Module I FYS3410 SPRING 2017

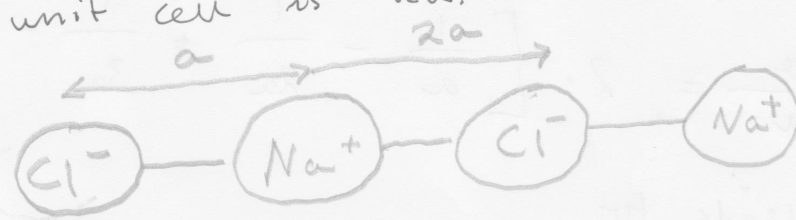
Candidacy number: 15

Assignment 1 a) The basis and unit cell for lattice

The basis is the set of atoms to be placed on each point of the lattice. In this case the basis is the Na^+ and Cl^- - ions.

For the unit cell we also define the lattice. And this leads us to:

The unit cell in (a) is a one-dimensional lattice. Since the distance between a Na^+ and Cl^- is = a, it gives that the distance between each unit cell is 2a.



b) An analytical expression for Madelung constant:

We are to derive an analytical expression for the Madelung constant, α.

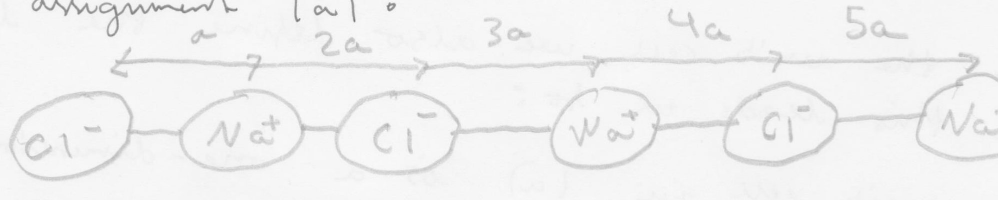
According to Kittel's book the definition of the Madelung constant is given by

$$\frac{\alpha}{R} = \sum_j{}' \frac{(\pm)}{r_j}$$

We place a negative ion as the reference point and the pluss sign will assign to the positive ion, while the negative one will be given to negative ions.

Furthermore, r_j, is the jth ion from the reference point and R is the nearest-neighbour distance.

This gives us bases on the figure below (taken from assignment 1a):



(Rough sketch)

We then get

$$\frac{\alpha}{a} = 2 \cdot \left[\frac{1}{a} - \frac{1}{2a} + \frac{1}{3a} - \frac{1}{4a} \pm \dots \right]$$

which leads to

$$(1) \quad \alpha = 2 \left[1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} \pm \dots \right]$$

The 2 factor is due to the fact that there are 2 ions (one to the left and one to the right at equal distance r_j)

(1) suggests that we have a series. And we that the alternating series converges if a_n decreases ($a_n > a_{n+1}$) and goes towards zero.

This gives us

$$(2) \quad \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n} \quad \text{(from basic mathematics)}$$

This is a rather common serie and is also found in the mandatory formula-book Rottmann for example, as well as in the curriculum.

The sum is therefore equal, from Rottmann, to $\ln 2$. And from (1) we get the answer:

$$\underline{\underline{\alpha = 2 \ln 2}} \quad \text{(we added the 2 factor}$$

c) We have to plot the evolution of the Madelung constant and analyze the trend for the corresponding cohesive energy evolution.

We use (2), but multiply it with the factor 2, to get the Madelung constant, to plot in Matlab. The code for Madelung constant evolution follows below.

$$\alpha = \frac{2 \cdot (-1)^{n+1}}{n} \quad \text{(the function)}$$

```
function [Madelung] = mad
    n = 1:50;
Madelung = 2*((-1).^(n+1)./(n));
plot(Madelung, 'r');
```

title ('Evolution of Madelung constant as a function of Unitcell size');

xlabel ('Unitcell');
ylabel ('Madelung');

The xlabel, ylabel and title were written on to the graph by using the insert - function on the figure tab. Plot itself follows as attachment 1.

Corresponding cohesive energy evolution:

The next part was to analyze the trend for the corresponding energy evolution.

Cohesion energy is the sum of the Coulomb (Madelung) and repulsion energy. Below is the coding and graph as attachment.

```
function [latticeenergy] = lattice
 z = 2;
 L = 1000; (eV)
 p = 0,32; (Å)
 R = 2,82; (Å)
 n = (1:50);

Madelung = 2* ((-1).^(n+1)./(n));

M = Madelung;

latticeenergy = (z*L*exp(-R/p) - (M))/(R);

plot (latticeenergy, 'b');
xlabel ('Unit cell');
ylabel ('Cohesive energy [eV]);
title ('Cohesive energy evolution');
end
```

d) From previous courses in material science / Chemistry it is explained that one can achieve equilibrium separation by minimizing the energy, and vice versa (implying that equilibrium distance gives minimal energy).

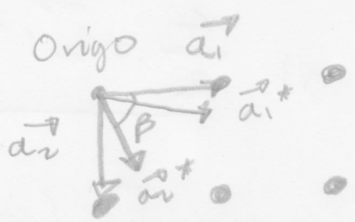
So therefore minimum energy should be a condition. From the graph in attachment 2, we also see that when the number of unitcells increases the equilibrium distance decreases since the crystal becomes more stabil.

Dessverre fikk jeg ikke tid til å legge til koden her.

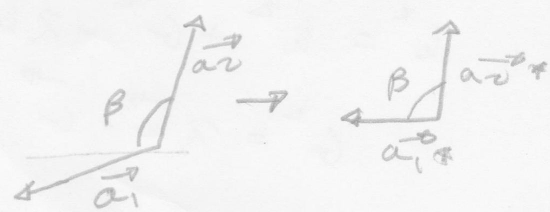
Assignment 4 a) The Miller indices are:

1. $(0\,2\,0)$
2. $(1\,2\,0)$
3. $(0\,1\,0)$
4. $(2\,1\,0)$
5. $(2\,0\,0)$
6. $(1\,0\,0)$

b) We are to make a drawing representing reciprocal lattice points corresponding to the planes in Fig 3. From



Lets put it this way



When we make the reciprocal lattice, we have to make sure that it contains the $\vec{a_1}$ and $\vec{a_2}$ vectors, but on the plane.

This leads to the planes

B) Since the wavevector is used, we understand that the Laue-condition is relevant for evaluating diffraction.

So that means that we have to show that the Laue-condition is not fulfilled.

Constructive interference occurs when $\vec{G} = \vec{k}' - \vec{k}$.

Since $\vec{k}' - \vec{k}$ is a reciprocal vector, so is $\vec{k} - \vec{k}'$.

We get

$$\vec{k} - \vec{k}' = G \Rightarrow \vec{k}' = \vec{k} - G$$

$$|\vec{k}| = |\vec{k}'| = |\vec{k} - \vec{G}| \quad \left(\begin{matrix}\text{Vi tar kvadratet på} \\ \text{begge side}\end{matrix}\right)$$

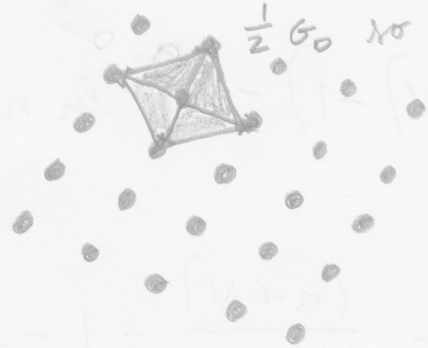
$$k^2 = k^2 + G^2 - 2\vec{k}\cdot\vec{G}$$

$$G^2 = 2\vec{k}\cdot\vec{G} \quad \text{som blir til} \quad \underline{\frac{G}{2} = \vec{k}\cdot\frac{\vec{G}}{G}} \quad (3)$$

(3) gives that the wave vector $\vec{k}$ (in our case $\vec{k}_g$) along the reciprocal lattice vector $\vec{G}$ must be half of the length of $\vec{G}$. Thereby $\vec{k}_g < \frac{1}{2}\vec{G}$ means no diffraction.

d) Basically the rule is valid for alle reciprocale points as long as the criteria of $\frac{1}{2}|\vec{G}|$ is fullfilled. Only projection to an another side is different. This gives us that $\frac{1}{2}|\vec{G}_{hkl}|$ for all G_{hkl}.

Now, we are to draw Brillouin zone concept for the same figure.



Assignment 7 a) We are to show that the minimum free energy in a crystal having N sites is reached only when a certain number of vacancies (n) are available.

We have the formula for free energy

$$G = U - TS + PV$$

Given that there is a crystal with $N+n$ latticepoints, since N represents atoms and n represents vacancies.

$V = (N+n)V_0$ where V_0 is the volume for each lattice point.

From statistical thermodynamics we have that W = configurationally distinct states

We place n vacancies in a $N+n$ lattice.

$$W = \binom{n+N}{n} = \binom{n+N}{N} = \frac{(n+N)!}{n!\,N!}$$

So we use $\ln x! \approx x(\ln x - 1)$ (3)

This leads us to Boltzmanns entropy law:

$$S = k_B \cdot \ln W \Rightarrow \frac{S}{k_B} = \ln W$$

$$\frac{S}{k_B} = \ln (n+N)! - (\ln n! + \ln N!)$$

Implementing (3) gives:

$$\frac{S}{k_B} = ((n+N) \cdot \ln (n+N) - 1) - (n \ln n - n$$

$$+ N \ln N - N)$$

$$\frac{\partial S}{\partial n} = k_B \left(\ln (n+N) - \frac{(n+N)}{n+N} - 1 - \ln n \right.$$

$$\left. -1 + 1 \right) = k_B \left(\ln \left(\frac{n+N}{n} \right) \right)$$

Equilibrium at $\frac{\partial G}{\partial n} = 0$

$$\ln \frac{(n+N)}{n} = \frac{\ln N}{n} \text{ for } N \gg n$$

that further gives

$$\frac{\partial G}{\partial n} = E_V - k_B T \cdot \ln \left(\frac{N}{n} \right) + PV_0 = 0$$

$$\Rightarrow n = N e \left(-\frac{PV_0 + E_V}{k_B T} \right)$$

b) The assignment is to derive an expression for the equilibrium concentration of vacancies (C_v).

We have that $C_v = \dfrac{n}{N}$ and from the previous assignment, we get:

$$C_v = e\left(-\frac{PV_0 + E_v}{k_B T}\right)$$

We can add an isotropic stress and get $\sigma = -P$ (for example like for hydrostatic stress).

This gives us

$$\underline{\underline{C_v = e\left(\frac{\sigma V_0 + E_v}{k_B T}\right)}}$$

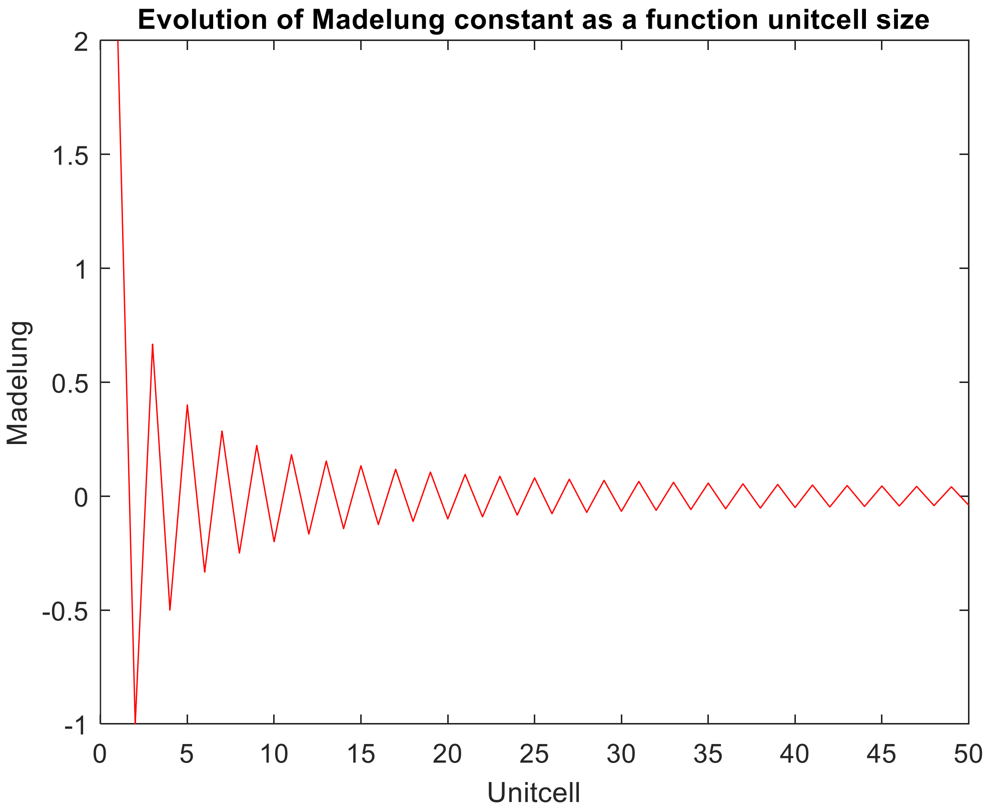
c) Activation energy can be calculated from the diffusion coefficients given by: $D = D_0 \exp(-E/k_B T)$ where E = activation energy. During

Energy is required to move neighbouring atoms elastically. That amount for the vacancy is called Activation energy.

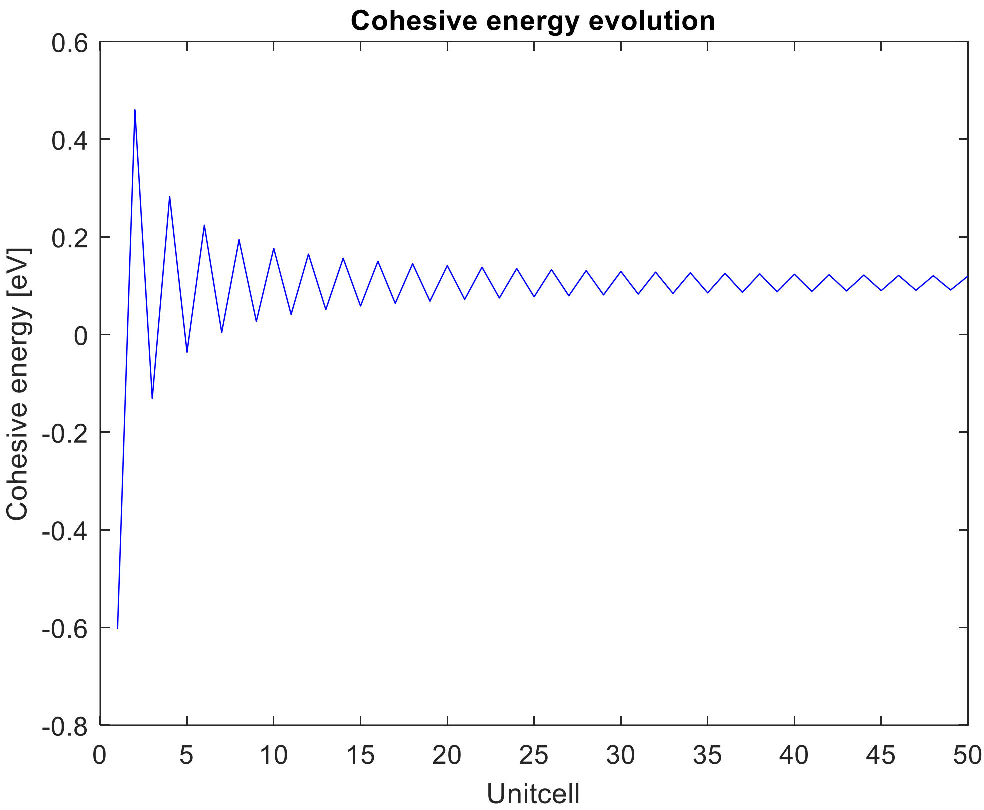
Activation volume is that at high temperatures more energy will be added, so that more vacancies are made.

ATTACHMENTS:

Graf 1:



Graf 2:



Cohesive energy evolution
Cohesive energy [eV]
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
0
5
10
15
20
25
30
35
40
45
50
Unitcell