Assignment 1: Solution

1. Cu₃Ag has fcc structure with $a = b = c = 3.74 \text{ Å}$. Atomic coordinates are:

   \[ \text{Ag in 1a at } (0, 0, 0) \]
   \[ 3\text{Cu in 3c at } (0, \frac{1}{2}, \frac{1}{2}), \left(\frac{1}{2}, 0, \frac{1}{2}\right), \text{ and } \left(\frac{1}{2}, \frac{1}{2}, 0\right), \]

and its projection along $\vec{c}$ shown in figure.

(a) Ag-Ag distance;
(i) first nearest neighbor at $a = 3.74 \text{ Å}$
(ii) second nearest neighbor at $\sqrt{2}a = 5.28 \text{ Å},$

Due date: Feb. 11, 2012, 5:00pm
(b) **Cu-cu distance:**
(i) first nearest neighbor at $a/\sqrt{2} = 2.64$ Å
(ii) second nearest neighbor at $a = 3.74$ Å,

(c) **Cu-Ag distance:**
(i) first nearest neighbor at $\sqrt{a^2/4 + a^2/3} = a/\sqrt{2} = 2.64$ Å.
(ii) second nearest neighbor at $\sqrt{5a^2/4 + a^2/4} = \sqrt{3a^2/2} = 4.58$ Å.

2. Fig (a) demonstrates the hexagonal close-packed structure. In addition to the two layers of atoms which form the base and upper face of the hexagon, there is also an intervening layer of atoms arranged such that each of these atoms rests over a depression between three atoms in the base. The unit cell with $a = b \neq c$, $\alpha = \beta = 90^0$, $\gamma = 120^0$ is shown in Fig (b). There are two spheres associated with each lattice point in the primitive hcp structure, one at $(0,0,0)$ and the other at $(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$. Consider Figs (b) and (c). In the hard spheres model, atoms touch. So $|\vec{A}| = 2R = a$, where $R$ is the atom’s radius. Note that $\vec{a}'$ is a new vector perpendicular to $\vec{b}$.
The vector \( \mathbf{B} = \frac{1}{3} \mathbf{a} + \frac{2}{3} \mathbf{b} \) and \( \mathbf{A} = \frac{1}{3} \mathbf{a} + \frac{2}{3} \mathbf{b} + \frac{1}{2} \mathbf{c} \). Remember that in hcp, \( \mathbf{a} \cdot \mathbf{b} \neq 0 \). From Fig (b), it is clear that \( \mathbf{a} \cdot \mathbf{b} = 0 \). Furthermore, the coordinates of \( \mathbf{a} \) and \( \mathbf{a}' \) are:

\[
\mathbf{a}' = |\mathbf{a}| \cos 30^\circ \hat{a}' \\
= \frac{\sqrt{3}}{2} a \hat{a}' , \\
\mathbf{a} = \frac{\sqrt{3}}{2} a \hat{a}' + |\mathbf{a}| \sin 30^\circ (-\hat{b}) \\
= \frac{\sqrt{3}}{2} a \hat{a}' - a \sin 30^\circ \hat{b} \\
= \frac{\sqrt{3}}{2} a \hat{a}' - \frac{a}{2} \hat{b} ,
\]

therefore \( \mathbf{A} \) can be written as,

\[
\mathbf{A} = \frac{1}{3} \mathbf{a} + \frac{2}{3} \mathbf{b} + \frac{1}{2} \mathbf{c} \\
= \frac{1}{3} (\frac{\sqrt{3}}{2} a \hat{a}' - \frac{a}{2} \hat{b}) + \frac{2}{3} \hat{a} + \frac{1}{2} \mathbf{c} \\
= \frac{\sqrt{3}}{6} a \hat{a}' + \frac{a}{2} \hat{b} + \frac{1}{2} \mathbf{c} ,
\]

and its magnitude is

\[
|\mathbf{A}| = \sqrt{\frac{3a^2}{36} + \frac{a^2}{4} + \frac{c^2}{4} = 2R = a} \\
\frac{3a^2 + 9a^2}{36} + \frac{c^2}{4} = a^2 \\
\frac{a^2}{3} + \frac{c^2}{4} = a^2 \\
\frac{c^2}{4} = a^2 (1 - \frac{1}{3}) \\
\frac{c^2}{4} = a^2 \frac{2}{3} \\
\frac{c}{a} = \sqrt{\frac{8}{3}}.
\]

This is the ideal \( c/a \) ratio in hcp.

(b) The crystallographic density of Ni is given by,

\[
\rho = \frac{\text{mass of Ni in the unit cell}}{\text{volume of unit cell}} ,
\]

so we need to evaluate the volume of the unit cell.

\[
\text{Volume of the unit cell} = \mathbf{a} \cdot \mathbf{b} \times \mathbf{c}.
\]
\[ \vec{a} \cdot (ac \sin 90^0) \hat{a}' = ac(\vec{a} \cdot \hat{a}') = \frac{c}{a} a^2 (\vec{a} \cdot \hat{a}') = \sqrt{\frac{8}{3}} a^2 (a \cos 30^0) = \sqrt{\frac{8}{3}} a^2 \frac{\sqrt{3}a}{2} = \frac{\sqrt{8}}{2} a^3 = \frac{2\sqrt{2}}{2} a^3 = \sqrt{2} a^3. \]

Given that; the atomic radius is 150 pm = 150 \times 10^{-12} m = 150 \times 10^{-10} cm; and for two spheres associated with each lattice point, \( a = 2R = 2(150 \times 10^{-10} \text{ cm}) = 3 \times 10^{-8} \text{ cm}, \) the volume of the unit cell becomes

\[ = \sqrt{2}(3 \times 10^{-8})^3 = \sqrt{2}(2.7 \times 10^{-23}) = 3.817 \times 10^{-23} \text{ cm}^3. \]

Now mass of the Ni atom = \[ \text{molar mass} \over \text{Avagadro's number} \]
\[ = \frac{58.693}{6.023 \times 10^{23}} = 9.744 \times 10^{-23} \text{ g}. \]

There are 2 Ni atoms per unit cell, so the mass of Ni in the unit cell = \( 2(9.744 \times 10^{-23}) = 1.949 \times 10^{-22} \text{ g}. \) Thus, the crystallographic density of Ni is

\[ \rho = \frac{1.949 \times 10^{-22}}{3.817 \times 10^{-23}} = 5.11 \text{ g cm}^{-3}. \]

The experimentally found density is 8.9 g cm\(^{-3}\).

3. Diamond has an \( F \)-lattice with atoms at the 8a positions;

\[ C_1 \equiv (0,0,0), \ C_2 \equiv (0,\frac{1}{2},\frac{1}{2}), \ C_3 \equiv (\frac{1}{2},0,\frac{1}{2}), \ C_4 \equiv (\frac{1}{2},\frac{1}{2},0), \ C_5 \equiv (\frac{3}{4},\frac{1}{4},\frac{3}{4}), \ C_6 \equiv (\frac{3}{4},\frac{3}{4},\frac{1}{4}), \ C_7 \equiv (\frac{1}{4},\frac{1}{4},\frac{1}{4}), \ C_8 \equiv (\frac{1}{4},\frac{3}{4},\frac{3}{4}). \]
Screw Symmetry Operation and Glide plane:

$4_1$ axis parallel to $\vec{c}$ is at $\left(\frac{1}{2}, \frac{1}{2}, 0\right)$ and diamond glide plane perpendicular to $4_1$ axis, is at $(x, y, \frac{1}{8})$ with $\vec{a} + \vec{b} \frac{1}{4}$ translation (see Fig (a)). In Seitz notation, the glide plane is written as $\{\sigma(x, y, \frac{1}{8})|\vec{a} + \vec{b} \frac{1}{4}\}$.

Fig (a) showing the screw $4_1$ axis and glide plane and 2 axis. Fig (b) showing a mirror plane normal to a 2-fold axis, shown already in (a).

Let’s take representative atom, say C$_7$, at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ and apply the $4_1$ screw operation successively resulting in:

$$
\begin{align*}
\text{after } 4_1 &: \quad \left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right) \rightarrow \left(\frac{1}{2}, 0, \frac{1}{2}\right) \\
\text{after } 4_1^2 &: \quad \left(\frac{1}{2}, 0, \frac{1}{2}\right) \rightarrow \left(\frac{3}{4}, \frac{3}{4}, \frac{3}{4}\right) \\
\text{after } 4_1^3 &: \quad \left(\frac{3}{4}, \frac{3}{4}, \frac{3}{4}\right) \rightarrow \left(\frac{1}{2}, \frac{1}{2}, 0\right), \quad \text{and} \\
\text{after } 4_1^4 &: \quad \left(\frac{1}{2}, \frac{1}{2}, 0\right) \rightarrow \left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right).
\end{align*}
$$
The glide plane, similarly, takes \( C_7 \equiv (\frac{1}{4}, \frac{1}{4}, \frac{1}{4}) \) to \( C_4 \equiv (\frac{1}{4}, \frac{1}{4}, 0) \) and so on. Note that in space group notation \( 2/m \) means that there is a mirror plane perpendicular to the 2-fold axis.

**Two fold Mirror plane Symmetry Operation (2/m):**

The two-fold axis of rotation is along a face diagonal \([\bar{1} 1 0]\). The two fold rotation along the face diagonal moves \((0, \frac{1}{2}, \frac{1}{2})\) to \((\frac{1}{2}, 0, \frac{1}{2})\).

Finally, the mirror plane perpendicular to the two fold axis, shown in (b), reflects \((0, \frac{1}{2}, \frac{1}{2})\) to \((\frac{1}{2}, 1, \frac{1}{2})\) which is same as \((\frac{1}{2}, 0, \frac{1}{2})\).

The zinc blende ZnS structure is closely related to that of diamond. ZnS crystallizes in the space group \( F\bar{4}3m \) and the basis is Zn at the \( 4a \) site at \((0, 0, 0)\) and S at the \( 4c \) site at \((\frac{1}{4}, \frac{1}{4}, \frac{1}{4})\) plus the equivalent positions due to the F-lattice;

\[
\begin{align*}
Zn_1 & \equiv (0, 0, 0), \quad Zn_2 \equiv (0, \frac{1}{2}, \frac{1}{2}), \quad Zn_3 \equiv (\frac{1}{2}, 0, \frac{1}{2}), \quad Zn_4 \equiv (\frac{1}{2}, \frac{1}{2}, 0), \\
S_1 & \equiv (\frac{3}{4}, \frac{1}{4}, \frac{3}{4}), \quad S_2 \equiv (\frac{3}{4}, \frac{3}{4}, \frac{1}{4}), \quad S_3 \equiv (\frac{1}{4}, \frac{1}{4}, \frac{1}{4}), \quad S_4 \equiv (\frac{1}{4}, \frac{3}{4}, \frac{3}{4}).
\end{align*}
\]

Unlike diamond, this structure does not have a screw axis or center of symmetry owing to the dissimilarity of the atoms.

Diamond has center of inversion at \((\frac{1}{8}, \frac{1}{8}, \frac{1}{8})\) (see Fig (7)). But zinc blende does not have center of inversion because of dissimilar atoms.

4. The crystal system is monoclinic, while the lattice is primitive. Operation E (or 1) takes the point in the top right within the unit cell to itself. Let’s label this point as P.

The \( 2_1 \) screw axis at \((0, \frac{1}{4}, 0)\) takes P to the point Q which is equivalent to the point R.
The centre of inversion at \((\frac{1}{2}, \frac{1}{2}, 0)\) transforms \(P\) to \(S\). There is also a b-glide plane at height \(z = 1/4\). The glide plane affects a reflection about the plane \((0, 0, \frac{1}{4})\), i.e., height \(z = 1/4\), followed by translation \(+\frac{1}{2}\mathbf{b}\). This transforms \(P\) to \(T\) in the neighboring cell at height \(z = +1/2\). This is equivalent to the point \(U\). Since all points are equivalent by lattice translations \(\pm 1\) units along \(\mathbf{c}\) axis, we write the point \(U\) with \(z\) coordinate \(\frac{1}{2}\), as is done in the International Tables.

These operations can also be seen from the space group name, \(P2_1/b\). The system is monoclinic. The nomenclature represents a \(2_1\) operation around the unique axis (which in our setting is the \(\mathbf{c}\) axis). There is then the glide plane normal to the \(2_1\) axis, where the over (/) sign shows perpendicularity.

5. Zinc sulfide crystallizes in two different atoms; wurtzite and zincblende.

**Tetrahedra in zinc blende**

Zinc blende crystallizes in the space group \(F\bar{4}3m\) and the basis is \(\text{Zn}\) at the \(4a\) site at \((0, 0, 0)\) and \(\text{S}\) at the \(4c\) site at \(\left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right)\) plus the equivalent positions due to the \(F\) centering. Consider various views of the unit cell shown below. We define the vectors \(\mathbf{p}_1\) through \(\mathbf{p}_4\) as shown.
All these lengths are in units of $a$,

\[
|\vec{p}_1| = [0 0 0] - \begin{bmatrix} \frac{1}{4} \\ \frac{1}{4} \\ \frac{1}{4} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix},
\]

\[
|\vec{p}_2| = \begin{bmatrix} \frac{1}{2} \\ \frac{1}{2} \\ 0 \end{bmatrix} - \begin{bmatrix} \frac{1}{4} \\ \frac{1}{4} \\ \frac{1}{4} \end{bmatrix} = \begin{bmatrix} \frac{1}{4} \\ \frac{1}{4} \\ -\frac{1}{4} \end{bmatrix},
\]

\[
|\vec{p}_3| = \begin{bmatrix} 0 \\ \frac{1}{2} \\ \frac{1}{2} \end{bmatrix} - \begin{bmatrix} \frac{1}{4} \\ \frac{1}{4} \\ \frac{1}{4} \end{bmatrix} = \begin{bmatrix} \frac{1}{4} \\ \frac{1}{4} \\ -\frac{1}{4} \end{bmatrix},
\]

\[
|\vec{p}_4| = \begin{bmatrix} \frac{1}{2} \\ 0 \\ \frac{1}{2} \end{bmatrix} - \begin{bmatrix} \frac{1}{4} \\ \frac{1}{4} \\ \frac{1}{4} \end{bmatrix} = \begin{bmatrix} \frac{1}{4} \\ -\frac{1}{4} \\ \frac{1}{4} \end{bmatrix}.
\]

All of these vectors have equal lengths,

\[
|\vec{p}_1| = |\vec{p}_2| = |\vec{p}_3| = |\vec{p}_4| = \sqrt{\frac{3}{16}} = \frac{\sqrt{3}}{4}.
\]

Angle between any two vectors, e.g., $\vec{p}_1$ and $\vec{p}_2$ is.

\[
\frac{3}{16} \cos \Phi = \frac{3}{16} \cos \Phi = -\frac{1}{16} - \frac{1}{16} + \frac{1}{16} = -\frac{1}{16},
\]

\[
\cos \Phi = -\frac{1}{3},
\]

\[
\Phi = \cos^{-1}\left(-\frac{1}{3}\right) = 109.47^\circ.
\]

Likewise, the angle between any two edges is the same at $109.47^\circ$, which is the tetrahedral angle.

**Tetrahedra in wurtzite**

The space group is $P6_3mc$, where Zn is at the $2b$ positions; $(0, 0, 0)$ and $(1/3, 2/3, 1/2)$ and S at $2b$ positions; $(0, 0, u)$ and $(1/3, 2/3, 1/2 + u)$ with $u = 3/8$.

**Fig (10):**

(a) Projection along $c^\parallel$

(b) Primitive unit cell
Coordinates of the vectors shown in Fig (b), written with respect to the standard hexagonal axes are,

\[ \vec{q}_1 = [0 \ 0 \ u] - \begin{bmatrix} 1 & 2 & 1 \\ 3 & 3 & 2 \end{bmatrix} = \begin{bmatrix} -1/3 - 2/3 \ u - 1/2 \end{bmatrix} = -\frac{2}{3} \vec{b} + (u - \frac{1}{2}) \vec{c} \]

\[ \vec{q}_2 = [1 \ 1 \ u] - \begin{bmatrix} 1 & 2 & 1 \\ 3 & 3 & 2 \end{bmatrix} = \begin{bmatrix} 2/3 \ 1/3 \ u - 1/2 \end{bmatrix} = \frac{2}{3} \vec{a} - \frac{1}{3} \vec{b} + (u - \frac{1}{2}) \vec{c}. \]

Now let’s introduce for the ease of computation, the orthogonal axes \( \{\vec{a}', \vec{b}, \vec{c}\} \),

\[
\vec{a} = \sqrt{3} \frac{a \hat{a}}{2} - \frac{a \hat{b}}{2} \\
\vec{b} = ab \\
\vec{c} = c \hat{c} = \sqrt{\frac{8}{3}} a \hat{c}.
\]

Also see Fig (c) of Q2!

\[ \Rightarrow \vec{q}_1 = -\frac{1}{3} \left( \frac{\sqrt{3}}{2} a \hat{a}' - \frac{a \hat{b}}{2} \right) - \frac{2}{3} \hat{a} \hat{b} - \frac{1}{8} \hat{c} \hat{c} \]

\[ = -\frac{\sqrt{3}}{6} a \hat{a}' + \left( \frac{a}{6} - \frac{2a}{3} \right) \hat{b} - \frac{1}{8} \sqrt{\frac{8}{3}} a \hat{c} \]

\[ \vec{q}_2 = \frac{2}{3} \left( \frac{\sqrt{3}}{2} a \hat{a}' - \frac{a \hat{b}}{2} \right) + \frac{1}{3} \hat{a} \hat{b} - \frac{1}{8} \sqrt{\frac{8}{3}} a \hat{c} \]

\[ = \frac{\sqrt{3}}{3} a \hat{a}' - \frac{a \hat{b}}{3} + \frac{1}{3} \hat{a} \hat{b} - \frac{1}{8} \sqrt{\frac{8}{3}} a \hat{c} \]

\[ = \frac{\sqrt{3}}{3} a \hat{a}' - \frac{1}{8} \sqrt{\frac{8}{3}} a \hat{c}, \]

where \( a' = a \cos 30^\circ = \frac{a \sqrt{3}}{2} \).

\[ |\vec{q}_1| = \sqrt{\frac{3}{36} a^2 + \left( \frac{a^2}{36} + \frac{4a^2}{9} - \frac{4a^2}{18} \right) + \frac{1}{64} \left( \frac{8}{3} \right) a^2} \]

\[ = \sqrt{\frac{4}{36} a^2 + \frac{16}{36} a^2 - \frac{8}{36} a^2 + \frac{1}{24} a^2} \]

\[ = \sqrt{\frac{a^2}{24} + \frac{a^2}{3}} = \sqrt{\frac{a^2 + 8a^2}{24}} = \sqrt{\frac{9a^2}{24}} = \sqrt{\frac{3}{8}} a \]

\[ |\vec{q}_2| = \sqrt{\frac{3}{9} a^2 + \frac{1}{64} \times \frac{8}{3} a^2} = \sqrt{\left( \frac{1}{3} + \frac{1}{24} \right) a^2} = \sqrt{\frac{3}{8}} a. \]

Due date: Feb. 11, 2012, 5:00pm
The angle between $\vec{q}_1$ and $\vec{q}_2$,

$$
\cos \Phi = \frac{\vec{q}_1 \cdot \vec{q}_2}{|\vec{q}_1||\vec{q}_2|} = \frac{\left(-\frac{\sqrt{3}}{6} a \hat{a}' + \left(\frac{a}{6} - \frac{2a}{3}\right) \hat{b} - \frac{1}{8} \sqrt{\frac{5}{3}} a \hat{c}\right) \cdot \left(\frac{\sqrt{3}}{3} a \hat{a}' - \frac{1}{8} \sqrt{\frac{5}{3}} a \hat{c}\right)}{\sqrt{\frac{3}{8} a} \times \sqrt{\frac{3}{8} a}}
$$

$$
= -\frac{3}{18} a^2 + \frac{1}{61} \times \frac{8}{3} a^2 = \frac{24}{61} - \frac{1}{6} = -\frac{1}{3}
$$

$$
\Phi = \cos^{-1} \left(-\frac{1}{3}\right) = 109.47^\circ,
$$

which is, once again, the tetrahedral angle. Hence the Zn-S coordination in both zincblende and wurtzite structure is tetrahedral.

6. **Pmc2$_1$: Primitive Orthorhombic**

1) The space group notation shows that in this crystal structure, there is a mirror plane perpendicular to the $\hat{a}$ axis.

2) $c$ is a glide plane perpendicular to the $\hat{b}$ axis. The plane produces a reflection followed by a translation along the $\hat{c}$ axis.

3) Finally, 2$_1$ is a screw axis along the $\hat{c}$ axis. The equivalent positions generated by the symmetry operations can be seen in accompanying projective diagram.

There are four equivalent positions in the unit cell

$$(x, y, z), \ (x, \bar{y}, z + 1/2), \ (\bar{x}, y, z), \ (\bar{x}, \bar{y}, z + 1/2),$$

which are the positions shown by A, B, C, D in the projective diagram. Check the International Tables!
The thick horizontal lines represent mirror planes. The vertical dotted lines are glide planes and the dgadic symbols are screw axes.

7. (a) Cuprite (Cu$_2$O) crystallizes in $Pn\overline{3}m$. Fractional coordinates:

\begin{align*}
\text{O in } & \ 2a \ \text{at } (0,0,0), \left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right) \\
\text{Cu in } & \ 4f \ \text{at } \left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right), \left(\frac{3}{4}, \frac{3}{4}, \frac{1}{4}\right), \left(\frac{3}{4}, \frac{1}{4}, \frac{3}{4}\right), \left(\frac{1}{4}, \frac{3}{4}, \frac{3}{4}\right).
\end{align*}

(b) There are two formula units per unit cell and one point per unit cell. There are four Cu atoms and two O atoms per unit cell.

\[a = 4.26 \text{ Å}, \ \text{volume of the unit cell} = \left(4.26 \times 10^{-10}\right)^3 \text{ m}^3 = 77.3 \times 10^{-30} \text{ m}^3.\]

(c) The density of the mineral is 6.1 g cm$^{-3}$.

\[
\text{mass per unit cell} = 6000 \times 77.3 \times 10^{-30} \text{ kg} = 4.638 \times 10^{-25} \text{ kg}
\]
\[
\text{mass of one formula unit} = \frac{(2 \times 63.5 + 32) \times 10^{-3}}{6.023 \times 10^{23}} = 2.64 \times 10^{-25} \text{ kg}
\]

Number of formula units per unit cell = 1.8,

which is consistent with the crystallographic information, 2 formula units per cell.

(d) The projection is drawn above. 4 diagonal (n) glide planes are shown in the projective view by dotted lines. For example a plane intersects at $x = 1/4$. Under the action of this glide plane, the operation \(\{\sigma(4 \ 0 \ 0)|\vec{b}_2 + \vec{c}\}\) transforms the O atom at $(0,0,0)$ to the position $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and so on.