# Problem Set 3

Crystal Structure, Reciprocal Lattice, and Scattering (plus tightbinding in 1d tacked on)

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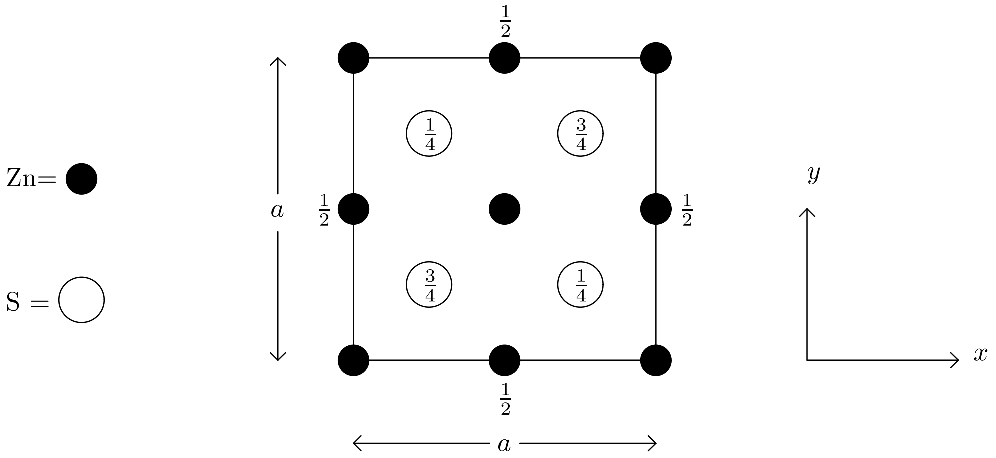
## 3.1. Crystal Structure



The diagram above shows a plan view of a structure of cubic ZnS (zinc blende) looking down the $z$ axis. The numbers attached to some atoms represent the heights of the atoms above the $z = 0$ plane expressed as a fraction of the cube edge $a$. Unlabeled atoms are at $z = 0$ and $z = a$.

(a) What is the Bravais lattice type

(b) Describe the basis

(c) Given that $a = 0.541$ nm, calculate the nearest-neighbor Zn-Zn, Zn-S, and S-S distances.

(d) Copy the drawing above, and show the [210] direction and the set of (210) planes.

(e) Calculate the spacing between adjacent (210) planes.

## 3.2. Directions and Spacings of Crystal Planes

▷ Explain briefly what is meant by the terms “Crystal Planes” and “Miller Indices” for the case where the axes of a lattice are all mutually orthogonal to each other.

▷ Show that the general direction $[hkl]$ in a cubic crystal is normal to the planes with Miller indices $(hkl)$.

▷ Is the same true in general for an orthorhombic crystal?

▷ Show that the spacing $d$ of the $(hkl)$ set of planes in a cubic crystal with lattice parameter $a$ is

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

▷ What is the generalization of this formula for an orthorhombic crystal?

## 3.3. ‡Reciprocal Lattice

(a) Define the term Reciprocal Lattice.

(b) Show that if a lattice in 3d has primitive lattice vectors $\mathbf{a_1}$, $\mathbf{a_2}$ and $\mathbf{a_3}$ then primitive lattice vectors for the reciprocal lattice can be taken as

$$\begin{aligned} \mathbf{b_1} &= 2\pi\frac{\mathbf{a_2}\times\mathbf{a_3}}{\mathbf{a_1}\cdot(\mathbf{a_2}\times\mathbf{a_3})} && (1)\\ \mathbf{b_2} &= 2\pi\frac{\mathbf{a_3}\times\mathbf{a_1}}{\mathbf{a_1}\cdot(\mathbf{a_2}\times\mathbf{a_3})} && (2)\\ \mathbf{b_3} &= 2\pi\frac{\mathbf{a_1}\times\mathbf{a_2}}{\mathbf{a_1}\cdot(\mathbf{a_2}\times\mathbf{a_3})} && (3) \end{aligned}$$

What is the proper formula in 2d?

(c) Define tetragonal and orthorhombic lattices. For an orthorhombic lattice, show that $|\mathbf{b_j}| = 2\pi/|\mathbf{a_j}|$. Hence, show that the length of the reciprocal lattice vector $\mathbf{G} = h\mathbf{b_1} + k\mathbf{b_2} + l\mathbf{b_3}$ is equal to $2\pi/d$, where $d$ is the spacing of the $(hkl)$ planes (see question 3.2.)

3.4. **Reciprocal Lattice and X-ray Scattering**

A two-dimensional rectangular crystal has a unit cell with sides $a_1 = 0.468$ nm and $a_2 = 0.342$ nm. A collimated beam of monochromatic X-rays with wavelength 0.166 nm is used to examine the crystal.

(a) Draw to scale a diagram of the reciprocal lattice.

▷ Label the reciprocal lattice points for indices in the range $0 \le h \le 3$ and $0 \le k \le 3$.

(b) Calculate the magnitude of the wavevectors $\mathbf{k}$ and $\mathbf{k}'$ of the incident and reflected X-ray beams, and hence construct on your drawing the "scattering triangle" corresponding to the Laue condition $\Delta\mathbf{k} = \mathbf{G}$ for diffraction from the (210) planes. (the scattering triangle includes $\mathbf{k}$, $\mathbf{k}'$ and $\Delta\mathbf{k}$).

(c) Draw the first and second Brillouin zones using the Wigner-Seitz construction.

3.5. ‡ **X-ray scattering II**

$BaTiO_3$ has a primitive cubic lattice and a basis with atoms having fractional coordinates

| | | | |
|---|---|---|---|
| Ba | (0,0,0) | | |
| Ti | $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ | | |
| O | $(\frac{1}{2},\frac{1}{2},0)$, | $(\frac{1}{2},0,\frac{1}{2})$, | $(0,\frac{1}{2},\frac{1}{2})$ |

▷ Sketch the unit cell.

▷ Show that the X-ray structure factor for the $(00l)$ Bragg reflections is given by

$$S_{hkl} = f_{Ba} + (-1)^l f_{Ti} + \left[1 + 2(-1)^l\right] f_O \qquad (4)$$

where $f_{\mathrm{Ba}}$ is the atomic form factor for Ba, etc.

▷ Calculate the ratio $I_{002}/I_{001}$, where $I_{hkl}$ is the intensity of the X-ray diffraction from the $(hkl)$ planes. You may assume that the atomic form factor is proportional to atomic number $(Z)$, and neglect its dependence on the scattering vector. [ $Z_{\mathrm{Ba}} = 56$, $Z_{\mathrm{Ti}} = 22$, $Z_{\mathrm{O}} = 8$ ]

3.6. ‡ **X-ray scattering and Systematic Absences**

(a) Explain what is meant by "Lattice Constant" for a cubic crystal structure.

(b) Explain why X-ray diffraction may be observed in first order from the (110) planes of a crystal with a body-centred cubic lattice, but not from the (110) planes of a crystal with a face-centred cubic lattice.

$\triangleright$ Derive the general selection rules for which planes are observed in bcc and fcc lattices.

(c) Show that these selection rules hold independent of what atoms are in the primitive unit cell, so long as the lattice is bcc or fcc respectively.

(d) A collimated beam of monochromatic X-rays of wavelength 0.162 nm is incident upon a powdered sample of the cubic metal palladium. Peaks in the scattered X-ray pattern are observed at angles of 42.3°, 49.2°, 72.2°, 87.4° and 92.3° from the direction of the incident beam.

$\triangleright$ Identify the lattice type

$\triangleright$ Calculate the lattice constant and the nearest-neighbor distance.

$\triangleright$ How well does this distance agree with the known data that the density of palladium is 12023 kg $\mathrm{m}^{-3}$? [Atomic mass of palladium = 106.4].

(e) How could you improve the precision with which the lattice constant is determined.

### 3.7. ‡ Neutron Scattering

(a) X-ray diffraction from sodium hydride (NaH) established that the Na atoms are arranged on a face-centred cubic lattice.

$\triangleright$ Why is it difficult to locate the positions of the H atoms using X-rays?

The H atoms were thought to be displaced from the Na atoms either by $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ or by $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, to form the ZnS (zinc blende) structure or NaCl (sodium chloride) structure, respectively. To distinguish these models a neutron powder diffraction measurement was performed. The intensity of the Bragg peak indexed as (111) was found to be much larger than the intensity of the peak indexed as (200).

$\triangleright$ Write down expressions for the structure factors $S_{hkl}$ for neutron diffraction assuming NaH has

(i) the sodium chloride (NaCl) structure

(ii) the zinc blende (ZnS) structure.

$\triangleright$ Hence, deduce which of the two structure models is correct for NaH. [Nuclear scattering length of Na $= 0.363 \times 10^5$nm; nuclear scattering length of H $= -0.374 \times 10^5$ nm]

(b) How does one produce monochromatic neutrons for use in neutron diffraction experiments?

$\triangleright$ What are the main differences between neutrons and X-rays?

$\triangleright$ Explain why (inelastic) neutron scattering is appropriate for observing phonons, but x-rays are not.

### 3.8. One Dimensional Tight Binding Model

This problem really belongs in problem set 2 due to its similarities with problems 2.5. and 2.6.. I recommend that you back up and review those problems before attempting this one. They are *extremely* similar to this.

(a) **Monatomic Solid:** Consider a one-dimensional tight binding model of electrons hopping between atoms. Let the distance between atoms be called $a$, and here let us label the atomic orbital on atom $n$ as $|n\rangle$ for $n = 1 \ldots N$ (and you may assume periodic boundary conditions). Suppose there is an on-site energy $\epsilon$ and a hopping matrix element $-t$. In other words, suppose $\langle n|H|m\rangle = \epsilon$ for $n = m$ and $\langle n|H|m\rangle = -t$ for $n = m \pm 1$.

$\triangleright$ Derive and sketch the dispersion curve for electrons. (Hint: Use the effective Schroedinger equations of problem 2.2.a. The resulting equation should look very similar to that of problem 2.5. above.)

$\triangleright$ How many different eigenstates are there in this system?

$\triangleright$ What is the effective mass of the electron near the bottom of this band?

$\triangleright$ What is the density of states?

$\triangleright$ If each atom is monovalent (it donates a single electron) what is the density of states at the fermi surface?

$\triangleright$ What then is the Pauli paramagentic (spin) susceptibility of the system? (See problem 1.6.).

$\triangleright$ What is the spin susceptibility if each atom is divalent?

(b) **Diatomic Solid:** Now consider a model of a diatomic solid as such

$$-A-B-A-B-A-B-$$

Suppose that the onsite energy of type $A$ is different from the onsite energy of type $B$. I.e, $\langle n|H|n\rangle$ is $\epsilon_A$ for $n$ being on a site of type $A$ and is $\epsilon_B$ for $n$ being on a site of type $B$. (All hopping matrix elements $-t$ are still identical to each other).

$\triangleright$ Calculate the new dispersion relation. (This is extremely similar to problem 2.6. above. If you are stuck, try studying that problem again.)

$\triangleright$ Sketch this dispersion relation in both the reduced and extended zone schemes.

$\triangleright$ What happens in the "atomic" limit when $t$ becomes very small.

$\triangleright$ What is the effective mass of an electron near the bottom of the lower band?

$\triangleright$ If each atom (of either type) is monovalent, is the system a metal or an insulator?