University of Zurich[UZH]

Solid State Physics
Exercise Sheet 4
Crystal Binding

HS19
Prof. Dr. Marta Gibert

Assistant: Gabriele De Luca

Received on 11th October
Discussed on 18th October

Noble gas crystals

Exercise 1 *Lennard-Jones potential*

1. Show that for a potential of the form $U(R) = -\frac{A}{R^m} + \frac{B}{R^n}$ an equilibrium structure can only be reached if $n > m$.
2. The potential energy of attraction between two atoms of noble gas separated by a distance R is of the form $\frac{A}{R^6}$ (van der Waals attraction) and the repulsive energy due to the overlapping of electronic orbitals is of the form $\frac{B}{R^{12}}$. The Lennard-Jones potential has the form:
$$U(R) = 4\epsilon\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right]. \tag{1}$$
Calculate the binding energy (cohesive energy) E_{B} and the equilibrium distance R_0 and describe qualitatively the role of ϵ and σ
3. Calculate the binding energy for a BCC and an FCC lattice

Ionic crystals

Exercise 2 *1D chains*

1. Consider a very long row of equidistant ions with alternating charges of $\pm 2q$. Determine the Madelung energy for an ion placed at the center of the chain and for another at the end.
2. Consider a linear crystal with the following basis: an ion A with charge $-2q$ at 0 and two ions B with charge $+q$ symmetrically located relative to A at 1/4 and –1/4. Find the Madelung energy at position A and position B.
(Hint: it is useful to regroup the terms BAB to evaluate the series...)

Exercise 3 *Stability of crystals*

In the alkali halides one can assume that the ions are hard spheres of radius r_+ (cation) and r_- (anion).

1. What inequality should the ratio r_-/r_+ satisfy so that in a simple cubic structure of CsCl type (basis 1 Cs at (0,0,0) and 1 Cl at (½,½,½)), the + and - ions are in contact along the diagonal without the largest Cl^- ions overlapping at the corners of the cube?
2. What inequality should the ratio r_-/r_+ satisfy so that in the FCC lattice of the NaCl type (basis 1 Na at (0,0,0) and 1 Cl at (½,0,0)), the ions of opposite signs located along the [100] direction are in contact without overlapping the biggest ions Cl^- located along the [110] direction?
3. Suppose that both CsCl and NaCl can crystallize in either a simple cubic lattice or a FCC lattice. For both hypotheses, find the distance R_0 between nearest neighbors of opposite signs and the lattice parameter a of the cube.
   Use $r_+(Na^+) = 0.98$ Å; $r_+(Cs^+) = 1.67$ Å; $r_-(Cl^-) = 1.81$ Å as ionic radius.
4. In the alkali halides the binding energy E_B can be approximately described by

$$E_B = (\frac{\alpha e^2}{4\pi\epsilon_0 r_0})(1 - \frac{\rho}{r_0}) \quad (2)$$

   where α is the Madelung constant and $\rho = 0.345$ Å. For both CsCl and NaCl, find the value of the ratio of cohesive energies for both simple cubic (SC) and face-centered cubic (FCC) lattices. Use $\alpha(SC) = 1.7626$; $\alpha(FCC) = 1.7476$. Discuss the results.