Experimental Physics 5 – Solid State Physics
WS23/24, Uni Leipzig | Prof. Alexander Tsirlin

Problem sheet 4: Bonding in crystals | **1.11.2023**

4.1. Pauling's exercise (4 P)

Help Linus Pauling to assess the structure of ionic crystals.

(a) Derive the minimum ratio of the cation and anion ionic radii (r_+/r_-) that allow the stable tetrahedral, octahedral, and cubic coordination of the cation.

(b) Use Pauling's rule and Shannon's ionic radii (for example, here) to determine the likely structure type(s) of the following compounds: KBr, TlI, and ZnTe. Consider the structure types discussed in the lecture: rocksalt, zinc blende, and CsCl-type.

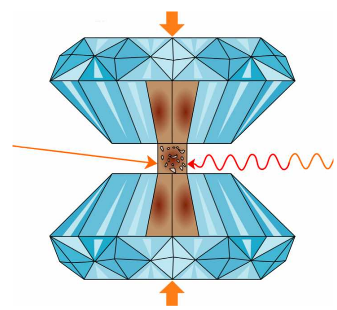
4.2. Combustion exercise (3 P)

Compute lattice energies of CaF_2, SrF_2, BaF_2 using their formation enthalpies of, respectively, -1228.0, -1216.3, and -1207.1 kJ/mol, as measured in combustion experiments. Explain the trend.

You will need ionization potentials and other thermodynamic parameters. They should not be hard to find.

4.3. Compression exercise (6 P)

(a) Express lattice energy of an ionic, rocksalt-type crystal A^+B^- as



$$E(r) = -\alpha e^2/(4\pi\varepsilon_0 r) + C/r^m$$

(per ion pair) and derive the corresponding bulk modulus. Follow the method used in lecture 8 for van der Waals crystals, but beware of prefactors. They are key to your success!

(b) Use the experimental bulk moduli for NaF (48 GPa), NaCl (24 GPa), NaBr (20 GPa), and NaI (15 GPa) to determine the m values for different anions. Explain the trend.

(c) Compute lattice energies (Madelung energy + repulsive energy, Born-Landé equation) for the aforementioned compounds.

4.4. Bonding exercise (3 P)

Retrieve the crystal structure of bromine. Analyze interatomic distances, identify the main covalent and van der Waals bonds assuming the covalent radius of 1.14 Å and the van der Waals radius of 1.85 Å for bromine.

You can list the interatomic distances and bond types, or plot the crystal structure with different bonds and paste the figure into your solution.

4.5. Van der Waals exercise (4 P)

Consider crystals of noble gases with the interatomic potential of the form $-A/r^6 + B/r^{12}$.

(a) Estimate A and B for neon, argon, and xenon using the lattice energies of -27 meV/atom, -89 meV/atom, and -172 meV/atom, respectively. Explain the trend.

(b) Determine an expression for the bulk modulus in terms of σ and ϵ at zero pressure and estimate the bulk modulus for neon, argon, and xenon.

The noble gases crystallize in the fcc structure. The corresponding lattice sums are $A_6 = 14.45$ and $A_{12} = 12.13$. You will also need lattice constants. Use the experimental values from the database taken at $4-5\,\mathrm{K}$.