vacancies in KCl increases (ii) concentration of Ag^+ interstitial in AgCl increases (iii) concentration of oxygen vacancies increases in ZrO_2 (iv) concentration of F- interstitial increases in CaF_2.