

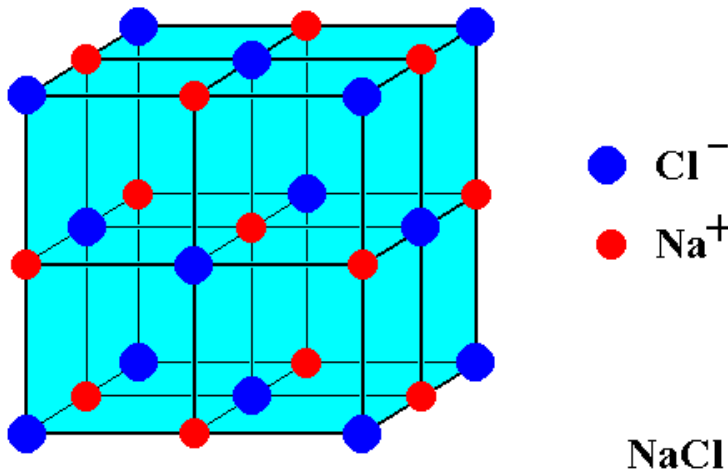
Lecture 6: Bonding in solids

Outline

- Review concepts from first 2 chapters of textbook using NaCl, an ionic solid
- Ionic Crystals (+/- charged ions)

Review of structure factor and concept of basis using NaCl, an ionic solid

The NaCl structure can be thought of as two interweaving FCC lattices (one for Na, one for Cl). Or you can think of it as drawing a FCC lattice of Cl ions and putting Na ions at every position in between.

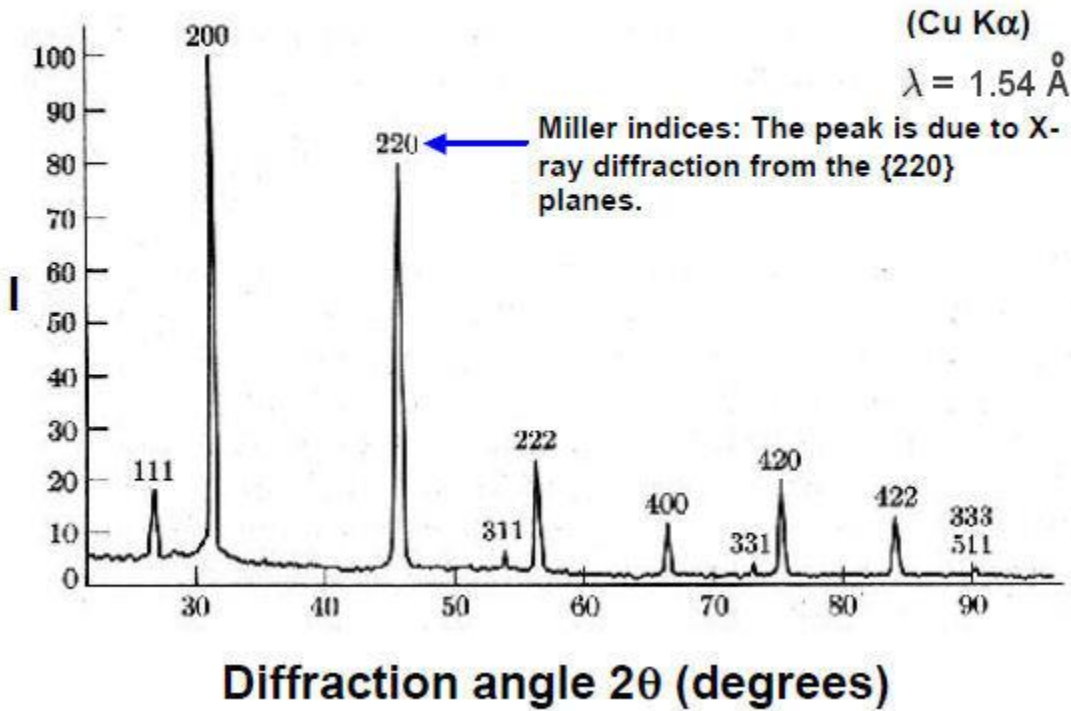


One can think of this structure in terms of a primitive FCC cell or a conventional FCC cell (a=length of side of cube, in both cases).

	Conventional	Primitive
<b>Lattice Vectors (FCC)</b>	$\mathbf{a}_1 = a\hat{x}$ $\mathbf{a}_2 = a\hat{y}$ $\mathbf{a}_3 = a\hat{z}$	$\mathbf{a}_1 = \frac{a}{2}(\hat{x} + \hat{y})$ $\mathbf{a}_2 = \frac{a}{2}(\hat{y} + \hat{z})$ $\mathbf{a}_3 = \frac{a}{2}(\hat{x} + \hat{z})$
<b>Atoms per cell (FCC)</b>	8 corner *1/8+ 6 face *1/2=4	<b>1</b>
<b>Atoms per cell (NaCl)</b>	8 corner *1/8+ 6 face *1/2 = <b>4 Cl</b> 1 center +12 edge*1/4 = <b>4 Na</b> <b>8</b>	Every Cl has a Na pair, so <b>2</b>
<b>Basis coordinates in terms of lattice vectors (NaCl)</b>	$\mathbf{r}_1 = \mathbf{0}$ $\mathbf{r}_2 = \frac{1}{2}(\mathbf{a}_1 + \mathbf{a}_2)$ $\mathbf{r}_3 = \frac{1}{2}(\mathbf{a}_2 + \mathbf{a}_3)$ $\mathbf{r}_4 = \frac{1}{2}(\mathbf{a}_1 + \mathbf{a}_3)$	$\mathbf{r}_1 = \mathbf{0}$ $\mathbf{r}_2 = \frac{1}{2}(\mathbf{a}_1 + \mathbf{a}_3 - \mathbf{a}_2)$ <p>note: find <math>\mathbf{r}_2</math> by finding the coordinate of the desired atom in terms of x,y,z and arrange <math>\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3</math> to get that answer</p>

$r_5 = \frac{1}{2}a_1$ $r_6 = \frac{1}{2}a_2$ $r_7 = \frac{1}{2}a_3$ $r_8 = \frac{1}{2}(a_1 + a_2 + a_3)$	⊗
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## XRD Pattern of NaCl Powder



First, let's use the angles where diffraction peaks are found to find the lattice constant of NaCl. The labels in the figure above are the Miller indices.

$$d_{hkl} = \frac{2\pi}{|\mathbf{G}_{hkl}|}$$

$|\mathbf{G}_{200}| = \left| 2 * \frac{2\pi}{a} \hat{x} \right| = \frac{4\pi}{a}$  (the Miller indices are most likely referenced to the conventional cell for this data set)

$d_{200} = \frac{a}{2}$  (which we could figure out otherwise, using procedure in book)

Plug into Bragg formula:

$$2d\sin\theta = n\lambda$$

$\lambda = 1.54 \text{ \AA}$  (we know this because the image is labeled Cu—K alpha and that is the wavelength of that emission line)

$2\theta = 32^\circ \rightarrow \theta = 16^\circ$  (estimate by looking at graph; note that the axis is labeled 2-theta because of the way experiments are done; the incidence angle is still given by theta)

$$d_{200} = 2.79 \text{ \AA} = \frac{a}{2}$$

$a = 5.59 \text{ \AA}$  (this is very close to value in literature, and the main error is from eyeballing the angle)

Lets do another plane (the 222).

$$G_{222} = \frac{4\pi}{a} \hat{x} + \frac{4\pi}{a} \hat{y} + \frac{4\pi}{a} \hat{z}$$

$$|G_{222}| = \frac{4\pi}{a} \sqrt{3}$$

$$d_{222} = \frac{2\pi}{\frac{4\pi\sqrt{3}}{a}} = \frac{a}{2\sqrt{3}}$$

$$\theta = \frac{57}{2} = 28.5^\circ$$

$$d_{222} = 1.61 \text{ \AA}$$

$a = 5.59 \text{ \AA}$  again

Second, lets discuss the relative intensity of peaks using structure factor (describes phase lag of diffracted wave from each atom in unit cell):

$$S_G = \sum_{j=1}^s f_j e^{-iG \cdot r_j}$$

The scattering intensity is proportional to  $|S_G|^2$  so it is ok if  $S_G$  is not real.

In terms of primitive lattice vectors, the positions of each of the atoms in the basis is given by:

$\mathbf{r}_j = x_j \mathbf{a}_1 + y_j \mathbf{a}_2 + z_j \mathbf{a}_3$  where  $x_j, y_j, z_j$  are fractional

$$\mathbf{G} \cdot \mathbf{r}_j = (v_1 \mathbf{b}_1 + v_2 \mathbf{b}_2 + v_3 \mathbf{b}_3) \cdot (x_j \mathbf{a}_1 + y_j \mathbf{a}_2 + z_j \mathbf{a}_3)$$

$$= 2\pi(v_1 x_j + v_2 y_j + v_3 z_j)$$

$$S_G(v_1 v_2 v_3) = \sum_{j=1}^s f_j e^{-2\pi i(v_1 x_j + v_2 y_j + v_3 z_j)}$$

Set the origin at the Cl atom in the back left corner (000)

The fractional coordinate of the Na atom next to it can be expressed as:  $\frac{1}{2}(\mathbf{a}_1 + \mathbf{a}_3 - \mathbf{a}_2)$

$$\mathbf{G} \cdot \mathbf{r}_j = (v_1 \mathbf{b}_1 + v_2 \mathbf{b}_2 + v_3 \mathbf{b}_3) \cdot (x_j \mathbf{a}_1 + y_j \mathbf{a}_2 + z_j \mathbf{a}_3) = 2\pi(v_1 x_j + v_2 y_j + v_3 z_j)$$

Thus,

$$S_{\mathbf{G}, \text{NaCl}} = f_{\text{Cl}} + f_{\text{Na}} e^{-i\pi(v_1 - v_2 + v_3)}$$

We cannot make the same simplification as before because the atomic form factors are different, but we can make general statements:

- If indices are all even or two odd and one even, the 2<sup>nd</sup> term will give a positive contribution to the sum
- If indices are all odd or two even and one off, the 2<sup>nd</sup> term will give a negative contribution to the sum, likely making  $|S_{\mathbf{G}}|^2$  (which we measure) smaller.

Comparing to the powder x-ray diffraction image we can see that the 111 peak is very small compared to the nearby 200 and ditto for the 311 vs 222. In general, we expect peaks to get smaller as we move to higher angle because higher-index planes contain fewer atoms, but the analysis we did above allows us to gain further insight into why some Bragg peaks are larger than others nearby.

If we are using x-rays to do our diffraction experiments, the form factor is proportional to Z (the atomic number). This is derived sketchily in your textbook, but we will take it as a given for this lecture. To be more specific, it is electrons which do the scattering so the number of electrons on each species of atoms is what matters. This might not be the same as the atomic number for **ionic solids** like NaCl, where the crystal structure is made up of charged species.

To summarize:

$$Z_{\text{Na}} = 11$$

$$Z_{\text{Cl}} = 17$$

$$\text{Electrons on Na}^+ = 10$$

$$\text{Electrons on Cl}^- = 18$$

### General commentary on crystal binding

In the first two chapters we learned vocabulary and formalism related to crystals, and learned one of the ways that scientists uncover the microscopic repeating structure of crystals (diffraction). In this chapter we step back and try to answer the question about why/how crystals hold themselves together in the first place.

Crystals are divided into 4 classes—ionic, covalent, van de waals, and metallic. These categories provide a useful framework for understanding crystal binding, but they are not the whole story. For example:

- ionic crystals can show some degree of covalent bonding (i.e. “electrons shared by neighboring atoms”)

- some of the most important contemporary manifestations of van der waals bonding are 'layered' materials which typically show covalent bonding within each layer but van der waals bonding between layers
- Metallic bonding, in certain circumstances (e.g. cold welding) can be thought of as a special case of Van der Waals bonding

Two concepts from this portion of the chapter are very important in modern solid state research/applications: the Lennard-Jones potential and the Madelung energy.

### Ionic Crystals

Definition: crystals made up of positive and negatively charged ions. Bonding results from electrostatic interactions of oppositely charged ions.

Coulomb potential between two point charges:  $\pm \frac{q^2}{r}$

Total coulomb interaction for ionic solid (consider one ion  $i$  and add up coulomb term between it and every other atom  $j$ ):

$$U_i = \sum_j U_{ij}$$

$$U_{ij} = \lambda e^{-r_{ij}/\rho} \pm q^2/r_{ij}$$

Where  $r_{ij}$  is separation between center of  $i$ -th atom and center of  $j$ -th atom.

But what's up with that first term? Where did it come from?

The first (exponential) term is an empirical term that is added to make sure that the atoms do not get too close together. The strength of this 'hard core repulsion' ( $\lambda$ ) and its range ( $\rho$ ) are constants to be determined from experiments. There is not necessarily a physical reason why we need to use an exponential; it is just the conventional choice among a number of functions that grow larger when  $r_{ij}/\rho$  is small.

Next steps:

- Total lattice energy: add up contributions from all atoms. There are  $2N$  ions (because we need same number of + or - to have neutrally charged solid at the end) but we double-count each pairwise interaction if we just add  $2N$  contributions together. Thus,  $U_{tot} = NU_i$
- Introduce new dimensionless quantity  $p_{ij}$  such that  $r_{ij} = p_{ij}R$ , where  $R$  is the nearest neighbor separation in the crystal.

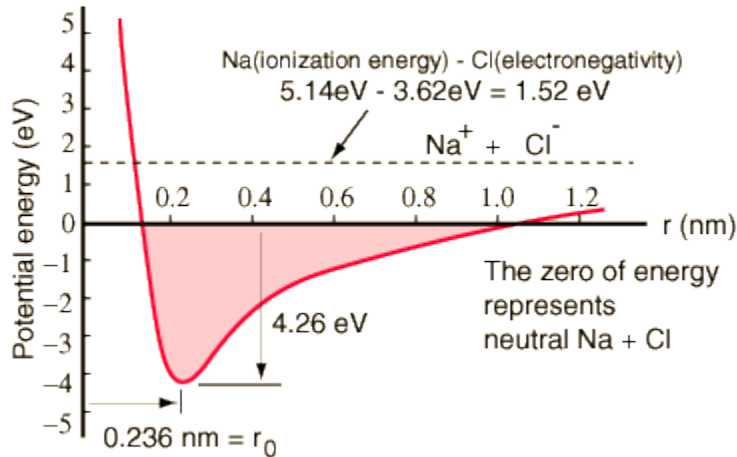
$$U_{ij} = \begin{cases} \lambda e^{-R/p} - \frac{q^2}{R} & \text{(nearest neighbors)} \\ \pm \frac{1}{p_{ij}} \frac{q^2}{R} & \text{(otherwise)} \end{cases}$$

$$U_{tot} = NU_i = N(z\lambda e^{-\frac{R}{\rho}} - \frac{\alpha q^2}{R})$$

Where  $z$  is the number of nearest neighbors an ion in the crystal has and  $\alpha$  is the **madelung constant**.

$$\alpha \equiv \sum_j \frac{(\pm)}{p_{ij}} \text{ (sum includes nearest neighbors)}$$

To give a stable crystal, it is necessary for  $\alpha$  to be positive (to *decrease* the potential energy, since the first term will always be positive)



At the equilibrium separation, the potential energy is at a **local minimum** so  $\frac{dU_{tot}}{dR} = 0$

$$N \frac{dU_i}{dR} = \frac{-Nz\lambda}{\rho} e^{-R/\rho} + \frac{N\alpha q^2}{R^2} = 0$$

$$R_0^2 e^{-R_0/\rho} = \rho \alpha q^2 / z\lambda$$

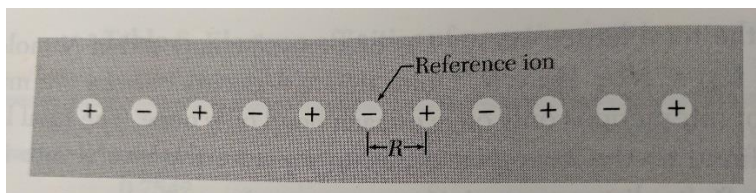
This equation determines the equilibrium separation between ions,  $R_0$

The total lattice energy of the crystal when all ions are at the equilibrium separation is given by:

$$U_{tot} = \frac{-N\alpha q^2}{R_0} \left(1 - \frac{\rho}{R_0}\right)$$

The prefactor,  $\frac{-N\alpha q^2}{R_0}$ , is the **madelung energy**. Physically, this represents the energy you save by taking all of your ions from a distance of infinity and configuring them into a crystal with equilibrium ion separation  $R_0$ . It turns out (experimentally determined) that  $\rho \sim 0.1R_0$ , so the quantities in the parenthesis contribute a factor of order one.

**Example:** evaluation of Madelung constant for 1D line of alternating charges.



$$\alpha = \sum_j \frac{\pm}{p_{ij}}$$

Divide both sides by R

$$\frac{\alpha}{R} = \sum_j \frac{\pm}{r_j}$$

$r_j$  is the distance to the  $j$ th ion from the reference ion (which we chose to be negative)

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

- Factor of 2 because there are symmetric contributions on left and right side of reference ion
- First term is *positive* (despite opposite charges) because we chose to express  $U_{tot}$  with the term containing the madelung constant being subtracted. To put it another way, opposite charges=attraction=stable crystals; positive  $\alpha$ =decrease in potential energy=stable crystal

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

The solution to this sum is found by noting that

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} \dots$$

$$\alpha = 2\ln 2 = 1.38$$

Unfortunately, this same procedure is exceedingly difficult in 3 dimensions, so people typically just look up the values (or calculate them numerically with a computer). As an example,  $\alpha_{NaCl} = 1.75$ . This number is dimensionless, and its significance is that it is one of the configuration-dependent parameters in the madelung energy.