PHY 752 Solid State Physics
11-11:50 AM MWF Olin 103

Plan for Lecture 18:

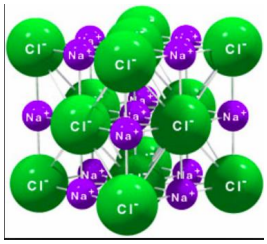
Reading: Chapter 6 in GGGPP
Electronic properties of selected materials

1. **Ionic crystals – Ewald summation and binding energy**
2. **Band structure**

3	Mon, 8/31/2015	Chap. 1.4	Tight binding models	#3
4	Wed, 9/02/2015	Chap. 1.6, 2.1	Crystal structures	#4
5	Fri, 9/04/2015	Chap. 2	Group theory	#5
6	Mon, 9/07/2015	Chap. 2	Group theory	#6
7	Wed, 9/09/2015	Chap. 2	Group theory	#7
8	Fri, 9/11/2015	Chap. 2	Group theory	#7
9	Mon, 9/14/2015	Chap. 2.4-2.7	Densities of states	#8
10	Wed, 9/16/2015	Chap. 3	Free electron model	#9
11	Fri, 9/18/2015	Chap. 4	One electron approximations to the many electron problem	#10
12	Mon, 9/21/2015	Chap. 4	One electron approximations to the many electron problem	#11
13	Wed, 9/23/2015	Chap. 4	Density functional theory	#12
14	Fri, 9/25/2015	Chap. 5	Implementation of density functional theory	#13
15	Mon, 9/28/2015	Chap. 5	Implementation of density functional theory	#14
16	Wed, 9/30/2015	Chap. 5	First principles pseudopotential methods	#15
17	Fri, 10/02/2015	Chap. 6	Example electronic structures	#16
18	Mon, 10/05/2015	Chap. 6	Ionic and covalent crystals	#17
19	Wed, 10/07/2015	Chap. 6	More examples of electronic structures	#18
20	Fri, 10/09/2015	Chap. 1-6	Review	Start exam
	Mon, 10/12/2015		No class	Take-home exam
	Wed, 10/14/2015		No class	Exam due before 10/19/2015
	Fri, 10/16/2015		Fall break -- no class	
23	Mon, 10/19/2015			

Ionic solids

Example -- NaCl



Ewald summation methods -- motivation

Consider a collection of point charges $\{q_i\}$ located at points $\{\mathbf{r}_i\}$. The energy to separate these charges to infinity($\mathbf{r}_i \to \infty$) is

$$W = \frac{1}{4\pi\epsilon_0} \sum_{(i,j;i>j)} \frac{q_i q_j}{|\mathbf{r}_i - \mathbf{r}_j|}.$$

Here the summation is over all pairs of (i, j), excluding $i = j$. It is convenient to sum over all particles and divide by 2 to compensate for the double counting:

$$W = \frac{1}{8\pi\epsilon_0} \sum_{i,j;i\neq j} \frac{q_i q_j}{|\mathbf{r}_i - \mathbf{r}_j|}.$$

Here the summation is over all pairs of $i, j,$ excluding $i = j$. The energy W scales as the number of particles N. As N $\to \infty$, the ratio W / N remains well-defined in principle, but difficult to calculate in practice.

Ewald summation methods – exact results for periodic systems

$$\frac{W}{N} = \sum_{\alpha\beta} \frac{q_\alpha q_\beta}{8\pi\varepsilon_0} \left(\frac{4\pi}{\Omega} \sum_{\mathbf{G}\neq\mathbf{0}} \frac{e^{-i\mathbf{G}\cdot\boldsymbol{\tau}_{\alpha\beta}}\, e^{-G^2/\eta}}{G^2} - \sqrt{\frac{\eta}{\pi}}\delta_{\alpha\beta} + \sum_{\mathbf{T}} \frac{\mathrm{erfc}(\frac{1}{2}\sqrt{\eta}\,|\,\boldsymbol{\tau}_{\alpha\beta} + \mathbf{T}\,|)}{|\,\boldsymbol{\tau}_{\alpha\beta} + \mathbf{T}\,|} \right) - \frac{4\pi Q^2}{8\pi\varepsilon_0 \Omega \eta}.$$

See lecture notes for details.

Summary of Ewald summation for electrostatic energy

Using identity: $\frac{1}{r} = \frac{\mathrm{erf}(\frac{1}{2}\sqrt{\eta}r)}{r} + \frac{\mathrm{erfc}(\frac{1}{2}\sqrt{\eta}r)}{r}.$

Electrostatic energy becomes:

$$W = \frac{1}{8\pi\varepsilon_0} \sum_{i\neq j} \frac{q_i q_j}{|\mathbf{r_i} - \mathbf{r_j}|} = \frac{1}{8\pi\varepsilon_0} \left(\sum_{i\neq j} \frac{q_i q_j \mathrm{erf}(\frac{1}{2}\sqrt{\eta}|\mathbf{r_i} - \mathbf{r_j}|)}{|\mathbf{r_i} - \mathbf{r_j}|} + \sum_{i\neq j} \frac{q_i q_j \mathrm{erfc}(\frac{1}{2}\sqrt{\eta}|\mathbf{r_i} - \mathbf{r_j}|)}{|\mathbf{r_i} - \mathbf{r_j}|} \right)$$

Summation in reciprocal space

Summation in real space

$$N \frac{4\pi}{\Omega} \left(\sum_{\mathbf{G}\neq\mathbf{0}} \frac{e^{-i\mathbf{G}\cdot\tau_{\alpha\beta}}\, e^{-G^2/\eta^2}}{G^2} + \frac{1}{2}\int_0^{\frac{1}{2}\sqrt{\eta}} \frac{du}{u^3} \right)$$

$$N \left(\sum_{\alpha\beta} q_\alpha q_\beta \sum_{\mathbf{T}} \frac{\mathrm{erf}(\frac{1}{2}\sqrt{\eta}|\tau_\alpha - \tau_\beta + \mathbf{T}|)}{|\tau_\alpha - \tau_\beta + \mathbf{T}|} - \sum_\alpha q_\alpha^2 \sqrt{\frac{\eta}{\pi}} \right),$$

Some details for singular term

$$\frac{W_{\text{sing}}}{N} = \sum_{\alpha\beta} \frac{q_\alpha q_\beta}{8\pi\varepsilon_0} \frac{4\pi}{\Omega} \frac{1}{2} \int_0^{\frac{1}{2}\sqrt{\eta}} \frac{du}{u^3} = \sum_{\alpha\beta} \frac{q_\alpha q_\beta}{8\pi\varepsilon_0} \frac{4\pi}{\Omega} \frac{1}{2} \int_{\frac{1}{2}\sqrt{\eta}}^{\infty} v dv$$

Suppose that $Q \equiv \sum_\alpha q_\alpha \neq 0$. W_{sing} diverges, representing the Coulomb interaction of an infinite amount of charge. In this case, we can however find the corresponding energy of a neutral system, where we subtract a compensating uniform charge density $\frac{Q}{\Omega}$ with

$$\frac{W_{\text{comp}}}{N} = -\frac{1}{8\pi\epsilon_0} \frac{Q^2}{N\Omega^2} \int d^3r \int d^3r' \frac{1}{|\mathbf{r}-\mathbf{r}'|} = -\frac{1}{8\pi\epsilon_0} \frac{Q^2}{\Omega} 2\pi \int_0^\infty r' dr'$$

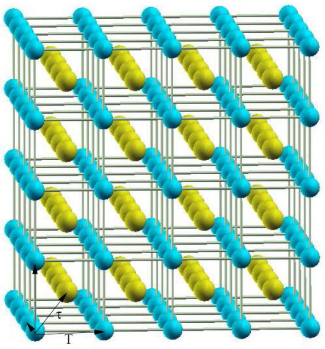
$$\frac{W_{\text{sing}}}{N} + \frac{W_{\text{comp}}}{N} = \frac{2\pi}{8\pi\epsilon_0} \frac{Q^2}{\Omega} \left(\int_{\frac{1}{2}\sqrt{\eta}}^{\infty} r' dr' - \int_0^{\infty} r' dr' \right)$$

$$= -\frac{2\pi}{8\pi\epsilon_0} \frac{Q^2}{\Omega} \int_0^{\frac{1}{2}\sqrt{\eta}} r' dr' = -\frac{4\pi}{8\pi\epsilon_0} \frac{Q^2}{\Omega\eta}$$

Ewald expansion formula:

$$\frac{W}{N} = \sum_{\alpha\beta} \frac{q_\alpha q_\beta}{8\pi\varepsilon_0} \left(\frac{4\pi}{\Omega} \sum_{\mathbf{G}\neq\mathbf{0}} \frac{e^{-i\mathbf{G}\cdot\boldsymbol{\tau}_{\alpha\beta}} e^{-G^2/\eta}}{G^2} - \sqrt{\frac{\eta}{\pi}} \delta_{\alpha\beta} + \sum_{\mathbf{T}} \frac{\operatorname{erfc}(\frac{1}{2}\sqrt{\eta}\,|\,\boldsymbol{\tau}_{\alpha\beta}+\mathbf{T}\,|)}{|\,\boldsymbol{\tau}_{\alpha\beta}+\mathbf{T}\,|} \right) - \frac{4\pi Q^2}{8\pi\varepsilon_0 \Omega\eta}.$$

Example for CsCl structure



$\tau_{\text{Cs}} = 0$ and $\tau_{\text{Cl}} = \frac{a}{2}(\hat{x}+\hat{y}+\hat{z})$.

$\mathbf{T}_1 = a\hat{x}$ $\mathbf{T}_2 = a\hat{y}$ $\mathbf{T}_3 = a\hat{z}$.

$\mathbf{G}_1 = \frac{2\pi}{a}\hat{x}$ $\mathbf{G}_2 = \frac{2\pi}{a}\hat{y}$ $\mathbf{G}_3 = \frac{2\pi}{a}\hat{z}$.

Evaluation of summation

$$\frac{W}{N}=\sum_{\alpha\beta}\frac{q_\alpha q_\beta}{8\pi\varepsilon_0}\left(\frac{4\pi}{\Omega}\sum_{\mathbf{G}\neq\mathbf{0}}\frac{e^{-i\mathbf{G}\cdot\boldsymbol{\tau}_{\alpha\beta}}\,e^{-G^2/\eta}}{G^2}-\sqrt{\frac{\eta}{\pi}}\delta_{\alpha\beta}+\sum_{\mathbf{T}}\frac{\mathrm{erfc}(\frac{1}{2}\sqrt{\eta}\,|\,\boldsymbol{\tau}_{\alpha\beta}+\mathbf{T}\,|)}{|\,\boldsymbol{\tau}_{\alpha\beta}+\mathbf{T}\,|}\right)-\frac{4\pi Q^2}{8\pi\varepsilon_0\Omega\eta}$$

$$\frac{W}{N}=\frac{q^2}{8\pi\varepsilon_0}(\mathcal{T}_1+\mathcal{T}_2),$$

$$\mathcal{T}_1\equiv\frac{4\pi}{\Omega}\sum_{\mathbf{G}\neq\mathbf{0}}2\frac{(1-e^{i\mathbf{G}\cdot\tau_{\mathrm{Cl}}})e^{-|\mathbf{G}|^2/\eta}}{|\mathbf{G}|^2}-2\sqrt{\frac{\eta}{\pi}}$$

$$\mathcal{T}_2\equiv\sum_{\mathbf{T}\neq\mathbf{0}}2\frac{\mathrm{erfc}(\frac{1}{2}\sqrt{\eta}|\mathbf{T}|)}{|\mathbf{T}|}-\sum_{\mathbf{T}}2\frac{\mathrm{erfc}(\frac{1}{2}\sqrt{\eta}|\tau_{\mathrm{Cl}}+\mathbf{T}|)}{|\tau_{\mathrm{Cl}}+\mathbf{T}|}.$$

Maple expressions

See Maple sheet

For this case, we find:

$$\frac{W}{N}=-\frac{e^2}{8\pi\epsilon_0}\left(\frac{4.070723105}{a}\right)$$ ← lattice constant

In terms of Madelung constant: $\frac{W}{N}=-\frac{e^2}{4\pi\epsilon_0}\left(\frac{\alpha_M}{R}\right)$

where for CsCl, $\alpha_M=1.7627$ ← nearest neighbor

For CsCl, $R=\frac{\sqrt{3}}{2}a$

$$\frac{4.070723105}{2a}=\frac{1.7627}{R}$$

NaCl structure

There are two kinds of sites – $\tau_{\mathrm{Na}}=0$ and $\tau_{\mathrm{Cl}}=\frac{a}{2}\hat{\mathrm{x}}$. The "primitive" lattice has the translation vectors:

$$\mathbf{T}_1=\frac{\mathrm{a}}{2}(\hat{\mathrm{x}}+\hat{\mathrm{y}})\;\;\mathbf{T}_2=\frac{\mathrm{a}}{2}(\hat{\mathrm{y}}+\hat{\mathrm{z}})\;\;\mathbf{T}_3=\frac{\mathrm{a}}{2}(\hat{\mathrm{x}}+\hat{\mathrm{z}}),\qquad(26)$$

and the reciprocal vectors:

$$\mathbf{G}_1=\frac{2\pi}{\mathrm{a}}(\hat{\mathrm{x}}+\hat{\mathrm{y}}-\hat{\mathrm{z}})\;\;\mathbf{G}_2=\frac{2\pi}{\mathrm{a}}(-\hat{\mathrm{x}}+\hat{\mathrm{y}}+\hat{\mathrm{z}})\;\;\mathbf{G}_3=\frac{2\pi}{\mathrm{a}}(\hat{\mathrm{x}}-\hat{\mathrm{y}}+\hat{\mathrm{z}}).\qquad(27)$$

Summary of Coulomb interaction energies

Note: In the rest of the lecture notes, we will resume the cgs Gaussian units used in your textbook

Coulombic interaction:

$$U_{\text{Coul}} = -N\alpha_M \frac{e^2}{R}$$

Convenient form for quantum repulsion:

$$U_{\text{Repul}} = N\frac{\lambda}{R^n}$$

Simple interaction model for ionic crystals

$$U_S(R) = N\left(\frac{\lambda}{R^n} - \alpha_M \frac{e^2}{R}\right).$$

At the equilibrium distance, we have

$$\left(\frac{dU_S}{dR}\right)_{R=R_0} = 0 \quad \text{hence} \quad \lambda = \frac{\alpha_M e^2}{n} R_0^{n-1}.$$

The cohesive energy $U_S(R_0)$ becomes

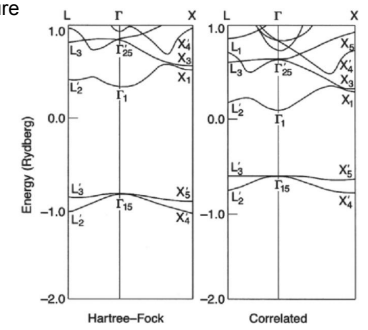
$$U_S(R_0) = -N\alpha_M \frac{e^2}{R_0}\left(1 - \frac{1}{n}\right).$$

Bulk modulus

$$B_0 = \frac{1}{18NR_0}\left(\frac{d^2U_S}{dR^2}\right)_{R=R_0} = (n-1)\frac{e^2\alpha_M}{18R_0^4}.$$

For NaCl structure

Band structure for NaCl



Empty Na bands

Filled Cl bands

Figure 6.7 Hartree-Fock and correlated energy bands of NaCl. The state Γ_{15} is the top of the valence bands and the state Γ_1 is the bottom of the conduction bands [With permission from Fig. 1, Phys. Rev. B *26*, 2056 (1982)].

How do you know if a material is ionic?

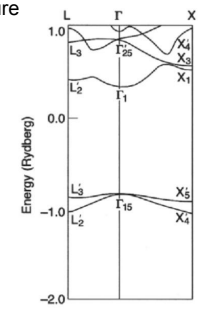
Atomic configurations (neutral)

Na: $1s^2\ 2s^2\ 2p^6$ 3s

Cl: $1s^2\ 2s^2\ 2p^6\ 3s^2$ $3p^5$

6 valence electrons

Band structure for NaCl



Empty Na bands

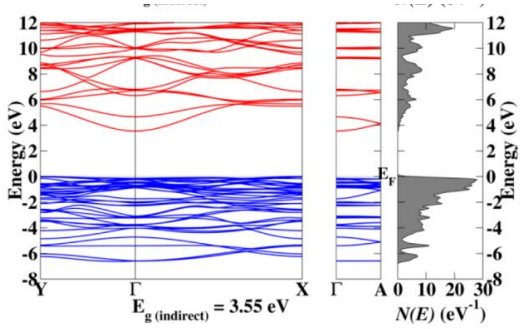
Na $3s^1 \rightarrow 3s^0$

Filled Cl bands; accommodate 6 electrons

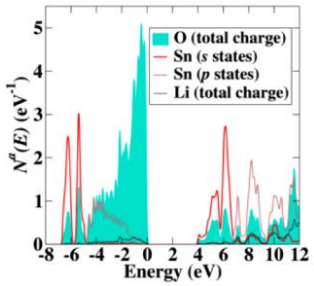
Cl $3p^5 \rightarrow 3p^6$

Electronic structure of Li_2SnO_3

Note: Valence bands must accommodate 72 valence electrons from 8 Li $2s^1$, 4 Sn $5s^25p^2$, and 12 O $2p^4$ atoms per unit cell

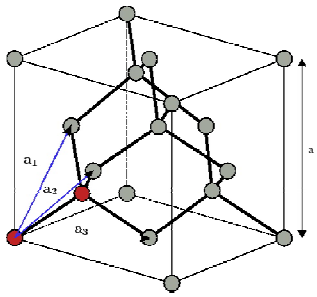


Partial density of states for Li_2SnO_3



Example of a non-ionic material

Diamond lattice (2 C atoms per unit cell)



Ref. PRB **2**, 2054 (1970)

Note: Valence bands must accommodate 8 valence electrons from two C $1s^2 2s^2 2p^2$ atoms per unit cell

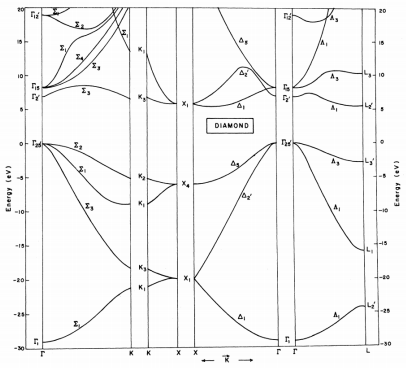
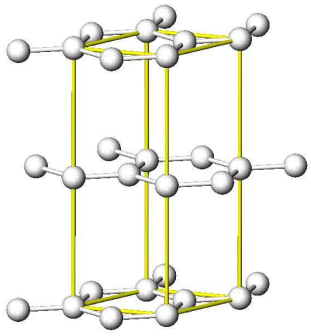


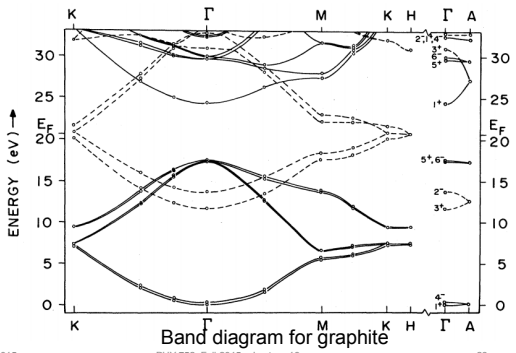
FIG. 1. Energy bands along principal symmetry lines.

Crystal structure of graphite (4 atoms per unit cell)



Ref. *PRB* **26**, 5382 (1982)

Note: Valence bands must accommodate 16 valence electrons from four C $1s^2 2s^2 2p^2$ atoms per unit cell



Band diagram for graphite