Crystal Structure

CRYSTAL BINDING
Lecture 7

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Crystal Binding (cont)

3.5.1 Energy of van der Waals Solid

Convert from pair-wise interactions by summing over all pairs.

- **pick an atom, label it 0,**
- **let energy of interaction of this atom with neighbour i at a distance r_i be $U(r_i)$**
- **total potential energy of the atom is**

$$U_0 = \sum_i U(r_i)$$

- **if there are N atoms altogether, each will have this same energy – but interaction $0 - i$ is the same as $i - 0$**
- **so total energy is**

$$U = \frac{N}{2} \sum_i U(r_i).$$

Separate structure (spatial arrangement) from scale (interatomic separation).

- **write $r_i = \rho_i r_0$, where r_0 is nearest neighbour distance, ρ_i is dimensionless**
- **then**

$$U(r_i) = 4\epsilon \left[\frac{1}{\rho_i^{12}} \left(\frac{\sigma}{r_0} \right)^{12} - \frac{1}{\rho_i^6} \left(\frac{\sigma}{r_0} \right)^6 \right].$$

- **summing,**

$$U = 2N\epsilon \left[A_{12} \left(\frac{\sigma}{r_0} \right)^{12} - A_6 \left(\frac{\sigma}{r_0} \right)^6 \right],$$

where

$$A_n = \sum_i \frac{1}{\rho_i^n}.$$

- **these lattice sums can be done for any structure.**

Structure	A_{12}	A_6
FCC	12.12188	14.45392
HCP	12.13229	14.45489
BCC	9.11418	12.25330

Note:

- **expect sum of $1/r^n$ to converge rapidly for large n**
- **A_{12} is dominated by the nearest neighbours (10 in FCC, HCP, 8 in BCC), but more distant neighbours affect A_6**

3.5.2 Equilibrium Separation

The equilibrium structure minimises the total energy: $\partial U/\partial r_0 = 0$.

$$\frac{\partial U}{\partial r_0} = -2N\epsilon \left[12A_{12}\frac{\sigma^{12}}{r_0^{13}} - 6A_6\frac{\sigma^6}{r_0^7} \right],$$

which is zero when

$$\frac{r_0}{\sigma} = \left(\frac{2A_{12}}{A_6} \right)^{1/6}$$

$\frac{r_0}{\sigma} = 1.09$ for FCC.

$$U = -\frac{A_6^2}{2A_{12}}\epsilon \quad \text{per atom.}$$

Typically about 0.01 to 0.1 eV per atom.

3.5.3 Choice of Structure

Expect structure to form crystals which have lowest energy, i.e. largest cohesive energy.
Strictly, Gibbs free energy,

$$G = U - TS + pV,$$

but assume $T = 0$ and $p = 0$. Neglect kinetic energy of atomic motion

	SC	BCC	HCP	FCC
A_6	8.4	12.25	14.45	14.45

in U.
	SC	BCC	HCP	FCC
A_{12}	6.2	9.11	12.13	12.12
$\frac{U}{N\epsilon}$	-5.69	-8.24	-8.61	-8.62

Note how close FCC and HCP are in energy – but FCC is favoured.

3.5.4 Bulk Modulus

We know energy as a function of separation: need to express as function of volume. For FCC structure, cubic lattice parameter a, nearest-neighbour separation $r_0 = a/\sqrt{2}$. Cubic unit cell, volume a^3, contains 4 atoms, so

$$\text{Volume per atom} = \frac{a^3}{4}$$
$$= \frac{r_0^3}{\sqrt{2}}.$$

Now we could use

$$\frac{\partial}{\partial V} = \frac{\partial r_0}{\partial V}\frac{\partial}{\partial r_0}$$

but it's easier to substitute

$$r_0 = 2^{1/6}V^{1/3}N^{-1/3}$$

in

$$U = 2N\epsilon \left[A_{12}\left(\frac{\sigma}{r_0}\right)^{12} - A_6\left(\frac{\sigma}{r_0}\right)^6 \right],$$

to get

$$U = 2N\epsilon \left[A_{12}\frac{\sigma^{12}N^4}{4V^4} - A_6\frac{\sigma^6 N^2}{2V^2} \right]$$

and hence

$$\frac{\partial^2 U}{\partial V^2} = 2N\epsilon \left[A_{12}\frac{20\sigma^{12}N^4}{4V^6} - A_6\frac{6\sigma^6 N^2}{2V^4} \right]$$

so

$$B = N\epsilon \left[A_{12}\frac{10\sigma^{12}N^4}{V^5} - A_6\frac{6\sigma^6 N^2}{V^3} \right].$$

But in equilibrium

$$r_0 = \sigma \left(\frac{2A_{12}}{A_6} \right)^{1/6},$$

so
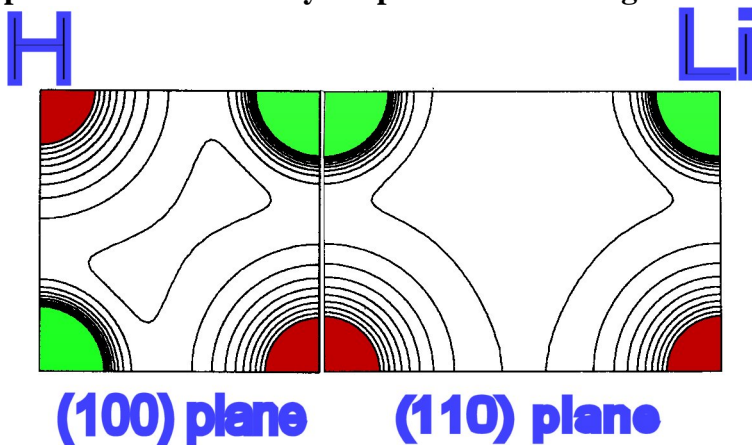
$$V = N\sigma^3 \sqrt{\left(\frac{A_{12}}{A_6} \right)}$$

and

$$B = N\epsilon \left[10A_{12}\sigma^{12}N^4 \times \frac{1}{N^5\sigma^{15}} \left(\frac{A_6}{A_{12}} \right)^{5/2} \right.$$
$$\left. - 6A_6\sigma^6 N^2 \times \frac{1}{N^3\sigma^9} \left(\frac{A_6}{A_{12}} \right)^{3/2} \right],$$

which simplifies to

$$B = \frac{4A_6^{5/2}\epsilon}{A_{12}^{3/2}\sigma^3}.$$

3.6   Ionic Crystals

The picture of an assembly of spherical ions is a good one:

(100) plane   (110) plane

(Theoretical calculations by Harker, checked against experiment)

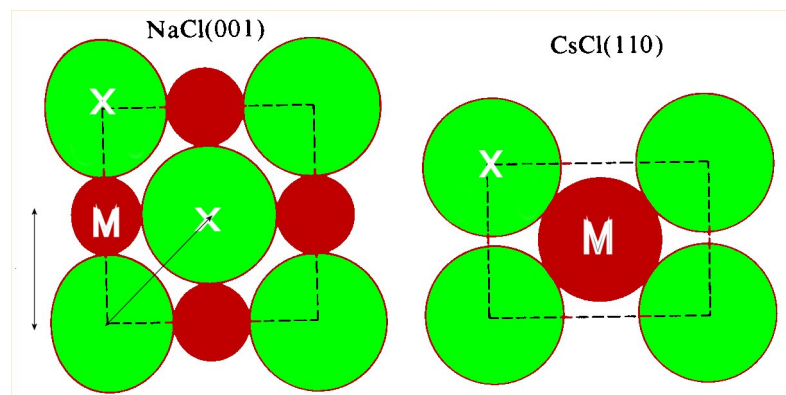### 3.6.1   Ionic Radii and Packing

In general, cation M^+ and anion X^- have different radii.
We expect lowest energy if we have as many cations as possible around each anion, and we avoid anions touching anions.
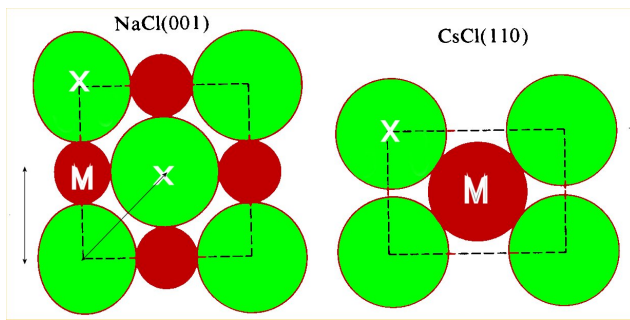**We know that for equal-sized spheres FCC gives high packing.**
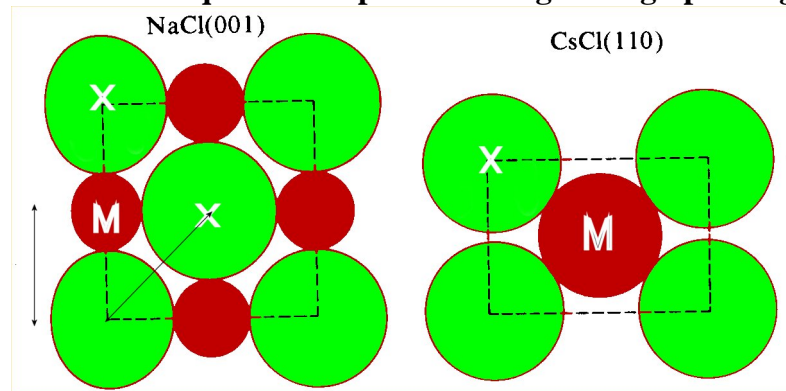
If we shrink the smaller ions, but keep the geometrical arrangement, eventually the larger ions will touch.

NaCl: X atoms touch if

$$r_{MX} = r_M + r_X$$
$$r_{XX} = \sqrt{2}r_{MX}$$
$$r_{XX} \leq 2r_X \rightarrow \sqrt{2}(r_M + r_X) \leq 2r_X$$
$$\frac{r_X}{r_M} \geq \frac{1}{\sqrt{2}-1}.$$

NaCl(001)   CsCl(110)

CsCl: X **atoms touch if**

$$r_{MX} = r_M + r_X$$
$$r_{XX} = \frac{2}{\sqrt{3}} r_{MX}$$
$$r_{XX} \leq 2r_X \rightarrow \frac{2}{\sqrt{3}}(r_M + r_X) \leq 2r_X$$
$$\frac{r_X}{r_M} \geq \frac{1}{\sqrt{3} - 1}.$$

Given a table of ionic radii, we can guess structures of compounds.

3.6.2 Ionic Lattice Sums

For a pair of ions,

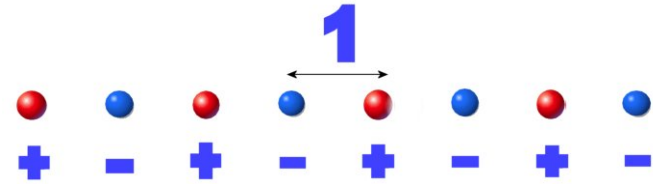$$U_{ij} = \frac{q_i q_j e^2}{4\pi\epsilon_0 r_{ij}} + U_{\text{rep}}(r_{ij}),$$

and summing as before gives

$$U = \frac{N}{2}\left[-\alpha_M \frac{e^2}{4\pi\epsilon_0 r_0} + U_{\text{rep}}\right].$$

α_M **is the** *Madelung constant*, **obtained by a lattice sum:**

$$-\alpha_M = \sum_i \frac{q_0 q_i}{\rho_i}.$$

3.6.3 Linear Chain

$$\alpha_M = 2\left[\frac{1}{1} - \frac{1}{2} + \frac{1}{3} - ....\right]$$

Note:

- **very slowly convergent**
- **only converges because it is an alternating series – try to sum only effect of, say, positive ions and get infinity**
- **Result:** $\alpha_M = 2\ln(2)$.

3.6.4 Three dimensions

Special mathematical tricks used to calculate Madelung constant.

- **Evjen method: sum neutral regions, using increasingly large cubes and only counting half of charges on face centres, quarter of cube edges, eighth of cube corners**
- **Ewald method: trick involving real space and reciprocal space**

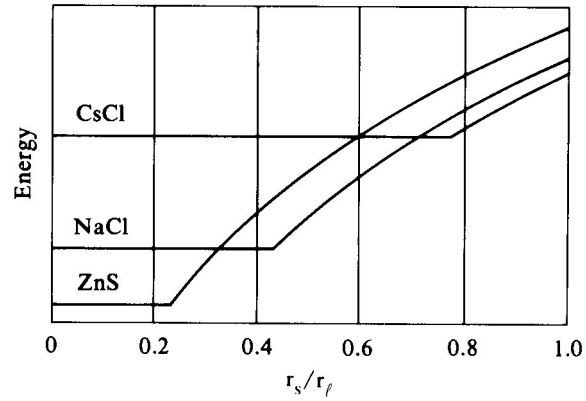| Structure	coordination number	α_M
CsCl	8	1.7627
NaCl	6	1.7476
Zinc blende (like GaAs)	4	1.6381
Wurtzite (hexagonal ZnS)	4	1.641

Higher coordination gives larger Madelung constant.

3.6.5   Ionic Structures

Structure will be that which minimises energy.

Energy increasingly negative as ions get closer – until like ions touch. Radius ratios (smaller r_s over larger r_l) give good guidance. Similar radii favour close packed structures – very different radii give more open, lower-coordinated (and more covalent) structures.

Summary

- **Binding Energy, Equilibrium Separation**
- **Lattice Sums**
- **Coulomb sums**
- **Minimum-energy structures**
- **Elasticity**

Next:

- **Lattice vibrations**