

Intro to Solid State Physics: Li Yang

Contents

1 Lecture 1/16/24

Chapter 1: Crystal Structure

Ideal crystal is constructed by the infinite repetition of identical structural groups of atoms. A group is called the basis. Detecting crystal structure started with x-rays due to the wavelength of the x-ray (≈ 1 angstrom) being comparable to the interatomic spacing in a crystal.

What is a *lattice*? 2D Bravais Lattices [Wikipedia](#) The famous graphene has a hexagonal (honeycomb structure) like lattice, but it does not have the center atom from the true hexagonal lattice. The primitive of this lattice is made of up two atoms than can be translated to form the lattice. Thus graphene is like a diatomic crystal.

3D Bravais Lattices There are 14 Bravais lattices in 3D. In both 2D and 3D, the primitive cells that make up the lattice must fill the least amount of space and have no 'holes' or 'extras' left over. The 2 most common lattices now are the Primitive Hexagonal for its symmetry and the Body Centered Cubic (BCC) which is the lattice of Silicon, the most important material today.

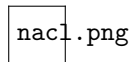


Figure 1.1: Sodium Chloride Structure (FCC)

Example Structures The lattice of Sodium Chloride is FCC as shown in Figure ??

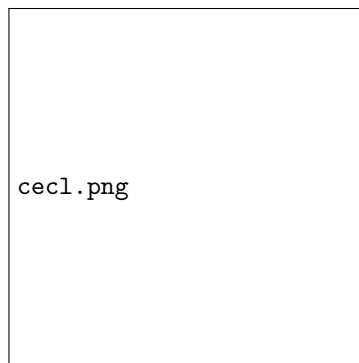


Figure 1.2: Cesium Chloride Structure (SC)

Figure ?? shows the lattice of Cesium Chloride which is SC.

2 Lecture 1/18

Chapter 2: Wave Diffraction and the Reciprocal Lattice

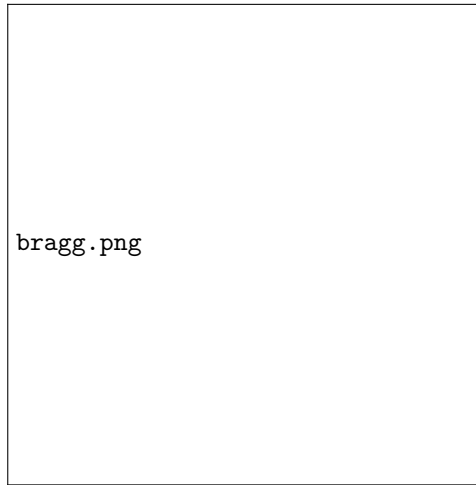


Figure 2.1: Bragg's Law

Scattering and Bragg's Law When two beams of same phase meet, they constructively interfere. When they are out of phase, they destructively interfere. The location of constructive interference, or path difference, is shown by the bold lines in Figure ???. The path difference is

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

known as Bragg's Law which is only valid for $\lambda \leq 2d$. In reality each lattice plane will reflect about $10^{-3} \sim 10^{-5}$ of the incident beam. Thus only about $10^3 \sim 10^5$ planes contribute to the diffraction. The periodicity of the lattice leads to a periodic observable. . .

aside: The electron wavefunction is not observable— ψ is a complex number, but the electron density, $\psi^*\psi$, is observable. Read about the quantized Hall effect (Queen:) and Superconductivity (King).

$$\psi(x+T) = \psi(x)e^{i\theta} n(x+T) = n(x)$$

Fourier Transform The discrete Fourier transform is useful for periodic functions.

$$\begin{aligned} n(x) &= \sum_{P \geq 0} \left[C_P \cos\left(\frac{2\pi}{a}x\right) + S_P \sin\left(\frac{2\pi}{a}x\right) \right] \\ &= \sum_p n_p e^{i \frac{2\pi}{a} p x} \end{aligned}$$

or in vector notation

$$n(\mathbf{r}) = \sum_{\mathbf{G}} n_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}}$$

Since $n(x)$ is real, there is a symmetry of the complex conjugate

$$n_p = n_{-p}^*$$

Inverse Fourier Transform

$$n_p = \frac{1}{a} \int_0^a n(x) e^{-i \frac{2\pi}{a} p x} dx$$

and in vector notation

$$n_G = \frac{1}{V} \int_{cell} n(\mathbf{r}) e^{-i \mathbf{G} \cdot \mathbf{r}} dV$$

Reciprocal Space Vectors The basis vectors of the reciprocal lattice are

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}; \quad \mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}; \quad \mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

where the denominator is the volume of the unit cell (parallelepiped) $\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3) = V_c$. Taking the dot product of a primitive vector with a reciprocal lattice vector gives

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij}$$

where the Kronecker delta tells us that the dot product is either 2π or 0. With this we can write the \mathbf{G} vector as a linear combination of the reciprocal lattice vectors

$$\mathbf{G} = v_1 \mathbf{b}_1 + v_2 \mathbf{b}_2 + v_3 \mathbf{b}_3$$

we can also show that

$$n(\mathbf{r} + \mathbf{T}) = n(\mathbf{r})$$

which means that this is invariant under translations.

Scattering amplitude

$$F = \int d\mathbf{r} n(\mathbf{r}) e^{i\mathbf{k} \cdot \mathbf{r}} e^{-i\mathbf{k}' \cdot \mathbf{r}}$$

where $|\mathbf{k}| = |\mathbf{k}'|$. In vector notation

$$\begin{aligned} F &= \int d\mathbf{r} \sum_{\mathbf{G}} n_G e^{i(\mathbf{G} - \mathbf{r}') \cdot \mathbf{r}} e^{-i\Delta\mathbf{k} \cdot \mathbf{r}} \\ &= \sum_{\mathbf{G}} n_G \int d\mathbf{r} e^{i(\mathbf{G} - \Delta\mathbf{k}) \cdot \mathbf{r}} \end{aligned}$$

where $\Delta\mathbf{k} = -(\mathbf{k} - \mathbf{k}')$. When $\mathbf{G} = \Delta\mathbf{k}$ we can rewrite to

$$\mathbf{k} + \Delta\mathbf{k} = \mathbf{k}'$$

in absolute value

$$|\mathbf{k} + \Delta\mathbf{k}| = |\mathbf{k}'| \rightarrow |\mathbf{k} + \Delta\mathbf{k}| = |\mathbf{k}| \rightarrow |\mathbf{k} + \mathbf{G}| = |\mathbf{k}|$$

and

$$(\mathbf{k} + \mathbf{G}) \cdot (\mathbf{k} + \mathbf{G}) = \mathbf{k} \cdot \mathbf{k} \rightarrow 2\mathbf{k} \cdot \mathbf{G} + \mathbf{G}^2 = 0$$

For the 1D crystal $G = 2\pi/a$. Since $\mathbf{k} \cdot \mathbf{G} = 2\pi/\lambda G \sin \theta$ and $2\mathbf{k} \cdot \mathbf{G} = \mathbf{G}^2$ We get

$$\begin{aligned} 2 \cdot \frac{2\pi}{\lambda} G \sin \theta &= \mathbf{G}^2 \\ \rightarrow \frac{4\pi}{\lambda} \sin \theta &= G \end{aligned}$$

since $G = 2\pi/a$ we get Bragg's Law

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

For the SC the reciprocal lattice is SC, but for BCC, the reciprocal lattice is different...

3 Lecture 1/23/24

Chapter 2: cont'd

Wigner-Seitz primitive cell: How to create the most symmetric primitive cell.

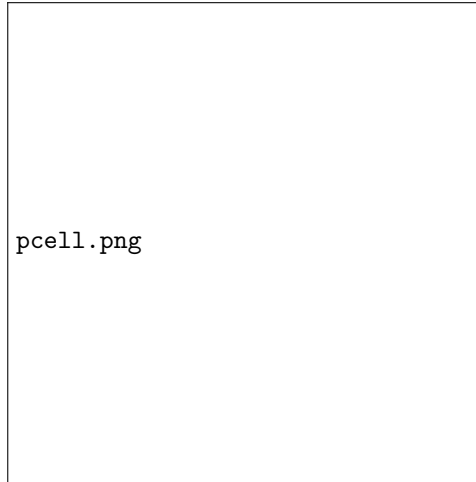


Figure 3.1: Wigner-Seitz Primitive Cell

Steps: Connect a given lattice point to all nearby lattice points. Bisect all lines. The area enclosed by the bisectors is the Wigner-Seitz primitive cell as shown in Figure ??.

Reciprocal Lattice of SC The lattice vectors (primitive translation vectors) are

$$\mathbf{a}_1 = a\hat{\mathbf{x}}, \quad \mathbf{a}_2 = a\hat{\mathbf{y}}, \quad \mathbf{a}_3 = a\hat{\mathbf{z}}$$

the reciprocal lattice vectors using the formula from last lecture are

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{V_c} = \frac{2\pi}{a} \hat{\mathbf{x}}, \quad \mathbf{b}_2 = \frac{2\pi}{a} \hat{\mathbf{y}}, \quad \mathbf{b}_3 = \frac{2\pi}{a} \hat{\mathbf{z}}$$

Reciprocal Lattice of BCC The lattice vectors are

$$\mathbf{a}_1 = \frac{a}{2}(-\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}), \quad \mathbf{a}_2 = \frac{a}{2}(\hat{\mathbf{x}} - \hat{\mathbf{y}} + \hat{\mathbf{z}}), \quad \mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}})$$

and the reciprocal lattice vectors are

$$\mathbf{b}_1 = \frac{2\pi}{a}(\hat{\mathbf{y}} + \hat{\mathbf{z}}), \quad \mathbf{b}_2 = \frac{2\pi}{a}(\hat{\mathbf{z}} + \hat{\mathbf{x}}), \quad \mathbf{b}_3 = \frac{2\pi}{a}(\hat{\mathbf{x}} + \hat{\mathbf{y}})$$

Reciprocal Lattice of FCC The lattice vectors are

$$\mathbf{a}_1 = \frac{a}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}}), \quad \mathbf{a}_2 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{z}}), \quad \mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}})$$

which is the same as the reciprocal space of BCC. Thus, the reciprocal lattice of FCC is BCC!

Brillouin Zone The first Brillouin zone is the Wigner-Seitz primitive cell of the reciprocal lattice.

Chapter 3: Crystal Binding and Elastic Constants

We are mostly interested in the E&M interaction between atoms on the energy scale of eV (e.g. the band gap of silicon is 1.2 eV).

There are 4 main types of bonds:

Metallic Bond Bonds between metals have weakly bound valence electrons. Hence the electrons move freely around like a fluid. This is why metals are good conductors.

Ionic Bond Bonds between metals and non-metals (e.g. NaCl). The opposing charges attract each other where the electrons form full shells and hence less conductivity.

Covalent Bond Bonds between non-metals (e.g. Si). The atomic orbitals defined by QM describes the bonds through the hybridization of the orbital wavefunctions (e.g. sp^3 in diamond). This is a very difficult problem to solve.

Van der Waals interaction Inert gases... e.g. He is interesting as it is a liquid at very low temperatures, and it is a boson (He-4 superfluid) and fermion (He-3) depending on the number of neutrons.

Hydrogen Bonding is very important in biology, but not in solid state physics.

Van der Waals interaction

Two types of energy to consider:

- Cohesive energy: Energy required to separate bound atoms. The cohesive energy of a solid is the sum of the cohesive energies of the bonds.
- Ionization energy: Energy required to remove an electron from an atom.

The ionization energy is larger because the Van der Waals interaction is a weaker bond. Given two inert gas atoms, there is no dipole or charge distribution contributing to the interactions between the atoms. In QM, there is no zero point energy, so we have to consider the atoms to not be perfect, but rather vibrate around a mean position. This is a dipole-dipole interaction.

dipole-dipole Given two electrons spaced by a distance R in a 1D lattice, one atom fluctuates by x_2 and the other by x_1 . The Hamiltonian of the unperturbed system is

$$H_o = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \frac{1}{2}Cx_1^2 + \frac{1}{2}Cx_2^2$$

The Coulomb interaction:

$$H_1 = \frac{e^2}{R} + \frac{e^2}{R+x_1-x_2} - \frac{e^2}{R+x_1} - \frac{e^2}{R-x_2}$$

Using Taylor expansion (2nd order) for small x_1 and x_2 we get

$$H_1 = -\frac{2e^2}{R^3}x_1x_2$$

Since this has 2 degrees of freedom, we have a 2x2 matrix with 2 eigenvalues diagonalized by the normal mode transform. This results in 2 Canonical Modes:

$$x_s = \frac{1}{\sqrt{2}}(x_1 + x_2) \quad x_a = \frac{1}{\sqrt{2}}(x_1 - x_2)$$

The total Hamiltonian is

$$\begin{aligned} H &= \frac{1}{2m} \left[\frac{1}{2}(p_s + p_a)^2 \right] + \frac{1}{2m} \left[\frac{1}{2}(p_s - p_a)^2 \right] - 2\frac{e^2}{R^3} \cdot \frac{1}{2}(x_s^2 - x_a^2) + \frac{1}{2}cx_1^2 + \frac{1}{2}cx_2^2 \\ &= \left[\frac{p_s}{2m} + \frac{1}{2} \left(c - \frac{2e^2}{R^3} \right) x_s^2 \right] + \left[\frac{p_a}{2m} + \frac{1}{2} \left(c + \frac{2e^2}{R^3} \right) x_a^2 \right] \end{aligned}$$

4 Lecture 1/25/24

Chapter 3: cont'd

The momenta of the harmonic oscillators from last time are also in the ofmr 2 modes:

$$p_s = \frac{1}{\sqrt{2}}(p_1 + p_2) \quad p_a = \frac{1}{\sqrt{2}}(p_1 - p_2)$$

The matrix form

$$\begin{pmatrix} E_o & 0 \\ 0 & E_o \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = \hbar\omega \begin{pmatrix} a \\ b \end{pmatrix}$$

$$\begin{vmatrix} E_o - \hbar\omega & \Delta \\ \Delta & E_o - \hbar\omega \end{vmatrix} = 0$$

solving for the eigenstates

$$\frac{1}{\sqrt{2}} \begin{pmatrix} a \\ b \end{pmatrix}, \quad \frac{1}{\sqrt{2}} \begin{pmatrix} a \\ -b \end{pmatrix}$$

The Hamiltonian of the single harmonic oscillator is

$$H_o = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2$$

thus we can compare the frequencies of the harmonic oscillator and the Van der Waals interaction

$$\omega = \sqrt{\frac{c \pm \frac{2e^2}{R^3}}{m}}$$

and we know the *zero-point energy* $1/2\hbar\omega$ or in this case

$$\frac{1}{2}\hbar\Delta\omega = \frac{1}{2}\hbar[\Delta\omega_s + \Delta\omega_a]$$

From the uncoupled sum and using Taylor expansion

$$\omega = \omega_o \left[1 \pm \frac{1}{2} \left(\frac{2e^2}{R^3 c} \right) \pm \frac{1}{8} \left(\frac{2e^2}{R^3 c} \right)^2 + \dots \right]$$

thus we get the interaction energy

$$\Delta U = \frac{1}{2}\hbar(\Delta\omega_s + \Delta\omega_a) = \frac{\hbar\omega_o}{2} \left[\frac{e^4}{c^2 R^6} \right] = -\frac{A}{R^6}$$

where the minus sign indicates an attractive force. We would expect the atoms to collapse, but this is not the case due to the Pauli exclusion principle (electrons cannot occupy the same state).

Pauli exclusion principle

As the atoms get closer, there is an overlap of the wavefunctions. If the wavefunctions are symmetric, the spin states must be anti-symmetric. Therefore anti-symmetric wavefunctions have symmetric spin states. This repulsive force from the Pauli exclusion principle is typically found empirically $\propto \frac{1}{R^{12}}$. Therefore the total potential is

$$U(R) = 4\epsilon \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \right]$$

AKA the Lennard-Jones potential. We could find the equilibrium distance by minimizing the potential $\frac{dU}{dR} = 0$. This is fine for inert gases that are spherical, but other molecules are depend on more than the scalar distance R . This decays faster than the scale of Coulombs Law $\propto \frac{1}{R^2}$. The total energy for a crystal is

$$E = \frac{1}{2}N(4\epsilon) \left[\sum_j' \left(\frac{\sigma}{P_{ij}R} \right)^{12} - \sum_j' \left(\frac{\sigma}{P_{ij}R} \right)^6 \right]$$

where the prime indicates that the sum is over the nearest neighbors. The fcc lattice

$$\sum_j' \left(\frac{1}{P_{ij}} \right)^{12} = 12.13188; \quad \sum_j' \left(\frac{1}{P_{ij}} \right)^6 = 14.45392$$

for the 12 nearest neighbors. Solving for the minimum energy $\frac{dU}{dR} = 0$ we get

$$R_o/\sigma = 1.09$$

Ionic Crystal

The Coulomb interaction:

$$\pm \frac{q^2}{r_{ij}}$$

The short-term interaction

$$\lambda e^{-r_{ij}/\rho}$$

thus the potential is

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

where at one site (one ion)

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

and the total energy is

$$U = NU_i$$

For N molecules

$$U_{ij} = \begin{cases} \lambda e^{-r_{ij}/\rho} - \frac{q^2}{r_{ij}} & \text{nearest neighbor} \\ \pm \frac{q^2}{r_{ij}} & \text{otherwise} \end{cases}$$

and the total energy is

$$U_{tot} = N \left[z e^{-R/\rho} - \alpha \frac{q^2}{R} \right] \quad \alpha = \sum_j' \frac{\pm}{p_{ij}}$$

where z is the number of nearest neighbors, and α is the Madelung constant. From this we can find the lattice constant by using

$$\frac{dU}{dR} = 0 \rightarrow R_o^2 e^{-R_o/\rho} = \alpha \rho \frac{q^2}{z\lambda}$$

solving for R_o and putting into the total energy equation we get

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

where we have a special term

$$-\frac{N\alpha q^2}{R_o}$$

known as the ‘Madelung Energy’.

5 Lecture 1/30/24

Chapter 3: Bonds Bonds and Bonds

From last time:

$$U_{ij} = \begin{cases} \lambda e^{-R/\rho} - \frac{q^2}{R} & \text{nearest neighbor} \\ \pm \frac{q^2}{p_{ij}R} & \text{otherwise} \end{cases}$$

where $p_{ij}R = r_{ij}$ and the total energy (sum) is

$$U_{tot} = N \left[z e^{-R/\rho} - \alpha \frac{q^2}{R} \right]$$

where z is the number of nearest neighbors, N is the total ions, and α is the Madelung constant:

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

At the equilibrium separation

$$\frac{dU}{dR} = 0 \rightarrow R_o^2 e^{-R_o/\rho} = \alpha \rho \frac{q^2}{z\lambda}$$

R_o is the equilibrium separation (position). Substituting this back into the total energy we get the empirical formal for the equilibrium energy (ground state):

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

where the first term outside the parenthesis is the Madelung energy

$$-\frac{N\alpha q^2}{R_o}$$

The Evaluation of Madelung Constant Letting R denote the distance between the ions, we can write the Madelung constant as

$$\begin{aligned} \frac{\alpha}{R} &= 2 \left[\frac{1}{R} - \frac{1}{2R} + \frac{1}{3R + \dots} \right] \\ &= \frac{2}{R} \left[1 - \frac{1}{2} + \dots \right] \end{aligned}$$