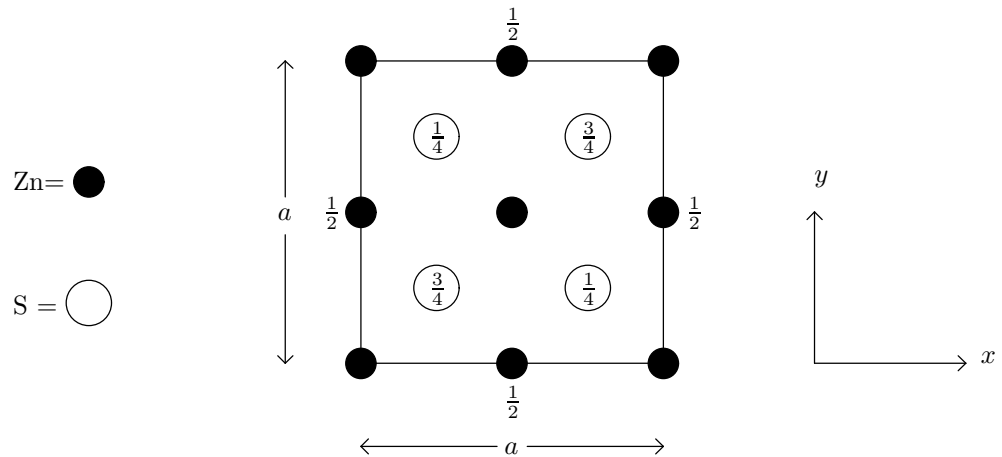


## Problem Set 3

### Crystal Structure, Reciprocal Lattice, and Scattering

#### 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  $z = a$ .

- What is the Bravais lattice type
- Describe the basis
- Given that  $a = 0.541$  nm, calculate the nearest-neighbor Zn-Zn, Zn-S, and S-S distances.
- Copy the drawing above, and show the  $[210]$  direction and the set of  $(210)$  planes.
- 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.”
- ▷ 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

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \quad (1)$$

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

$$\mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \quad (3)$$

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  $0 \leq h \leq 3$  and  $0 \leq k \leq 3$ .  
 (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<sub>3</sub> has a primitive cubic lattice and a basis with atoms having fractional coordinates

$$\begin{array}{l} \text{Ba} \quad [0,0,0] \\ \text{Ti} \quad [\frac{1}{2}, \frac{1}{2}, \frac{1}{2}] \\ \text{O} \quad [\frac{1}{2}, \frac{1}{2}, 0], \quad [\frac{1}{2}, 0, \frac{1}{2}], \quad [0, \frac{1}{2}, \frac{1}{2}] \end{array}$$

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

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

where  $f_{Ba}$  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. [ $Z_{Ba} = 56$ ,  $Z_{Ti} = 22$ ,  $Z_O = 8$ ]

### 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.
- ▷ 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  $42.3^\circ$ ,  $49.2^\circ$ ,  $72.2^\circ$ ,  $87.4^\circ$  and  $92.3^\circ$  from the direction of the incident beam.
- ▷ Identify the lattice type
- ▷ Calculate the lattice constant.
- ▷ If you assume there is only a single atom in the basis, how well does this lattice constant agree with the known data that the density of palladium is  $12023 \text{ kg m}^{-3}$ ? [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.

▷ 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 (zincblende) 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).

▷ 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.

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

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

▷ What are the main differences between neutrons and X-rays?

▷ Explain why (inelastic) neutron scattering is well suited for observing phonons, but x-rays are not.