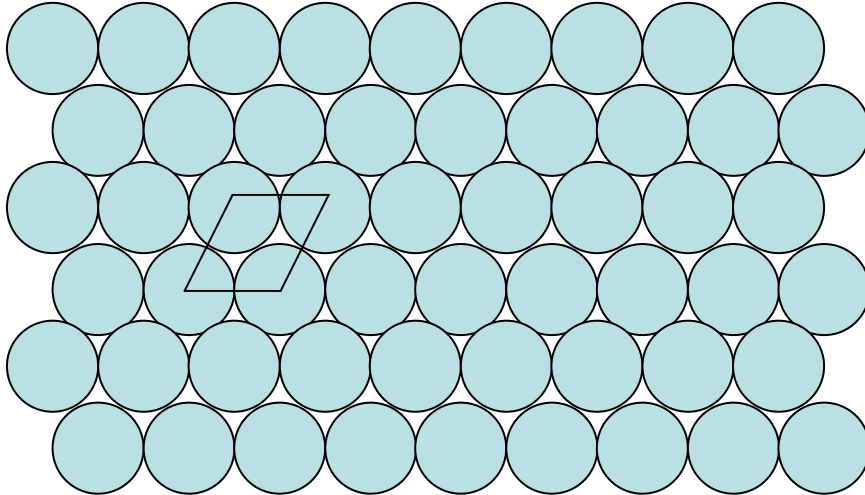**Solution manual for colloquium tasks for MEF 3000 / MEF 4000**

Task 1: Sphere packing

1.1. The two dimensional unit cell of a close packed layer is illustrated by the box below.

1.2. The length of the two axes in the unitcell above is identical, viz. |a| = |b|

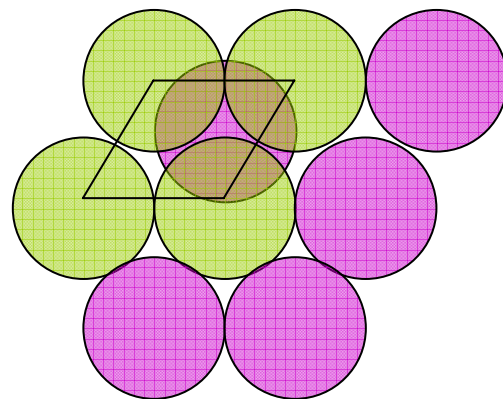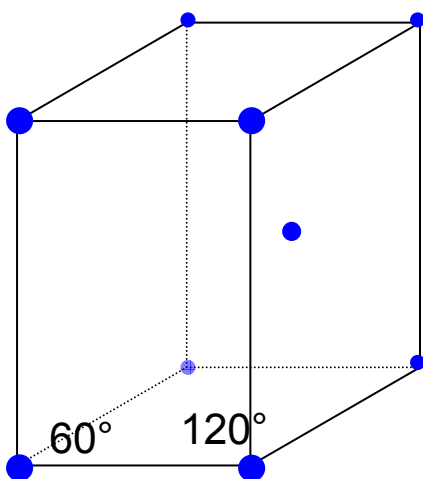The angle between the axes is by convention chosen to be 120° and not 60°.

The coordinates that represent the whole structure can be given by (0,0,0)

1.3. .
    B (1/3,2/3)
    C (2/3,1/3)

1.4. .

1.5. The real problem here is to calculate the height of a tetrahedra. The c-axis of a hexagonal close packed structure is equal to the height of two tetrahedrons. One approach (there are many) is shown below.

x is the height of a regular triangle
n is the shortest distance from the edge of the base to the center of the tetrahedra base.
m is as equal the longest distance.

The aim is to express m in terms of radius and use the 90 degree triangle m, 2r and height to find the height of the triangle.

First x is expressed in terms of r.
Then the relation of the two triangles r,m,n and x,2r,r is used to express m in terms of r.

This is used together with the 90 degree tiangle m,2r,height to find the height.
The height is equal to c/2, and a = 2r. The ratio is thus calculated.

$$x = (n + m)$$

$$x = \sqrt{4r^2 - r^2} = r\sqrt{3}$$

$$\frac{x}{2r} = \frac{r}{m} \Rightarrow m = \frac{2r}{\sqrt{3}}$$

$$\left(\frac{c}{2}\right) = \sqrt{4r^2 - \frac{4r^2}{3}} = r\sqrt{\frac{8}{3}}$$

$$c/a = \frac{2r\sqrt{\frac{8}{3}}}{2r} = \sqrt{\frac{8}{3}} \approx 1.632$$

1.6. (a) 1 octahedrahole and 2 tetrahedraholes
(b) 1 octahedrahole and 2 tetrahedraholes (with restrictions, only one in a pair filled at the same time), 1 trigonal bipyramidal hole
(c) 2 trigonal prismatic holes

Task 2:

2.1. Octahedra, tetrahedra and trigonal prismatic. There are restrictions concerning the tetrahedras and trigonal prismatic. Two tetrahedra make one trigonal prismatic hole, hence these can not be filled at the same time. Also T+ and T- tetrahedras can not be filled at the same time, hence only half of the tetrahedra holes can be filled at the same time.

2.2.

	All oct	all tetr	½ tetr.
hcp	NiAs	-	wurtsitt
ccp	NaCl	CaF_2	zink-blende

2.3. Consider 2-dimensional layers of dense packed spheres stacked along the c-axis. For …AB… packing: If all octahedra holes are filled one gets NiAs-structure. In this case every second layer should systematically be empty. One then obtains CdI_2 type structure. If the packing system had been according to …ABC… ccp packing, then $CdCl_2$ would have formed.

There will be strong bondings within the layers of (CdI6)4- octahedra connected along their edges. There will be weaker van der Waals forces between the layers I-I.

2.4. Regard a layer with filled octahedra holes as for the $CdCl_2$-type structure. Compare this with the densepacking layer in 1.1. Imagine that the darker (red) circles resemble empty octahedras while the others are filled. That is: around each empty hole there should be a ring of filled ones. ScCl3 is built of such layers with v.d. Waals forces between them.

2.5. Cs_2O is the anti-type for the CdI_2 type structure. Hence, the Cd-cation is replaced by O-anion, and I-anion by Cs-cation. In this structure, there will be Cs-Cs metal interactions. In the same way Na_2O is the anti type for the CaF_2 type structure.

2.6. Ni_2As

2.8. The structure is buildt of face sharing octahedra. Atoms in octahedra positions will feel repulsion or contractions from their same kind due to the short M-M distance. Pure metals has not got any atom in octahedra positions. Würtstitt-type phases has only filled half of the tetrahedra positions and they only share corners with other tetrahedra positions. These are too distant from each other to interact.

Task 3: Theme: Spherepacking and simple structures

3.1.
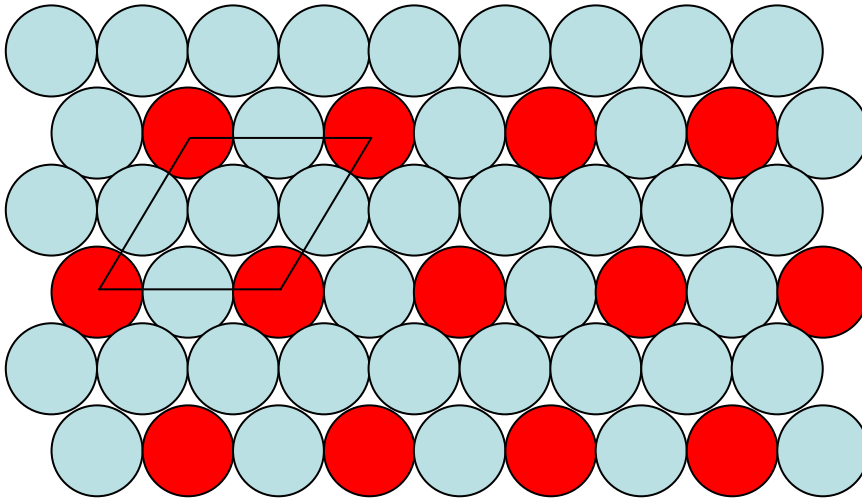
3.2. Generally for dense spherepacking: 1 octahedra hole pr. packing sphere. 4 packing spheres (1X and 3Y) will thus generate 4 octahedraholes.

3.3. 1 set of octahedra holes with only Y surroundings and 3 octahedra holes of X_2Y_4 where X are in trans positions.

3.4. There will be repulsion (unacceptable) if M is in contact with X sphere. Therefore only one set of octahedra holes are useful of those found under 1.3.

3.6.
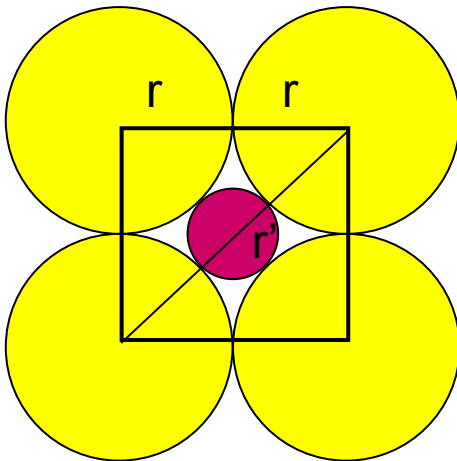
$(2r+2r')^2 = (2r)^2+(2r)^2 => \sqrt{8}\ r = 2r+2r'$

$r' = 0.5*(\sqrt{8}-2)r => 1.12\ \text{Å}$

3.7. Evaluate R_{kation} / R_{anion}:
$R_{Na+} / R_{O2-} = 0.929$
$R_{Nb5+} / R_{O2-} = 0.557$

In order to posses octahedra position: $0.414 < R_{kation}/R_{anion} < 0.732$.
Viz. Nb^{5+} in octahedra holes

3.8. Formula units: $Z = 1$
When $Z = 1$ the Bravais lattice must be primitive

3.9.
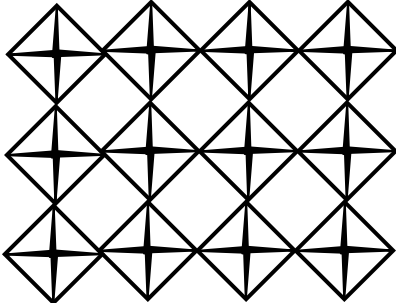
3.10. The coordiatnion for the cations in ABO_3 are:
A in octahedra hole surrounded by 6 oxygen.
B is together with oxygen a packing sphere and is surrounded by only oxygens, hence 12 coordination.

Together the cations make $6+12 = 18$ oxygen bonds. These are divided equally (vi at least assume so) between the different oxygens. Hence one oxygen has $18/3 = 6$ bonds. $(6/3 = 2)$ stem from A atoms and $(12/3 = 4)$ stem from oxygen.

This general case applies only for compounds with pure cation-anion bonds, hence no cation-cation or anion-anion bonds. Does not apply for metallic systems.

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

4.1. (a) M_2X_9
(b) M_2X_{10}
(c) M_2X_{11}
(d) M_3X_{12}
(e) M_3X_{13}

4.2. Al_2Cl_6, Two tetrahedra with one common edge.
$Cr_2O_7^{2-}$, Two tetrahedra with one common corner
Mn_2O_7, Two tetrahedra with one common corner
SO_3 , Infinite chains of cornersharing tetrahedras
CrO_3 , Infinite chains of cornersharing tetrahedras.

4.3. Isolated octahedra: MO_6
Limit: MO_5

4.4. (a) SiO_4^{4-} : Monomers of tetrahedras.
(b) $KAlSiO_4$ (both Al and Si adopts tetrahedra environments),
End up with effective $(Al,Si)O_2^{1-}$ composition. Expect then corner sharing tetrahedra in three dimensions.
(c) $Sc_2Si_2O_7$, $Si_2O_7^{6-}$ unit, expect dimeric tetrahedras sharing one common corner.

(d) $MnSiO_3$, SiO_3^{2-}, expect infinite chains or rings, that is 2 out of four corners are shared.

(e) $CaMgSi_2O_6$, $Si_2O_6^{4-}$, or SiO_3, expect infinite chains or rings, viz. Two out of four corners are shared.

(f) $CaAl_2(OH)_2(Si_2Al_2)O_{10}$, After removing the other cations one get: $(Si_2Al_2)O_{10}$, viz. M_4O_{10}, $MO_{2.5}$, Expect twodimensional layers where three out of four corners are shared.

4.5.   (a) SiO_4^{4-}
       (b) $Si_2O_7^{6-}$
       (c) SiO_3^{2-}
       (d) SiO_3^{2-}
       (e) $SiO_{2.5}^{1-}$
       (f) SiO_2

4.6.   The CdI_2 structure is built of edge sharing octahedra within twodimensional planes. One octahedra is connected to six other octahedras.

Task 5:

5.1.
       NaCl: Intuitively ionical bonding, small charge, large ions. Burt the structure type can also hold materials with some covalent character such as TiC.

       Zink Blende: Somewhat more covalent than würtsite, and more covalent than NaCl-type

       Fluorite: Ionic character.

   Würtsite: Somewhat covalent.

       NiAs: Covalent character.

       CsCl: Ionic.

5.2.   The NH_4^+ ions arrange themselves inside the cubes so that the four tetrahedrally coordinated hydrogens go towards each corner. Will then have two different sets of corners, four with hydrogen towards them and four without. This is done with a high degree of symmetry. At higher temperatures the ammonium ion rotates and becomes uniform.

Task 6:

6.1. $R_{Be}/R_O = 0.330$ Hence most suitable in a tetrahedral position with CN = 4
       $R_{Ca}/R_O = 0.91935$ Hence most suitable in CN=8, cubic positions or as a packing sphere, CN=12.
       $R_O/R_{Ba} = 0.8266$ Hence most suitable in CN=8, cube positions

6.2. The ratio of cation to anion in octahedra holes are calculated from:
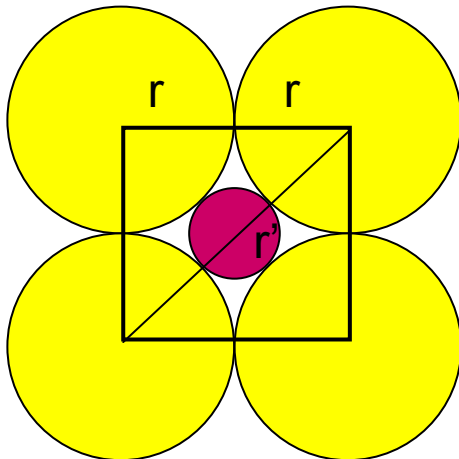
$(2r+2r')^2 = (2r)^2 + (2r)^2 \Rightarrow \sqrt{8}\, r = 2r+2r'$

$r' = 0.5*(\sqrt{8}-2)r \Rightarrow r'/r = 0.414$

It will not be beneficial that the cation is smaller than this ratio, since it would imply that anion-anion interactions occurred.

For CN = 8.

The length of a room diagonal in a cube can be expressed as $\sqrt{3}$ * cell edge. Cell edge is 2*r viz: room diagonal = $\sqrt{3}*2r = 2*(r+r')$

Viz. $r' = (\sqrt{3}-1)r \Rightarrow r'/r = 0.732$

6.3.

$S_{Ba} = 0.78, \Delta S_c^{Ba} = 1.93$
$S_O = 5.21, \Delta S_c^O = 4.75$

$Sb = \sqrt{(0.78*5.21)} = 2.016$

$\Delta S_{Ba} = 2.016 - 0.78 = 1.236$
$\Delta S_O = 5.21 - 2.016 = 3.194$

$\delta_{Ba} = 1.236/1.93 = \textbf{0.64}$
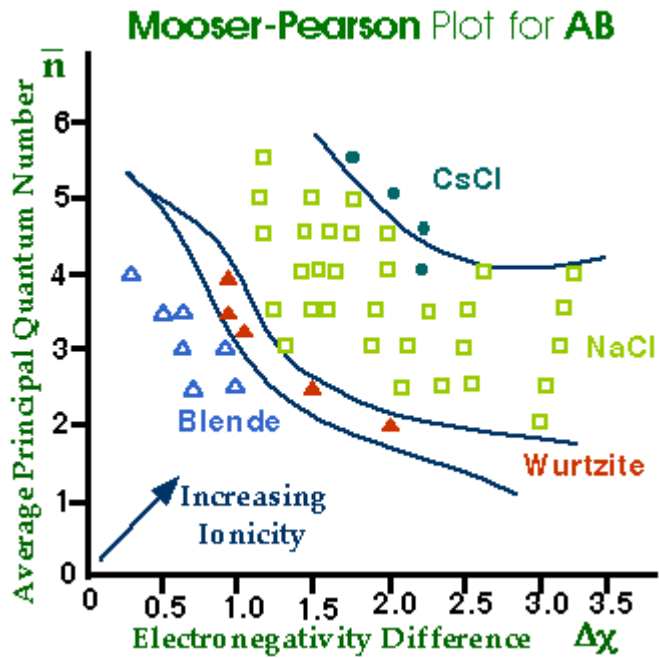$\delta_O = 3.194/5.21 = \textbf{0.61}$

6.4. The partial charge increases as the ionicity increases. The difference in electronegativity increases with the line Be-Sr. Also the possibility to polarize and ionize these cations increase.

6.5. Increasing degree of covalency as the charges increases on the ions. TiC is virtually a covalent materials while LiF is ionic.
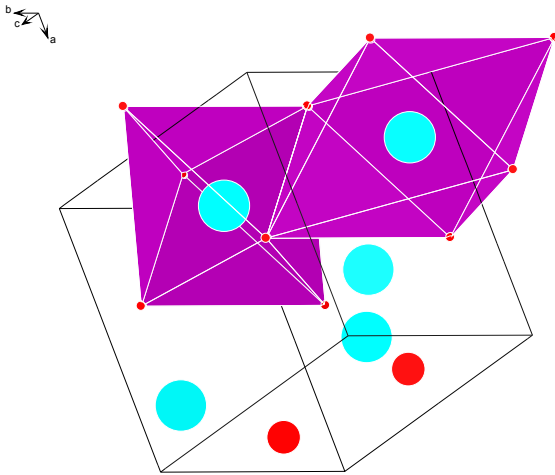
6.6. BeO, N = 2, $\Delta X = 1.5-3.5 = 2$, Wurtsitt

CaO, N = 3, ΔX = 1.0-3.5 = 2.5, NaCl
LiF, N = 2, ΔX = 1.0-4.1 = 3.1, NaCl
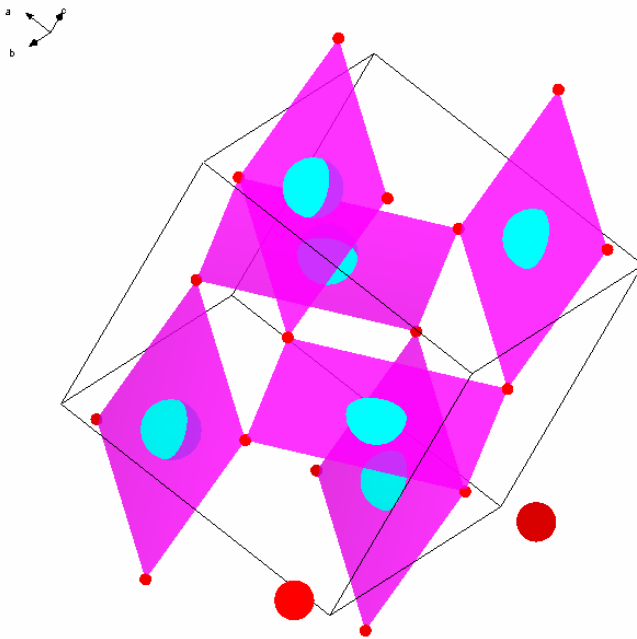TiC, N = 3, ΔX = 1.3-2.5 = 1.2, NaCl

Mooser-Pearson Plot for **AB**

6.7.   The structure for CuO is deformed due to that Cu has a Cu d^9 configuration and thus experiences a Jahn-Teller deformation.
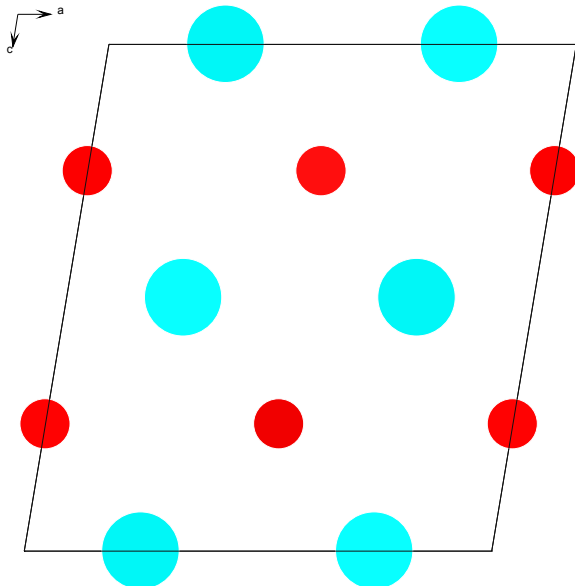
Cu-O: 2 x 1.947 Å + 2 x 1.948 Å + 2 x 2.766 Å
Rather enlongated octahedras or essentially square plannar geometry.

6.8.   Both Ni an Pt are d^8 elements in this oxidation state and expected to be influenced by Jahn-Teller distortion. However, this effect is stronger for the 4d (Pd) and 5d (Pt) elements than for 3d (Ni) elements. This is why PtO is distorted strongly and NiO not.

6.9.   Sn has valency of (+II) in this composition and hence one lone pair of electrons. (Sn can be oxidized to Sn^{4+}). This electron pair acts as an inert pair that takes up space in the structure.

Task 7:

7.1. $Fe(1) = a^3 = 2.8865^3 = 24.050\ Å^3$
      $Fe(2) = a^3 = 3.6660^3 = 49.269\ Å^3$
      $Fe(3) = a^3 = 2.9378^3 = 25.355\ Å^3$
      $Fe(4) = a^2*cos(30)*c = 20.473\ Å^3$

7.2. $Fe(1)$: Z = 2; V/Z = 12.025
      $Fe(2)$: Z = 4; V/Z = 12.317
      $Fe(3)$: Z = 2; V/Z = 12.678
      $Fe(4)$: Z = 2; V/Z = 10.236

7.3. $D = Z*m_v/N_A*V$
      Al (26.982 g/mol): Z = 4, V = a^3 = 4.0488^3 = 66.371 $Å^3$, D = 2.700 g/cm^3
      Mg (24.305 g/mol): Z = 2, V = $a^2*cos(30)*c$ = 46.461 $Å^3$, D = 1.737 g/cm3
      Fe (55.847 g/mol): Z = 2, V = a^3 = 2.8865^3 = 24.050 $Å^3$, D = 7.712 g/cm^3

7.4. Cu: Cubic F
      Mg: Hexagonal P
      W: Cubic I

7.5. Cu: Cubic F with Cu in (0,0,0), centrocymmetric
      Mg: Hexagonal P with Mg in (1/3,2/3,1/4 og 2/3,1/3,3/4), centrosymmetric
   W: Cubic I, with W in (0,0,0), centrosymmetric

7.6. $Fe(1)$: W : h+k+l = 2n
      $Fe(2)$: Cu : h+k=2n, h+l=2n, k+l=2n
      $Fe(3)$: W : h+k+l = 2n
      $Fe(4)$: Mg : 2h-hl = 2n, hhl = 2n, h-2hl = 2n

7.7. a) 6-fold screwaxis with ½ translation along the screwaxis
      b) 6-fold skruakse with ½ translation along the screwaxis and a mirrorplane normal to the screwaxis
      c) mirrorplane
      d) 3-fold rotoinversion axis
      e) glide mirrorplane with ½ translation along c-axis

7.8. 6/mmm

7.9.

6/mmm
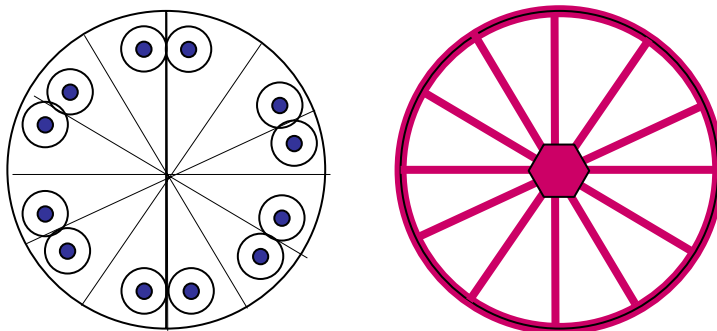
Special position lies on a symmetry element and is thus not multiplicated fully.
General position lies not on symmetry elements. In total 24 general positions.

Task 8:

8.1.   a≠b≠c, α=β=γ=90° => Orthorombic crystal system.
P notes primitive lattice.
Corresponding point group: mmm

8.2.   Z = 2

8.3.   Mg 4(g): (0.2903, 0.3901, 0), (0.7097, 0.6099, 0), (0.2097, 0.8901, 0.5), (0.7903, 0.1099,0.5)
C(1) 2(d): (0,0.5,0.5), (0.5,0,0)
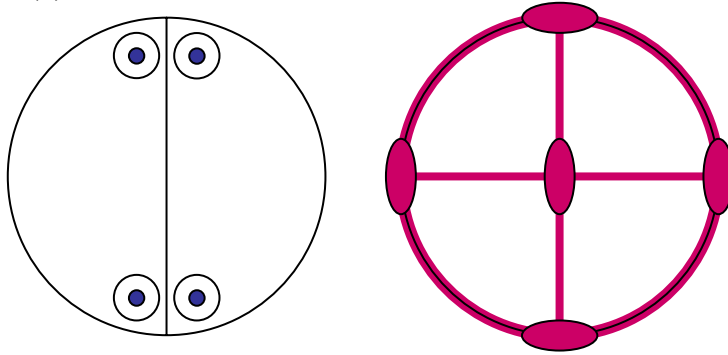C(2) 4(g): (0.1188, 0.2930, 0.5), (0.8812, 0.7070, 0.5), (0.3812, 0.7930, 0), (0.6188, 0.2070, 0)
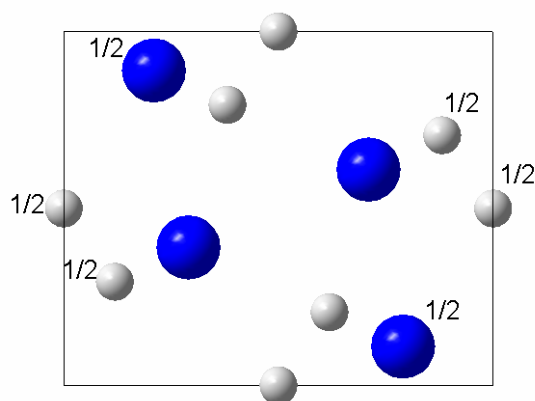
8.4.   Mg, m
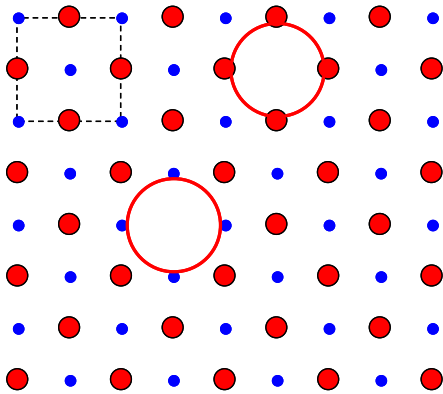C(1) 2/m
C(1) m

8.7.

8.8.   ½

8.9.

8.10. The distance between the C-atoms are: 1.332 Å
The geometry is a straight C-C-C chain.

The charge of a C$_3$ chain must be -4.
The isoelectronic gas molecule is H2C=C=CH2.
8.11.   The bonding characteristics is close to double bonds.

Sett 9:

9.1.   The (100) for NaCl-type structure

A cation vacancie is associated with a -1 charge.
An anion vacancie is associated with a +1 charge.

9.2. $N_V = N \cdot C \cdot e^{(-\Delta H/2RT)}$

$$\frac{N_{V(298K)}}{N_{V(1300K)}} = \frac{N \cdot C \cdot e^{(-\Delta H/2R(298K))}}{N \cdot C \cdot e^{(-\Delta H/2R(1300K))}} = \frac{e^{(-\Delta H/2R(298K))}}{e^{(-\Delta H/2R(1300K))}} = e^{(-\Delta H/2R(298K))-(-\Delta H/2R(298K))}$$

$$= e^{\Delta H/2R\left(\frac{1}{1300K}-\frac{1}{298K}\right)} = e^{200kJ\cdot mol^{-1}/2\cdot 8.314 J\cdot K^{-1}mol^{-1}\left(\frac{1}{1300K}-\frac{1}{298K}\right)} = 3.08\cdot 10^{-14}$$

Note: The book "Understanding solids…" disregards the constant C.

9.3.   In one mole NaBr there are 6.022·10^{23} NaBr units.
There are thus 6.022·10^{13} NaBr units per defect.
There are four NaBr formula units per unit cell, which gives 6.022·10^{13} / 4=
1.506·10^{13} unitcells per defect. These may make a supercell with cell lengths of
$^3\sqrt{1.506\cdot 10^{13}}$ = 24692 unitcells. This is the average distance between the Schottky
defects.

9.4.   At 1300K the number of defects per atom becomes:

$$\frac{N_V}{N} = e^{(-\Delta H/2RT)} = e^{-200kJ\cdot mol^{-1}/2\cdot 8.314 J\cdot K^{-1}mol^{-1}\left(\frac{1}{1300K}\right)} = 9.6\cdot 10^{-5}\ \frac{defects}{atom}$$

There goes 8 atoms per unitcell -> 7.7·10^{-4} defects/unitcell
The inverse of this number gives number of unitcell/defect = 13021 unitcell/defect
The size of the supercell becomes: $^3\sqrt{13021}$ = 24 unitcells.

24 unitcells may seem a long distance, but considering that it is a relatively high

temperature so that the mobility is high, it is a large probability that these defects will interact with each other and form clusters.

However at room temperature and for the situation in 1.3. is should be reasonable to assume point defects.
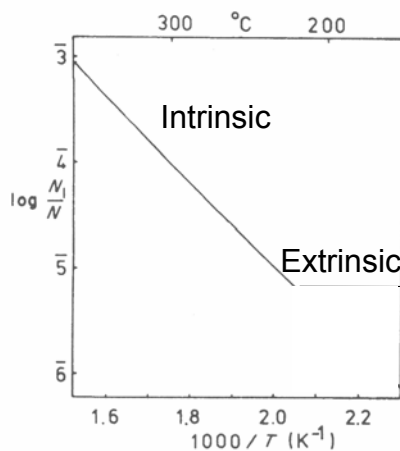
Note: KBr melts at 734 °C. = 1007 K

9.5.   Na-Vacancies: $Na_{1-2x}Mn_xV_xBr$

Insert $x = 0.005$:

Na-Vacancies: $Na_{0.99}Mn_{0.005}V_{0.005}Br$

9.6.

9.7.   By introduction of Mn^{2+}, the amount of vacancies will increase. Since these vacancies contribute to the conduction mechanism, the conduction should therefore increase.

Task 10:

10.1.   Frenkel defects will dominate.

10.2.   Na must enter tetrahedral holes, and there are totally 8 tetrahedral holes in a unitcell of NaBr.

The possible movement paths are to enter a tetrahedral position and then to exit it through another face. The most open paths are through the faces constructed by three anions.

10.4.   AgBr should have the largest ionic conductivities. The fact that Frenkel defects dominate for this compound indicates that it is not that hard for the cations to enter the tetrahedral positions. This helps the diffusion.

Task 11:

11.7 Use the Arrhenius dependency and note that nickel is a charge neutral metal so that vacancies can be formed alone, viz. does not have to be formed in pairs as is the case for ionic compounds.

$$\frac{N_V}{N} = e^{(-\Delta H/RT)} = e^{-97.3kJ \cdot mol^{-1} / 8.314 J \cdot K^{-1} mol^{-1} \left(\frac{1}{1373K}\right)} = 1.99 \cdot 10^{-4} \frac{defects}{atom}$$

11.10 First find the fraction of vacancies in this metal:

$$\frac{N_V}{N} = e^{(-\Delta H/RT)} = e^{-72.4kJ \cdot mol^{-1} / 8.314 J \cdot K^{-1} mol^{-1} \left(\frac{1}{873K}\right)} = 4.65 \cdot 10^{-5} \frac{defects}{atom}$$

How many atoms are there per m^3?

Molar weight of Al is: 26.98 g/mol:

Number of atoms in 1 m^3 = N_A*2698 kg m^{-3} / 26.98 g mol^{-1} = 6.022 10^{23} atoms mol^{-1} * 100000 mol m^{-3} = 6.022 10^{28} atoms m^{-3}.

The number of defects will then be: 6.022 10^{28} atoms m^{-3} * 4.65 10^{-5} defects $atom^{-1}$ = 2.80 10^{24} defects m^{-3}.

11.11

$$\frac{N_V}{N} = e^{(-\Delta H/2RT)} = e^{-244kJ \cdot mol^{-1} / 2 \cdot 8.314 J \cdot K^{-1} mol^{-1} \left(\frac{1}{T}\right)}$$

11.14

From the table 3.4 one notes that ΔH_f = 1.81 10^{-19} J

By multiplying with N_A one obtaines the molar value = 6.022 10^{23} * 1.81 10^{-19} = 109 kJ/mol.

The volume of one unit cell is $(0.576 \text{ nm})^3$ = 1.911 10^{-28} m^3

The number of cells in one m^3 is the inverse of this = 1/(1.911 10^{-28} m^3) = 5.23 10^{27} cells m^{-3}. The number of interstitial positions are four times this number = 2.09 10^{28}. Note that there is an equal number of silver atoms as interstitial positions and $(N*N')^{1/2}$ thus becomes N.

The fraction of defects are given by:

$$\frac{N_V}{(N \cdot N')^{1/2}} = e^{(-\Delta H/2RT)} = e^{-109kJ \cdot mol^{-1} / 2 \cdot 8.314 J \cdot K^{-1} mol^{-1} \left(\frac{1}{673K}\right)} = 3.24 \cdot 10^{-10}$$

The absolute number of interstitial defects are then given by: 3.24 10^{-10} * 2.09 10^{28} m^{-3} = 6.78 10^{18} m^{-3}

11.20 The volume of one unit cell is $(0.417 \text{ nm})^3$ = 7.251 10^{-29} m^3

The number of cells in one m^3 is the inverse of this = 1/(7.251 10^{-29} m^3) = 1.379 10^{28} cells m^{-3}. The number of possible number of nickel vacancies are four times this number = 5.52 10^{28}. Multiplying this with the fraction 1.25 10^{-4} gives the number of vacancies of 6.9 10^{24} m^{-3}.

11.23 By taking a basis that 1 mol% is 1 mol one gets:

9 mol% Y_2O_3 = 18 mol Y and 27 mol O

91 mol% ZrO2 = 91 mol Zr and 182 mol O

This gives something with a composition of: $Y_{18}Zr_{91}O_{209}$

We note that Y^{3+} substitutes for Zr^{4+} and the charge is compensated by making anion vacancies. The sum of the metal composition should therefore be 1. We divide the composition by (18+91) = 109 and obtains $Y_{0.165}Zr_{0.835}O_{1.917}$

Hypothetically: Another charge compensating mechanism would be to make cation interstitials. In this case it would be the Zr^{4+} ions that should go to interstitial positions. The O lattice should remain intact and given the value 2. This can be obtained by dividing the first obtained composition by 209/2 = 104.5 and obtain: $Y_{0.172}Zr_{0.871}O_2$

11.24 By taking a basis that 1 mol% is 1 mol one gets:

10 mol% CaO = 10 mol Ca and 10 mol O

90 mol% Bi_2O_3 = 180 mol Bi and 270 mol O

This gives something with a composition of: $Ca_{10}Bi_{180}O_{280}$

We note that Ca^{2+} substitutes for Bi^{3+} and the charge is compensated by making anion vacancies. The sum of the metal composition should therefore be 1. We divide the composition by (10+180) = 190 and obtains $Ca_{0.05263}Bi_{0.9473}O_{1.4737.}$ However, we want to have the formula on the same form as Bi_2O_3 and thus multiplies it by two, obtaining: $Ca_{0.105}Bi_{1.895}O_{2.947}$

The difference in charge between Bi^{3+} and Ca^{2+} is +1, and the charge compensated by each vacancy (O^{-2}) is -2. The number of vacancies are thus half of the Ca content, viz. 0.105/2 = 0.0526.

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

(a) A = LiBr, B = $CaBr_2$? -> Li^+ substitutes for Ca^{2+} giving Br^- vacancies.

(b) A = $CaBr_2$, B = LiBr? -> Ca^{2+} substitutes for Li^+ giving Li^+ vacancies.

(c) A = MgO, B = Fe_2O_3? -> Mg^{2+} substitutes for Fe^{3+} giving O^{2-} vacancies.

(d) A = MgO, B = NiO? -> Mg^{2+} substitutes for Ni^{2+}

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? -> Cd^{2+} substitutes for Na^+ giving Na^+ vacancies

(b) A = NaCl, B = $CdCl_2$? -> Na^+ substitutes for Cd^{2+} giving Cl^- vacancies

(c) A = Sc_2O_3, B = ZrO_2? -> Sc^{3+} substitutes for Zr^{4+} giving O^{2-} vacancies

(d) A = ZrO_2, B = HfO_2? -> Zr^{4+} substitutes for Hf^{4+}

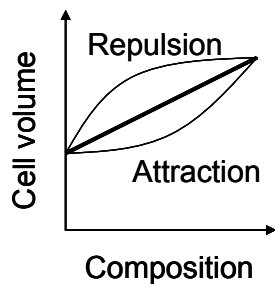**Task 12:**

12.1. UO_{2+x} with CaF_2 type structure to begin with.
Anion interstitials
12.2. W_nO_{3n-1} with ReO_3 type structure for WO_3
Crystallographic shear defects where all anion vacancies are located in defined planes. This collapses the structures in this region.
12.3.   AgCl with NaCl type structure
Frenkel defects
12.4.   RbBr with NaCl type structure
Schottky defects
12.5. $ZrC_{0.1}$ with hcp type structure to begin with
Carbon interstitials
12.6. $Ni_{1-x}O$ as analog $Fe_{1-x}O$ but with a smaller extent of none stoichiometry.
Cation vacancies together with cation interstitials.
12.7. $Mn_{1.1}Sb$ with partly filled NiAs-type structure.
Mn goes in to additional trigonal bipyramidal holes. This approaches the Ni_2In type structure.
12.8. α-Fe with some dissolved carbon
Cation interstitials
12.9. $LaCoO_{2.98}$ with perovskite type structure
Anion vacancies
12.10. Rent Cu
Long range defects such as edge defects, line defects and further.

Task 13:

13.1.   (i) Al_2O_3 and Cr_2O_3,
$Al_{2-x}Cr_xO_3$
(ii) NaCl and NaBr,
$NaCl_{1-x}Br_x$
(iii) Fe and Co,
$Fe_{1-x}Co_x$
(iv) $LaCrO_3$ and $LaCoO_3$.
$LaCr_{1-x}Co_xO_3$
13.2.

A positive deviation indicates repulsion in the solid solution.

13.3.

Task 14:

14.1.
If the solid solubility involves end members that have different placements of the

atoms in the base structures, then a solid solubility will induce intermediate situations that can be regarded as defects. If the solubility is by aliovalent substitution, then defects must be created in order to preserve the charge neutrality.

14.2. (i) $K_{1-2x}Ca_xCl$

(ii) AgCl with increasing temperature.

 Or $AgCl_{1-2x}O_x$

(iii) $Zr_{1-x}Ca_xO_{2-x}$

(iv) $Ca_{1-x}Y_xF_{2+x}$