

Sources

U. Müller, *Inorganic Structural Chemistry*, John Wiley & Sons, Chichester, England, 1993  
 A.R. West, *Basic Solid State Chemistry*, 2<sup>nd</sup> Edition, John Wiley & Sons, New York, 1999.

Useful resources and information for some of the following problems include:

- *International Tables for Crystallography, Volume A*, <https://it.iucr.org>
- *VESTA*, <http://jp-minerals.org/vesta/en/download.html>, distributed without charge for academic users
- *IUPAC Commission, Atomic Weights of the Elements 2021*, <https://iupac.qmul.ac.uk/AtWt/>
- Avogadro's number:  $N_A = 6.022 \times 10^{23}$

**Elements**

- (1) Calculate the densities (in g/cm<sup>3</sup>) of the following allotropes of carbon. Briefly discuss the variation in these values.

Graphite-2H  $hP4$   $a = 2.464 \text{ \AA}$ ,  $c = 6.711 \text{ \AA}$ ,  $\gamma = 120^\circ$

$$\text{Density} = \frac{(4)(12.01 \text{ g/mol}) / 6.022 \times 10^{23} \text{ mol}^{-1}}{[(2.464 \text{ \AA})^2 (6.711 \text{ \AA}) \sin 120^\circ] (10^{-8} \text{ cm/\AA})^3} = \frac{7.9781 \times 10^{-23} \text{ g}}{3.5286 \times 10^{-23} \text{ cm}^3} = 2.261 \text{ g/cm}^3$$

Graphite-3R  $hR2$   $a = 3.635 \text{ \AA}$ ,  $\alpha = 39.82^\circ$  (Primitive cell)

$$\text{Density} = \frac{3.9890 \times 10^{-23} \text{ g}}{1.7741 \times 10^{-23} \text{ cm}^3} = 2.248 \text{ g/cm}^3$$

Diamond  $cF8$   $a = 3.567 \text{ \AA}$

$$\text{Density} = \frac{1.5956 \times 10^{-22} \text{ g}}{4.5385 \times 10^{-23} \text{ cm}^3} = 3.516 \text{ g/cm}^3$$

Buckminsterfullerene  $cF240$   $a = 14.16 \text{ \AA}$

$$\text{Density} = \frac{4.7868 \times 10^{-21} \text{ g}}{2.8392 \times 10^{-21} \text{ cm}^3} = 1.686 \text{ g/cm}^3$$

Densities increase as the structures change from molecular (buckminsterfullerene) to layered (graphite) to 3-d network (diamond).

- (2) Calculate the densities (in g/cm<sup>3</sup>) and average molar volumes (L/mol) for the following sequence of 5<sup>th</sup> period elements at 298 K. Discuss any trends you see in the results.

Ag ( $cF4$ )  $a = 4.0863 \text{ \AA}$

$$\text{Density} = \frac{7.1649 \times 10^{-22} \text{ g}}{6.8232 \times 10^{-23} \text{ cm}^3} = 10.50 \text{ g/cm}^3; \quad \text{Molar Volume} = \frac{AW}{1000 \rho} = 0.0103 \text{ L/mol}$$

Cd ( $hP2$ )  $a = 2.9794 \text{ \AA}$ ,  $c = 5.6186 \text{ \AA}$ ,  $\gamma = 120^\circ$

$$\text{Density} = \frac{3.7334 \times 10^{-22} \text{ g}}{4.3193 \times 10^{-23} \text{ cm}^3} = 8.644 \text{ g/cm}^3; \quad \text{Molar Volume} = 0.0130 \text{ L/mol}$$

In ( $tI2$ )  $a = 3.2509 \text{ \AA}$ ,  $c = 4.9474 \text{ \AA}$

$$\text{Density} = \frac{3.8133 \times 10^{-22} \text{ g}}{5.2286 \times 10^{-23} \text{ cm}^3} = 7.293 \text{ g/cm}^3; \quad \text{Molar Volume} = 0.0157 \text{ L/mol}$$

Sn ( $tI4$ )  $a = 5.8318 \text{ \AA}$ ,  $c = 3.1819 \text{ \AA}$

$$\text{Density} = \frac{7.8851 \times 10^{-22} \text{ g}}{1.0822 \times 10^{-22} \text{ cm}^3} = 7.286 \text{ g/cm}^3; \quad \text{Molar Volume} = 0.0163 \text{ L/mol}$$

Sb (*hR6*)  $a = 4.3084 \text{ \AA}$ ,  $c = 11.2740 \text{ \AA}$   $\gamma = 120^\circ$   
**Density** =  $\frac{1.2132 \times 10^{-21} \text{ g}}{1.8123 \times 10^{-22} \text{ cm}^3} = 6.694 \text{ g/cm}^3$ ; **Molar Volume** = **0.0182 L/mol**

Te (*hP3*)  $a = 4.457 \text{ \AA}$ ,  $c = 5.929 \text{ \AA}$   $\gamma = 120^\circ$   
**Density** =  $\frac{6.3567 \times 10^{-22} \text{ g}}{1.0200 \times 10^{-22} \text{ cm}^3} = 6.232 \text{ g/cm}^3$ ; **Molar Volume** = **0.0205 L/mol**

I (*oS8*)  $a = 7.255 \text{ \AA}$ ,  $b = 4.795 \text{ \AA}$ ,  $c = 9.780 \text{ \AA}$   
**Density** =  $\frac{1.6859 \times 10^{-21} \text{ g}}{3.4022 \times 10^{-22} \text{ cm}^3} = 4.955 \text{ g/cm}^3$ ; **Molar Volume** = **0.0256 L/mol**

These densities steadily decrease from Ag to I as their structures vary from densely packed to molecular packings. Likewise, the molar volumes increase steadily I. Ag is cubic close packed. Although Cd is hexagonally close packed, the distance between adjacent close packed layers is extended as compared to ideal 3-d close packing. The main group metals In and Sn and the semimetals Sb and Te adopt more open atomic packings with Sb and Te based, respectively, on 3-connected layers and 2-connected spiral chains. Iodine is a packing of I<sub>2</sub> molecules.

- (3) The following elements adopt structures that are distortions of HCP, CCP, or BCC. Given the unit cell parameters and atomic positions, determine the element's density (in g/cm<sup>3</sup>) and the coordination environment of the atom. Discuss how each structure compares to one of HCP, CCP, or BCC.

Cd (*hP2*)  $a = 2.979 \text{ \AA}$ ,  $c = 5.619 \text{ \AA}$ ,  $\gamma = 120^\circ$ ; Cd atoms at  $(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$  and  $(\frac{2}{3}, \frac{1}{3}, \frac{3}{4})$ .

**Density** = **8.645 g/cm<sup>3</sup>**; **6 neighbors in the *ab*-plane at 2.979 \AA**  
**6 neighbors above/below *ab*-plane at 3.294 \AA**  
**HCP-related; expanded *c*-axis compared to *a*-axis.**

Hg (*hR3*)  $a = 3.458 \text{ \AA}$ ,  $c = 6.684 \text{ \AA}$ ,  $\gamma = 120^\circ$ ; Hg atoms at  $(0,0,0)$ ,  $(\frac{2}{3}, \frac{1}{3}, \frac{1}{3})$  and  $(\frac{1}{3}, \frac{2}{3}, \frac{2}{3})$ .

**Density** = **15.401 g/cm<sup>3</sup>**; **6 neighbors in the *ab*-plane at 3.458 \AA**  
**6 neighbors above/below *ab*-plane at 2.992 \AA**  
**CCP-related; compressed along the *body-diagonal* of the cubic cell.**

In (*tI2*)  $a = 3.251 \text{ \AA}$ ,  $c = 4.947 \text{ \AA}$ ; In atoms at  $(0,0,0)$  and  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ .

**Density** = **7.293 g/cm<sup>3</sup>**; **4 neighbors in the *ab*-plane at 3.251 \AA**  
**8 neighbors above/below *ab*-plane at 3.377 \AA**  
**CCP-related; expanded along one axis (*c*-axis) of the cubic cell.**

Pa (*tI2*)  $a = 3.925 \text{ \AA}$ ,  $c = 3.238 \text{ \AA}$ ; Pa atoms at  $(0,0,0)$  and  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ .

**Density** = **15.382 g/cm<sup>3</sup>**; **6 neighbors in the *ab*-plane at 3.458 \AA**  
**6 neighbors above/below *ab*-plane at 2.992 \AA**  
**CCP-related; compressed along the *body-diagonal* of the cubic cell.**

Zn (*hP2*)  $a = 2.659 \text{ \AA}$ ,  $c = 4.937 \text{ \AA}$ ,  $\gamma = 120^\circ$ ; Zn atoms at  $(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$  and  $(\frac{2}{3}, \frac{1}{3}, \frac{3}{4})$ .

**Density** = **7.183 g/cm<sup>3</sup>**; **6 neighbors in the *ab*-plane at 2.659 \AA**  
**6 neighbors above/below *ab*-plane at 2.907 \AA**  
**HCP-related; expanded *c*-axis compared to *a*-axis.**

- (4) At ambient pressure and temperature, manganese adopts the most complex structure among all elements. Before reaching its melting point of 1519 K, the solid undergoes three transitions: (1) at 1000 K,  $\alpha$ -Mn (*cI58*)  $\rightarrow$   $\beta$ -Mn (*cP20*); (2) at 1373 K,  $\beta$ -Mn (*cP20*)  $\rightarrow$   $\gamma$ -Mn (*cF4*, FCC); and (3) at 1411 K,  $\gamma$ -Mn (*cF4*, FCC)  $\rightarrow$   $\delta$ -Mn (*cI2*, BCC).

- (a) At 1000 K, the lattice constants for  $\alpha$ -Mn and  $\beta$ -Mn are, respectively, 9.092 Å and 6.477 Å. Evaluate their densities (in g/cm<sup>3</sup>) and molar volumes (in L/mol). Determine the change in molar volume at the transition temperature of 1000 K.

$\alpha$ -Mn:      Density = 7.040 g/cm<sup>3</sup>; Molar Volume = 0.00780 L/mol

$\beta$ -Mn:      Density = 6.715 g/cm<sup>3</sup>; Molar Volume = 0.00818 L/mol

$\Delta V_{\text{mol}} = V_{\text{mol}}(\beta) - V_{\text{mol}}(\alpha) = +0.00038 \text{ L/mol}$

- (b) At 1519 K, the lattice constant for  $\delta$ -Mn is 3.092 Å and density of Mn(*l*) is 5.95 g/cm<sup>3</sup>. Evaluate the density (in g/cm<sup>3</sup>) of  $\delta$ -Mn and molar volumes (in L/mol) of  $\delta$ -Mn and Mn(*l*) at 1519 K. Determine the change in molar volume at the melting point.

$\delta$ -Mn:      Density = 6.172 g/cm<sup>3</sup>; Molar Volume = 0.00890 L/mol

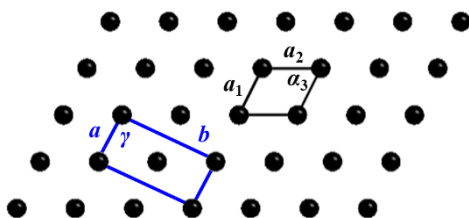
Mn(*l*):      Density = 5.95 g/cm<sup>3</sup>; Molar Volume = 0.00923 L/mol

$\Delta V_{\text{mol}} = V_{\text{mol}}(l) - V_{\text{mol}}(\delta) = +0.00033 \text{ L/mol}$

### Symmetry

- (5) For each of the following primitive unit cells of 2-d lattices, identify the rotational symmetry and determine the conventional unit cell.

- (a)  $a_1 = 3.00 \text{ \AA}$ ,  $a_2 = 2.68 \text{ \AA}$ ,  $\alpha_3 = 63.44^\circ$



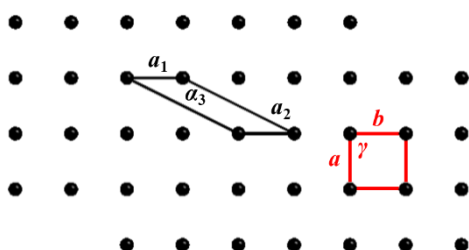
The lattice is *centered-rectangular* with a rectangular unit cell:

$a = a_1 = 3.00 \text{ \AA}$

$b = 2a_2 \sin \alpha_3 = 4.79 \text{ \AA}$

$\gamma = 90^\circ$

- (b)  $a_1 = 4.00 \text{ \AA}$ ,  $a_2 = 8.94 \text{ \AA}$ ,  $\alpha_3 = 153.43^\circ$



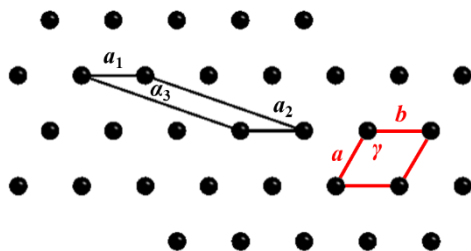
The lattice is *tetragonal* with a square-shaped unit cell:

$a = a_1 = 3.00 \text{ \AA}$

$b = a_2 \sin \alpha_3 = 3.00 \text{ \AA}$

$\gamma = 90^\circ$

(c)  $a_1 = 3.46 \text{ \AA}$ ,  $a_2 = 9.16 \text{ \AA}$ ,  $\alpha_3 = 160.89^\circ$



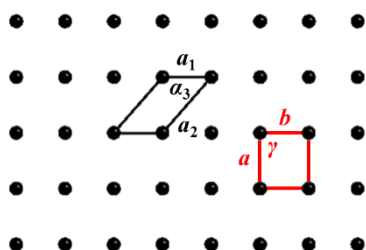
The lattice is *hexagonal* with a rhombus-shaped unit cell:

$$a = a_1 = 3.46 \text{ \AA}$$

$$b = 2a_1 \sin \alpha_3 = 3.46 \text{ \AA}$$

$$\gamma = 120^\circ$$

(d)  $a_1 = 3.50 \text{ \AA}$ ,  $a_2 = 5.32 \text{ \AA}$ ,  $\alpha_3 = 48.81^\circ$



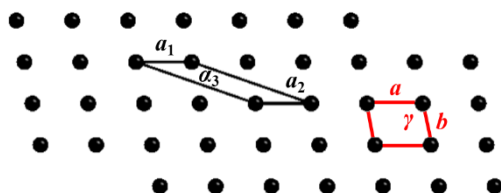
The lattice is *rectangular* with a unit cell:

$$a = a_1 = 3.00 \text{ \AA}$$

$$b = a_2 \sin \alpha_3 = 4.00 \text{ \AA}$$

$$\gamma = 90^\circ$$

(e)  $a_1 = 3.50 \text{ \AA}$ ,  $a_2 = 7.94 \text{ \AA}$ ,  $\alpha_3 = 160.89^\circ$



The lattice is *oblique* with a conventional unit cell:

$$a = a_1 = 3.50 \text{ \AA}$$

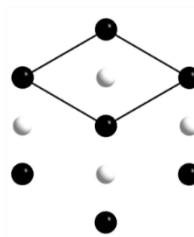
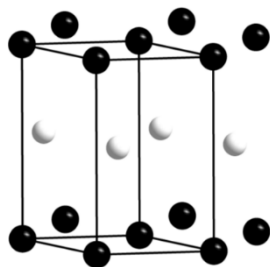
$$b = a_2 \sin \alpha_3 = 2.65 \text{ \AA}$$

$$\gamma = 100.9^\circ$$

(6) Considering the geometry and symmetry of various crystallographic lattices:

(a) Explain why there is no body-centered hexagonal lattice.

The point symmetry at every lattice point must be the same and the highest point symmetry allowed for the crystal system, i.e., the holohedral symmetry. Therefore, a “body-centered” hexagonal lattice should have symmetry  $6/mmm$  at the corners and center of its unit cell. However, the center of the hexagonal unit cell only has point symmetry  $2/m$  as these diagrams emphasize: (left) a perspective view with  $c$ -axis vertical; and (right) projection down the  $c$ -axis. The lighter shaded circles are the body-centered positions.



- (b) Show that face-centered (*F*) and body-centered (*I*) tetragonal lattices are the same lattice.

The relationship between these two lattices can be shown by an illustration. The standard setting is body-centered tetragonal (BCT), with its unit cell shown by black lines. A face-centered tetragonal (“FCT”) unit cell is emphasized by the red lines. Therefore, BCT can be transformed into “FCT” and vice versa.

The transformation from “FCT” to BCT must be a matrix with only integer matrix elements with the additional proviso that its inverse matrix, which takes BCT to “FCT”, also has only integer matrix elements.

Let the “FCT” unit cell be the orthogonal lattice vectors  $a, b, c$ . The primitive “FCT” unit cell vectors are:

$$\mathbf{a}_1 = \frac{1}{2}\mathbf{b} + \frac{1}{2}\mathbf{c}, \quad \mathbf{a}_2 = \frac{1}{2}\mathbf{a} + \frac{1}{2}\mathbf{c}, \quad \mathbf{a}_3 = \frac{1}{2}\mathbf{a} + \frac{1}{2}\mathbf{b}.$$

Likewise, let the BCT unit cell be the orthogonal lattice vectors  $a', b', c'$ . The primitive BCT unit cell vectors are:

$$\mathbf{a}'_1 = -\frac{1}{2}\mathbf{a}' + \frac{1}{2}\mathbf{b}' + \frac{1}{2}\mathbf{c}', \quad \mathbf{a}'_2 = \frac{1}{2}\mathbf{a}' - \frac{1}{2}\mathbf{b}' + \frac{1}{2}\mathbf{c}', \quad \mathbf{a}'_3 = \frac{1}{2}\mathbf{a}' + \frac{1}{2}\mathbf{b}' - \frac{1}{2}\mathbf{c}'.$$

The “FCT” lattice vectors are related to the BCT lattice vectors by:  $a = a' - b'$ ,  $b = a' + b'$ ,  $c' = c$ .

Then, the relationships between primitive “FCT” vectors and primitive BCT vectors are:

$$\begin{aligned} \mathbf{a}_1 &= \frac{1}{2}(\mathbf{a}' + \mathbf{b}') + \frac{1}{2}\mathbf{c}' = \mathbf{a}'_1 + \mathbf{a}'_2 + \mathbf{a}'_3 & \mathbf{a}'_1 &= \mathbf{a}_1 - \mathbf{a}_3 \\ \mathbf{a}_2 &= \frac{1}{2}(\mathbf{a}' - \mathbf{b}') + \frac{1}{2}\mathbf{c}' = \mathbf{a}'_2 & \mathbf{a}'_2 &= \mathbf{a}_2 \\ \mathbf{a}_3 &= \frac{1}{2}(\mathbf{a}' + \mathbf{b}') + \frac{1}{2}(\mathbf{a}' - \mathbf{b}') = \mathbf{a}'_2 + \mathbf{a}'_3 & \mathbf{a}'_3 &= -\mathbf{a}_2 + \mathbf{a}_3 \end{aligned}$$

Therefore, the transformations between the two perspective lattice definitions are

$$(\mathbf{a}_1 \quad \mathbf{a}_2 \quad \mathbf{a}_3) = (\mathbf{a}'_1 \quad \mathbf{a}'_2 \quad \mathbf{a}'_3) \begin{pmatrix} 1 & 0 & 0 \\ 1 & 1 & 1 \\ 1 & 0 & 1 \end{pmatrix}; \quad (\mathbf{a}'_1 \quad \mathbf{a}'_2 \quad \mathbf{a}'_3) = (\mathbf{a}_1 \quad \mathbf{a}_2 \quad \mathbf{a}_3) \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & -1 \\ -1 & 0 & 1 \end{pmatrix}$$

NOTE: 
$$\begin{pmatrix} 1 & 0 & 0 \\ 1 & 1 & 1 \\ 1 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & -1 \\ -1 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & -1 \\ -1 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 1 & 1 & 1 \\ 1 & 0 & 1 \end{pmatrix}$$

- (c) Show that base-centered (*C*) and body-centered (*I*) monoclinic lattices are the same lattice.

By illustration, we see that the *C*-centered monoclinic (CCM) lattice, with unit cell vectors  $a, b$ , and  $c$ , can be transformed into an *I*-centered (“ICM”) lattice with unit cell vectors  $a', b', c'$ .

Let the CCM unit cell be the lattice vectors  $a, b, c$ . The primitive CCM unit cell vectors are:

$$\mathbf{a}_1 = \frac{1}{2}\mathbf{a} - \frac{1}{2}\mathbf{b}, \quad \mathbf{a}_2 = \frac{1}{2}\mathbf{a} + \frac{1}{2}\mathbf{b}, \quad \mathbf{a}_3 = \mathbf{c}.$$

Likewise, let the “ICM” unit cell vectors be  $a', b', c'$ . The primitive “ICM” unit cell vectors are:

$$\mathbf{a}'_1 = -\frac{1}{2}\mathbf{a}' + \frac{1}{2}\mathbf{b}' + \frac{1}{2}\mathbf{c}', \quad \mathbf{a}'_2 = \frac{1}{2}\mathbf{a}' - \frac{1}{2}\mathbf{b}' + \frac{1}{2}\mathbf{c}', \quad \mathbf{a}'_3 = \frac{1}{2}\mathbf{a}' + \frac{1}{2}\mathbf{b}' - \frac{1}{2}\mathbf{c}'.$$

The “ICM” lattice vectors are related to the CCM lattice vectors by:  $a' = a - c$ ,  $b' = b$ ,  $c' = c$ .

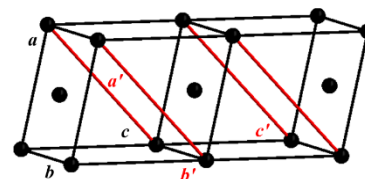
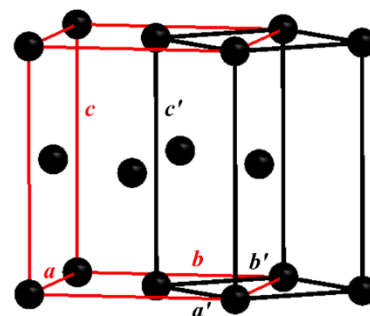
Then, the relationships between primitive “ICM” vectors and primitive CCM vectors are:

$$\begin{aligned} \mathbf{a}'_1 &= -\frac{1}{2}(\mathbf{a} - \mathbf{c}) + \frac{1}{2}\mathbf{b} + \frac{1}{2}\mathbf{c} = -\frac{1}{2}\mathbf{a} + \frac{1}{2}\mathbf{b} + \mathbf{c} = -\mathbf{a}_1 + \mathbf{a}_3 & \mathbf{a}'_1 &= \mathbf{a}'_2 \\ \mathbf{a}'_2 &= \frac{1}{2}(\mathbf{a} - \mathbf{c}) - \frac{1}{2}\mathbf{b} + \frac{1}{2}\mathbf{c} = \frac{1}{2}\mathbf{a} - \frac{1}{2}\mathbf{b} = \mathbf{a}_1 & \mathbf{a}'_2 &= \mathbf{a}'_1 + \mathbf{a}'_2 + \mathbf{a}'_3 \\ \mathbf{a}'_3 &= \frac{1}{2}(\mathbf{a} - \mathbf{c}) + \frac{1}{2}\mathbf{b} - \frac{1}{2}\mathbf{c} = \frac{1}{2}\mathbf{a} + \frac{1}{2}\mathbf{b} - \mathbf{c} = \mathbf{a}_2 - \mathbf{a}_3 & \mathbf{a}'_3 &= \mathbf{a}'_1 + \mathbf{a}'_2 \end{aligned}$$

Therefore, the transformations between the two different lattice definitions are

$$(\mathbf{a}'_1 \quad \mathbf{a}'_2 \quad \mathbf{a}'_3) = (\mathbf{a}_1 \quad \mathbf{a}_2 \quad \mathbf{a}_3) \begin{pmatrix} -1 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & -1 \end{pmatrix}; \quad (\mathbf{a}_1 \quad \mathbf{a}_2 \quad \mathbf{a}_3) = (\mathbf{a}'_1 \quad \mathbf{a}'_2 \quad \mathbf{a}'_3) \begin{pmatrix} 0 & 1 & 1 \\ 1 & 1 & 1 \\ 0 & 1 & 0 \end{pmatrix}$$

NOTE: 
$$\begin{pmatrix} -1 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & -1 \end{pmatrix} \begin{pmatrix} 0 & 1 & 1 \\ 1 & 1 & 1 \\ 0 & 1 & 0 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 0 & 1 & 1 \\ 1 & 1 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} -1 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & -1 \end{pmatrix}$$



- (d) Show that the primitive rhombohedral unit cell  $a_1 = a_2 = a_3 = a$  and  $\alpha_1 = \alpha_2 = \alpha_3 = \alpha$  generates the standard trigonal lattice with  $a' = b' \neq c'$  and  $\alpha' = \beta' = 90^\circ$ ,  $\gamma' = 120^\circ$ . Determine  $a'$  and  $c'$  in terms of  $a$  and  $\alpha$ .

By construction,  $a' = a_1 - a_3$ ,  $b' = -a_1 + a_2$ , and  $c' = a_1 + a_2 + a_3$ .

$$\begin{aligned} \text{Length of } a' &= \sqrt{a' \cdot a'} = \sqrt{(a_1 - a_3) \cdot (a_1 - a_3)} \\ &= \sqrt{(a_1 \cdot a_1) + (a_3 \cdot a_3) - 2(a_1 \cdot a_3)} \\ &= \sqrt{a^2 + a^2 - 2a^2 \cos \alpha} = \sqrt{2a^2(1 - \cos \alpha)} = 2a \sin(\alpha/2) \end{aligned}$$

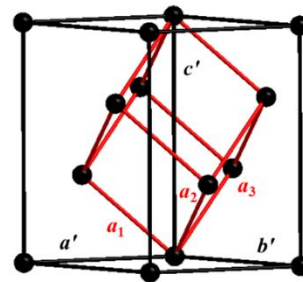
$$\begin{aligned} \text{Length of } b' &= \sqrt{b' \cdot b'} = \sqrt{(-a_1 + a_2) \cdot (-a_1 + a_2)} \\ &= \sqrt{(a_1 \cdot a_1) + (a_2 \cdot a_2) - 2(a_1 \cdot a_2)} = \text{Length of } a' \end{aligned}$$

$$\begin{aligned} \text{Length of } c' &= \sqrt{c' \cdot c'} = \sqrt{(a_1 + a_2 + a_3) \cdot (a_1 + a_2 + a_3)} \\ &= \sqrt{(a_1 \cdot a_1) + (a_2 \cdot a_2) + (a_3 \cdot a_3) + 2(a_1 \cdot a_2) + 2(a_1 \cdot a_3) + 2(a_2 \cdot a_3)} \\ &= \sqrt{a^2 + a^2 + a^2 + 2a^2 \cos \alpha + 2a^2 \cos \alpha + 2a^2 \cos \alpha} = \sqrt{3a^2(1 + 2 \cos \alpha)} = \sqrt{6}a \cos(\alpha/2) \end{aligned}$$

$$\begin{aligned} \text{Angle between } a' \text{ and } c': a' \cdot c' &= (a_1 - a_3) \cdot (a_1 + a_2 + a_3) = a_1 \cdot (a_1 + a_2 + a_3) - a_3 \cdot (a_1 + a_2 + a_3) \\ &= (a^2 + 2a^2 \cos \alpha) - (a^2 + 2a^2 \cos \alpha) = 0 = a'c' \cos \beta; \quad \beta = 90^\circ \end{aligned}$$

$$\begin{aligned} \text{Angle between } b' \text{ and } c': b' \cdot c' &= (-a_1 + a_2) \cdot (a_1 + a_2 + a_3) = a_2 \cdot (a_1 + a_2 + a_3) - a_1 \cdot (a_1 + a_2 + a_3) \\ &= a' \cdot c' = 0 = b'c' \cos \alpha; \quad \alpha = 90^\circ \end{aligned}$$

$$\begin{aligned} \text{Angle between } a' \text{ and } b': a' \cdot b' &= (a_1 - a_3) \cdot (-a_1 + a_2) = (a_1 \cdot a_2) + (a_1 \cdot a_3) - (a_1 \cdot a_1) - (a_2 \cdot a_3) \\ &= a^2 \cos \alpha - a^2 = -2a^2 \sin^2(\alpha/2) = a'b' \cos \gamma = (2a \sin(\alpha/2))^2 \cos \gamma; \\ &\cos \gamma = -1/2; \quad \gamma = 120^\circ \end{aligned}$$



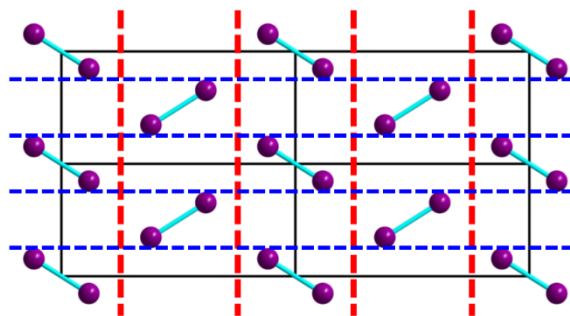
- (7) For each of the following space groups, identify (i) the crystal class, (ii) the lattice type, (iii) the point group of the space group in International and Schönflies notations, (iv) the symmetry operations specified in the symbol, (v) whether the group is centrosymmetric or noncentrosymmetric, and (vi) the highest point symmetry in the unit cell using both International and Schönflies notations.

Crystal Class	Lattice Type	Point Group of the Space Group	Inversion	Highest Point Symmetry	
(a) $P 1 2_1/a 1$ (#14; not the conventional space group designation)	Monoclinic	Primitive	$2/m = \mathcal{C}_{2h}$	Centrosymmetric	$\bar{1} = \mathcal{C}_i$
					$2_1$ -screw axis parallel to $b$ ; axial glide plane perpendicular to $b$ and shift by $a/2$
(b) $C 1 2/m 1$ (#12)	Monoclinic	Base-Centered	$2/m = \mathcal{C}_{2h}$	Centrosymmetric	$2/m = \mathcal{C}_{2h}$
					$2$ -fold axis parallel to $b$ ; reflection plane perpendicular to $b$
(c) $P n a 2_1$ (#33)	Orthorhombic	Primitive	$mm2 = \mathcal{C}_{2v}$	Non-centrosymmetric	$1 = \mathcal{C}_1$
					$2_1$ -screw axis parallel to $c$ Diagonal glide plane perpendicular to $a$ and shift by $(b+c)/2$ Axial glide plane perpendicular to $b$ and shift by $a/2$
(d) $I 2_1/b 2_1/c 2_1/a \equiv Ibca$ (#73)	Orthorhombic	Body-Centered	$mmm = \mathcal{D}_{2h}$	Centrosymmetric	$\bar{1} = \mathcal{C}_i$
					$2_1$ -screw axis parallel to $a$ ; axial glide plane perpendicular to $a$ and shift by $b/2$ $2_1$ -screw axis parallel to $b$ ; axial glide plane perpendicular to $b$ and shift by $c/2$ $2_1$ -screw axis parallel to $c$ ; axial glide plane perpendicular to $c$ and shift by $a/2$

Crystal Class	Lattice Type	Point Group of the Space Group	Inversion	Highest Point Symmetry
(e) $I 4_1$ (#80)				
Tetragonal	Body-Centered	$4 = C_4$	Non-centrosymmetric	$1 = C_1$
4 <sub>1</sub> -screw axis parallel to <i>c</i>				
(f) $I 4_1/a 2/m 2/d \equiv I 4_1/amd$ (#141)				
Tetragonal	Body-Centered	$4/mmm = D_{4h}$	Centrosymmetric	$mmm = D_{2h}$
4 <sub>1</sub> -screw axis parallel to <i>c</i> ; axial glide plane perpendicular to <i>c</i> and shift by <i>a</i> / <i>2</i>				
2-fold axes parallel to <i>a</i> and <i>b</i> ; reflection planes perpendicular to <i>a</i> and <i>b</i>				
2-fold axes parallel to <i>a</i> + <i>b</i> and <i>a</i> - <i>b</i> ; diamond glide planes perpendicular to <i>a</i> + <i>b</i> and <i>a</i> - <i>b</i>				
(g) $P 3 m 1$ (#156)				
Trigonal	Primitive	$3m = C_{3v}$	Non-centrosymmetric	$3m = C_{3v}$
3-fold axis parallel to <i>c</i>				
Reflection planes perpendicular to <i>a</i> and <i>b</i>				
(h) $P \bar{3} 2/m 1 \equiv P\bar{3}m1$ (#164)				
Trigonal	Primitive	$\bar{3}m = D_{3d}$	Centrosymmetric	$\bar{3}m = D_{3d}$
$\bar{3}$ -fold axis parallel to <i>c</i>				
2-fold axes parallel to <i>a</i> and <i>b</i> ; reflection planes perpendicular to <i>a</i> and <i>b</i>				
(i) $P \bar{6} 2 m$ (#189)				
Hexagonal	Primitive	$\bar{6}2m = D_{3h}$	Non-centrosymmetric	$\bar{6}2m = D_{3h}$
$\bar{6}$ -fold axis parallel to <i>c</i>				
2-fold axes parallel to <i>a</i> and <i>b</i>				
Reflection planes parallel to <i>a</i> and <i>b</i>				
(j) $P 6_3/m 2/m 2/c \equiv P6_3/mmc$ (#194)				
Hexagonal	Primitive	$6/mmm = D_{6h}$	Centrosymmetric	$\bar{3}m = D_{3d}$ $\bar{6}2m = D_{3h}$
6 <sub>3</sub> -screw axis parallel to <i>c</i> ; reflection plane perpendicular to <i>c</i>				
2-fold axes parallel to <i>a</i> and <i>b</i> ; reflection planes perpendicular to <i>a</i> and <i>b</i>				
2-fold axes perpendicular to <i>a</i> and <i>b</i> ; axial glide planes parallel to <i>a</i> and <i>b</i> and shift by <i>c</i> / <i>2</i>				
(k) $F 2/m \bar{3} \equiv Fm\bar{3}$ (#202)				
Cubic	Face-Centered	$m\bar{3} = T_h$	Centrosymmetric	$m\bar{3} = T_h$
2-fold axes parallel to <i>a</i> , <i>b</i> , and <i>c</i> ; reflections perpendicular to <i>a</i> , <i>b</i> , and <i>c</i>				
$\bar{3}$ -fold axes parallel to <i>a</i> + <i>b</i> + <i>c</i> (body-diagonals of a cube)				
(l) $F 4_1/d \bar{3} 2/m \equiv Fd\bar{3}m$ (#227)				
Cubic	Face-Centered	$m\bar{3}m = O_h$	Centrosymmetric	$\bar{4}3m = T_d$
4 <sub>1</sub> -screw axes parallel to <i>a</i> , <i>b</i> , and <i>c</i> ; diamond glide planes perpendicular to <i>a</i> , <i>b</i> , and <i>c</i>				
$\bar{3}$ -fold axes parallel to <i>a</i> + <i>b</i> + <i>c</i> (body-diagonals of a cube)				
2-fold axes perpendicular to <i>a</i> + <i>b</i> ,... (face-diagonals of a cube); reflection planes perpendicular to <i>a</i> + <i>b</i> ,... (face-diagonals of a cube)				

- (8)  $I_2(s)$  is a molecular solid that crystallizes in the space group  $Cmce$  (#64) with  $a = 7.14 \text{ \AA}$ ,  $b = 4.69 \text{ \AA}$ ,  $c = 9.78 \text{ \AA}$ , and I atoms at sites  $8f$  with  $x = 0$ ,  $y = 0.1543$ ,  $z = 0.1174$ . (From Müller)

- (a) Draw the  $x = 0$  plane for four contiguous unit cells and show the glide reflection planes.



- (b) What is the I–I bond length (in  $\text{\AA}$ ) in crystalline iodine?

**From the drawing and the fractional coordinates:**

$$d(\text{I-I}) = \sqrt{(2 \cdot 0.1543 \cdot 4.69 \text{ \AA})^2 + (2 \cdot 0.1174 \cdot 9.78 \text{ \AA})^2} = 2.714 \text{ \AA}$$

- (c) How many  $I_2$  molecules are there in one unit cell?

**Since there are 8 I atoms per unit cell, there are 4  $I_2$  molecules per unit cell.**

- (d) What is the density (in  $\text{g/cm}^3$ ) of crystalline iodine?

$$\text{Density} = \frac{1.6859 \times 10^{-21} \text{ g}}{3.2750 \times 10^{-22} \text{ cm}^3} = 5.15 \text{ g/cm}^3$$

- (e) What is the point symmetry of each  $I_2$  molecule in the crystal?

**The center of each  $I_2$  corresponds to a lattice point, which includes the origin (0, 0, 0). The point group at the origin is  $2/m = C_{2h}$ , which includes a 2-fold rotation axis with respect to the  $a$ -axis, a reflection perpendicular to the  $a$ -axis, and an inversion center.**

- (9)  $W\text{OBr}_4$  adopts a structure in space group  $I4$  (#79) with  $a = 9.002 \text{ \AA}$ ,  $c = 3.935 \text{ \AA}$ . The asymmetric unit is W (0, 0, 0.0779), O (0, 0, 0.529), Br (.2603, 0.0693, 0). (From Müller)

- (a) Describe the shape of the environment surrounding each W atom and evaluate the W–Br, W–O, and O–W–Br angle(s).

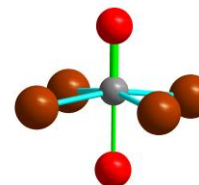
**Each W atom is surrounded by 2 O atoms along the  $c$ -axis and 4 Br atoms in approximately the  $ab$ -plane to give a *distorted octahedral* coordination environment. There are two distinct W–O distances and four equal W–Br distances:**

$$d_1(\text{W-O}) = (0.529 - 0.0779)(3.935 \text{ \AA}) = 1.775 \text{ \AA}$$

$$d_2(\text{W-O}) = (0.0779 - (-0.471))(3.935 \text{ \AA}) = 2.160 \text{ \AA}$$

$$d(\text{W-Br}) = \sqrt{(0.2603 \cdot 9.002 \text{ \AA})^2 + (0.0693 \cdot 9.002 \text{ \AA})^2 + (0.0779 \cdot 3.935 \text{ \AA})^2} = 2.444 \text{ \AA}$$

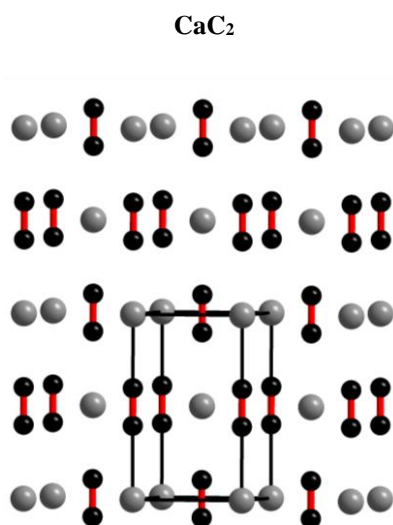
$$\text{O-W-Br} = 180^\circ - \arccos((0.0779 \cdot 3.935 / 2.444)) = 180^\circ - 82.79^\circ = 97.21^\circ$$



- (b) What is the point symmetry of the  $W\text{OBr}_4$  molecule in the crystal and what would the point symmetry be in the gas phase? Explain any differences.

**In the crystal, the molecular point symmetry is  $C_4$  while in the gas phase it would be  $C_{4v}$ . The additional reflections are lost when the molecules pack into the crystal, an effect most likely arising from anion–anion repulsions.**

- (10)  $\text{CaC}_2$  and  $\text{MoSi}_2$  are *isopointal* structures because they adopt the same space group  $I4/mmm$  (#139) and their atoms occupy the same Wyckoff sites, but their structures are distinctly different. Using the crystallographic data of the two compounds, discuss their structural differences:



$$a = 3.8858 \text{ \AA}, c = 6.4005 \text{ \AA}$$

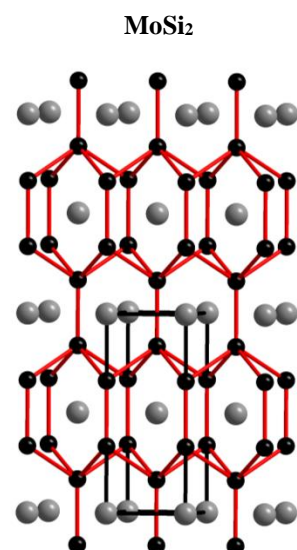
Ca at  $2a$  (0,0,0)

C at  $4e$  (0, 0, 0.3987)

$$d(\text{C-C}) = 1.297 \text{ \AA} (1\times); 3.343 \text{ \AA} (4\times)$$

$$d(\text{Ca-C}) = 2.552 \text{ \AA} (2\times); 2.823 \text{ \AA} (8\times)$$

NaCl-type packing of  $\text{Ca}^{2+}$  and  $\text{C}_2^{2-}$  species. All  $\text{C}_2^{2-}$  units are oriented along the  $c$ -axis, so there is a tetragonal elongation along  $c$ . The C-C distance in each  $\text{C}_2^{2-}$  unit is somewhat longer than in a typical  $\text{C}\equiv\text{C}$  triple bond arising from the cation environment.



$$a = 3.2056 \text{ \AA}, c = 7.8450 \text{ \AA}$$

Mo at  $2a$  (0,0,0)

Si at  $4e$  (0, 0, 0.3353)

$$d(\text{Si-Si}) = 2.584 \text{ \AA} (1\times); 2.632 \text{ \AA} (4\times)$$

$$d(\text{Mo-Si}) = 2.630 \text{ \AA} (2\times); 2.609 \text{ \AA} (8\times)$$

3-d network of Si atoms, which are 5-bonded in a square-pyramidal arrangement. Mo atoms occupy 10-atom bicapped tetragonal prismatic cages. Through-space Mo-Mo bonding is minimal because all Mo-Mo distances are rather long compared to normal bonding distances.

- (11) An important intermetallic compound involves a combination of samarium and cobalt. Its space group is  $P6/mmm$  (#191) with lattice constants  $a = 4.94 \text{ \AA}$  and  $c = 3.96 \text{ \AA}$ . The asymmetric unit has samarium atoms at (0, 0, 0); cobalt atoms at ( $\frac{1}{3}$ ,  $\frac{2}{3}$ , 0); and cobalt atoms at ( $\frac{1}{2}$ , 0,  $\frac{1}{2}$ ).

- (a) Determine the empirical formula of this compound;

For the space group  $P6/mmm$  (#191), Sm atoms occupy  $1a$  sites ( $D_{6h}$ ) and Co atoms occupy  $2c$  ( $D_{3h}$ ) and  $3g$  ( $D_{2h}$ ) sites. The unit cell formula is  $\text{SmCo}_5$ , which is the empirical formula.

- (b) Calculate the density (in  $\text{g/cm}^3$ ) of this compound;

$$\text{FW}(\text{SmCo}_5) = 150.36 + 5(58.933) = 445.025 \text{ g/mol}$$

$$\text{Mass in unit cell (g)} = (445.025 \text{ g/mol})/6.022 \times 10^{23} = 7.390 \times 10^{-22} \text{ g}$$

The unit cell is for a *hexagonal lattice*:  $a = b = 4.94 \text{ \AA}$ ,  $c = 3.96 \text{ \AA}$ ,  $\alpha = \beta = 90^\circ$ ,  $\gamma = 120^\circ$ .

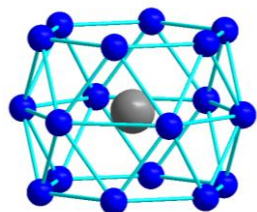
Therefore, the volume of the unit cell = area of base  $\times$  height =  $(ab \sin 120^\circ)(c)$

$$\text{Volume of unit cell (\AA}^3) = [(4.94 \text{ \AA})^2 \sin 120^\circ](3.96 \text{ \AA}) = 83.691 \text{ \AA}^3$$

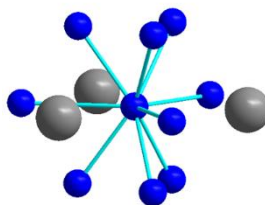
$$\text{Volume of unit cell (cm}^3) = (83.691 \text{ \AA}^3)(1 \text{ cm} / 10^8 \text{ \AA})^3 = 83.691 \times 10^{-24} \text{ cm}^3$$

$$\text{Density (g/cm}^3) = \text{Mass in unit cell (g)} / \text{Volume of unit cell (cm}^3) = 8.830 \text{ g/cm}^3.$$

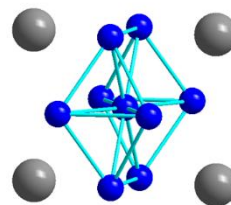
- (c) For each atom in the asymmetric unit, determine all first-, second-, and third-nearest neighbors, i.e., determine the coordination polyhedron for each site.



**Sm: 18-coordinate**  
 Sm–Co1: 2.85 Å (6×)  
 Sm–Co2: 3.17 Å (12×)

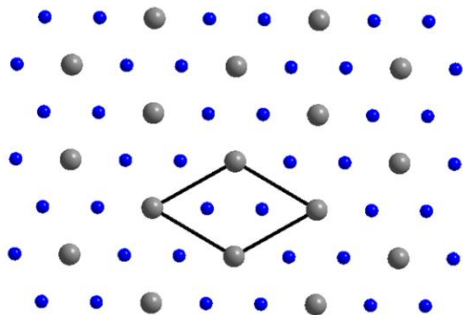


**Co1: 9- + 3-coordinate**  
 Co1–Sm: 2.85 Å (3×)  
 Co1–Co1: 2.85 Å (3×)  
 Co1–Co2: 2.44 Å (6×)

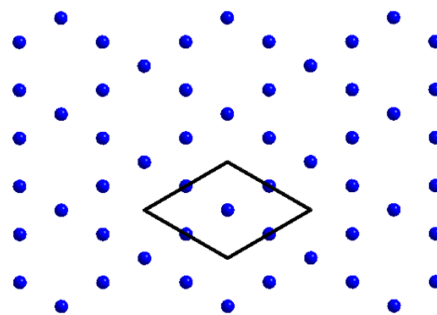


**Co2: 8- + 4-coordinate**  
 Co2–Sm: 3.17 Å (4×)  
 Co2–Co2: 2.47 Å (4×)  
 Co2–Co1: 2.44 Å (4×)

- (d) Draw the planes of atoms at  $z = 0$  and  $z = \frac{1}{2}$  for four contiguous unit cells. Label the atoms.

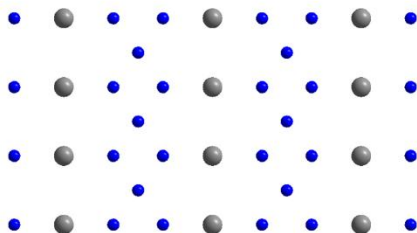


**(001) at  $z = 0$**   
 Sm: large gray circles  
 Co: small blue circles

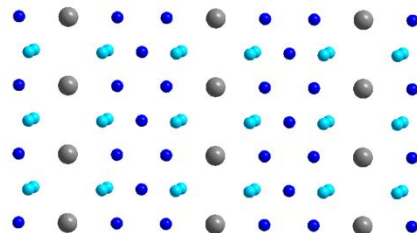


**(001) at  $z = \frac{1}{2}$**   
 Co: small blue circles

- (e) Draw the (110) plane of atoms for four contiguous unit cells. Label the atoms.



**(110) Section**



**(110) Section in perspective, showing planes of Co atoms just above and below**

- (12) A compound of lanthanum (gadolinium) and carbon adopts a cubic unit cell,  $a = 8.817(3)$  Å ( $8.322(1)$  Å), and space group  $I\bar{4}3d$  (#220). The asymmetric unit has just two atoms: lanthanum (gadolinium) at (0.053, 0.053, 0.053) and carbon at (0.300, 0,  $\frac{1}{4}$ ).

- (a) Determine the empirical formula of this compound.

**RE = La or Gd**

**RE atoms occupy 16c sites ( $x, x, x$ ); C atoms occupy 24d sites ( $x, 0, \frac{1}{4}$ ).**

**The formula of one unit cell is RE<sub>16</sub>C<sub>24</sub>.**

**The empirical formula is RE<sub>2</sub>C<sub>3</sub>.**

- (b) What is the density (in  $\text{g}/\text{cm}^3$ ) of this compound?

$\text{La}_2\text{C}_3$ :  $\text{FW}(8 \text{ La}_2\text{C}_3) = 2510.80 \text{ g/mol}$

Mass in unit cell (g) =  $(2510.80 \text{ g/mol}) / (6.0221 \times 10^{23}) = 4.169 \times 10^{-21} \text{ g}$

Volume of unit cell ( $\text{cm}^3$ ) =  $(8.817 \text{ \AA})^3 = 685.429 \text{ \AA}^3 / 10^{24} = 685.429 \times 10^{-24} \text{ cm}^3$

Density ( $\text{g}/\text{cm}^3$ ) = Mass in unit cell (g) / Volume of unit cell ( $\text{cm}^3$ ) =  $6.082 \text{ g}/\text{cm}^3$ .

$\text{Gd}_2\text{C}_3$ :  $\text{FW}(8 \text{ Gd}_2\text{C}_3) = 2804.24 \text{ g/mol}$

Mass in unit cell (g) =  $(2804.24 \text{ g/mol}) / (6.0221 \times 10^{23}) = 4.657 \times 10^{-21} \text{ g}$

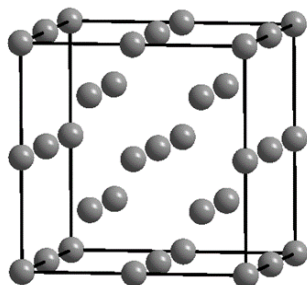
Volume of unit cell ( $\text{\AA}^3$ ) =  $(8.3221 \text{ \AA})^3 = 576.367 \text{ \AA}^3$

Volume of unit cell ( $\text{cm}^3$ ) =  $(8.3221 \text{ \AA})^3 = 576.367 \text{ \AA}^3 / 10^{24} = 576.367 \times 10^{-24} \text{ cm}^3$

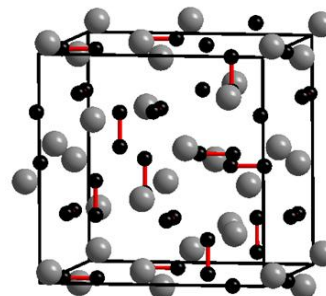
Density ( $\text{g}/\text{cm}^3$ ) = Mass in unit cell (g) / Volume of unit cell ( $\text{cm}^3$ ) =  $8.080 \text{ g}/\text{cm}^3$ .

- (c) Describe the packing of lanthanum (gadolinium) atoms in the structure. What voids are occupied by carbon atoms? (HINT: the coordinates for lanthanum (gadolinium) are close to 0.)

The coordinates for RE are quite close to (0, 0, 0), which remain  $16c$  sites. The ideal packing of RE atoms can be determined by setting the RE fractional coordinates to (0, 0, 0), shown on the left:



RE at (0, 0, 0)



RE at (0.053, 0.053, 0.053)

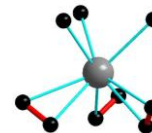
Therefore, RE atoms form distorted BCC packing. The C atoms occupied octahedral holes. The idealized fractional coordinates would be  $(\frac{1}{4}, 0, \frac{1}{4})$ , but they shift to form C–C dimers.

- (d) Each C atom is 6-coordinate with La. What is the coordination number for La by C?

$$2 \langle \text{CN} \rangle_{\text{La}} = 3 \langle \text{CN} \rangle_{\text{C}} = 3(6) = 18$$

$\langle \text{CN} \rangle_{\text{La}} = 9$ : each La is 9-coordinated by C.

The 9-coordinate environment involves 3 side-on C–C (6 neighboring C atoms) and 3 end-on C–C (3 neighboring C atoms)



- (e) Hydrolysis of this compound produces lanthanum (gadolinium) oxide and ethylene as the major products. Write the balanced chemical equation for this reaction using the empirical formula of the compound.

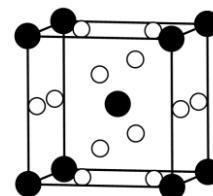


- (f) Write an ionic formulation for this compound, using the appropriate cation and anion. Explain your assignments of oxidation numbers to lanthanum and carbon.

The common oxidation state for RE metals is  $3+$ , which occurs for RE in the oxides  $\text{RE}_2\text{O}_3$ . In ethylene, the formal oxidation state of C is  $-2$  with a C=C double bond. Since the hydrolysis reaction is not a redox reaction, we can assume that carbon occurs as the dimer,  $\text{C}_2^{4-}$  in  $\text{RE}_2\text{C}_3$ . Then, since  $\text{RE}_2\text{C}_3 = \text{RE}_4\text{C}_6 = \text{RE}_4(\text{C}_2)_3$ , we have  $(\text{RE}^{3+})_4(\text{C}_2^{4-})_3$ .

- (13) An important intermetallic compound involves a combination of titanium and antimony. Its space group is  $Pm\bar{3}n$  (#223) with a lattice constant  $a = 5.218 \text{ \AA}$  at ambient conditions. The asymmetric unit has antimony atoms at  $2a$  sites and titanium atoms at  $6c$  sites.

- (a) Use the accompanying grid of a unit cell to sketch a projection of the structure. Use filled circles ● for Sb and open circles ○ for Ti.



**In this figure, Sb atoms are green, Ti atoms are red.**

- (b) Determine the empirical formula of this compound.

**Unit cell contains  $Ti_6Sb_2$ , so the empirical formula is  $Ti_3Sb$ .**

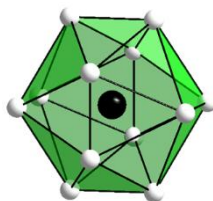
- (c) Calculate the density (in  $g/cm^3$ ) of this compound at ambient conditions.

$$\text{Mass of unit cell} = [6(47.867) + 2(121.76)] / 6.022 \times 10^{23} = 8.8131 \times 10^{-22} \text{ g}$$

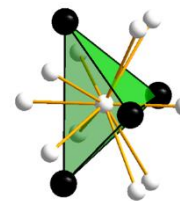
$$\text{Volume of unit cell} = (5.218 \text{ \AA})^3 = 142.073 \text{ \AA}^3 = 142.073 \times 10^{-24} \text{ cm}^3$$

$$\text{Density} = (8.8131 \times 10^{-22} \text{ g}) / (142.073 \times 10^{-24} \text{ cm}^3) = 6.203 \text{ g/cm}^3$$

- (d) Describe the coordination environments at the Sb and Ti atoms.

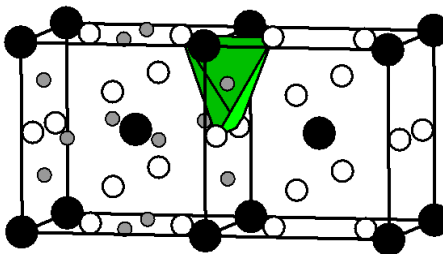


**Around Sb: 12-coordinate  
 distorted icosahedron by Ti**



**Around Ti: 4-coordinate  
 distorted tetrahedron by Sb  
 + 10 Ti atoms**

- (e) This compound reacts with hydrogen to form a hydride. H atoms prefer to bond to Ti atoms and not Sb atoms, so they will occupy voids in this structure formed by only Ti atoms. Use your picture in part (a) and the International Tables to identify the Wyckoff site best suited for H atoms. If all of these tetrahedral holes are occupied by H atoms, what is the resulting empirical formula?



**By placing two unit cells next to one another, tetrahedral voids formed by 4 Ti atoms become apparent. The centers of these tetrahedra have the coordinates  $(\frac{1}{4}, \frac{1}{2}, 0)$ , etc., which are the  $6d$  sites in the unit cell.**

**The unit cell of this intermetallic hydride is  $Ti_6Sb_2H_6$ ; the empirical formula is  $Ti_3SbH_3$ .**

- (14) A compound of cobalt and arsenic adopts a cubic structure with space group  $Im\bar{3}$  (#204) and lattice constant  $a = 8.195(3) \text{ \AA}$  at ambient temperature. The asymmetric unit has cobalt at  $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$  and arsenic at  $(0, 0.1503, 0.3401)$ .

(a) Determine the empirical formula of this compound.

**Co atoms occupy 8c sites  $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ ; As atoms occupy 24g sites  $(0, y, z)$ .**

**The formula of one unit cell is  $\text{Co}_8\text{As}_{24}$ .**

**The empirical formula is  $\text{CoAs}_3$ .**

(b) How many formula units are there in one unit cell?

**$\text{Co}_8\text{As}_{24} = 8 \text{ CoAs}_3$ . There are 8 formula units per unit cell.**

(c) What is the density (in  $\text{g/cm}^3$ ) of this compound?

**Mass of unit cell =  $8[(58.933) + 3(74.922)] / 6.022 \times 10^{23} = 3.7688 \times 10^{-21} \text{ g}$**

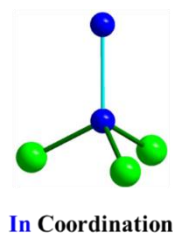
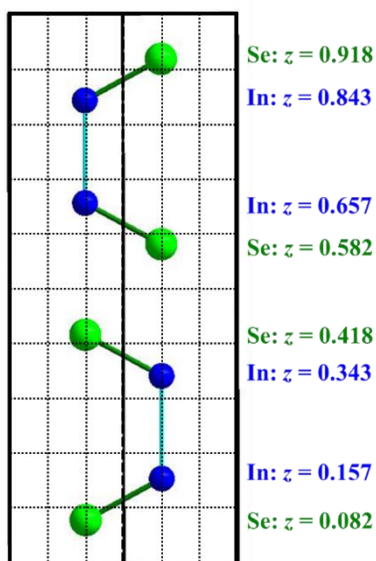
**Volume of unit cell =  $(8.195 \text{ \AA})^3 = 550.360 \text{ \AA}^3 = 550.360 \times 10^{-24} \text{ cm}^3$**

**Density =  $(3.7688 \times 10^{-21} \text{ g}) / (550.360 \times 10^{-24} \text{ cm}^3) = 6.848 \text{ g/cm}^3$**

(d) The compound is semiconducting, and cobalt atoms are octahedrally coordinated by arsenic. Given these facts, write a formulation of the compound that provides a precise description of the structure. What is the local coordination environment for each arsenic atom?

**Octahedrally coordinated Co atoms are best assigned as  $d^6 \text{ Co}^{3+}$ . As a result, each As atom is formally  $\text{As}^-$ , which is isoelectronic with Se. Therefore, As is 2-bonded to other As atoms to satisfy the octet rule and 2-bonded to Co atoms to satisfy the connectivity. Since the Co atoms form a simple cubic network, the As atoms must bridge every edge and form 4-membered rings. Therefore,  $\text{CoAs}_3$  can be formulated as  $(\text{Co}^{3+})_8(\text{As}_4^{4-})_6$ .**

- (15) InSe forms a hexagonal structure, with space group  $P6_3/mmc$  (#194) and lattice constants  $a = 4.05 \text{ \AA}$ , and  $c = 16.93 \text{ \AA}$ . The asymmetric unit contains In atoms at Wyckoff sites  $(\frac{1}{3}, \frac{2}{3}, 0.157)$  and Se atoms at Wyckoff sites  $(\frac{1}{3}, \frac{2}{3}, 0.918)$ . Use the accompanying grid to draw a (110) plane of atoms. From its structure, describe the coordination at each In site, at each Se site, and discuss its chemical formulation using oxidation states.

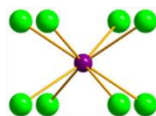
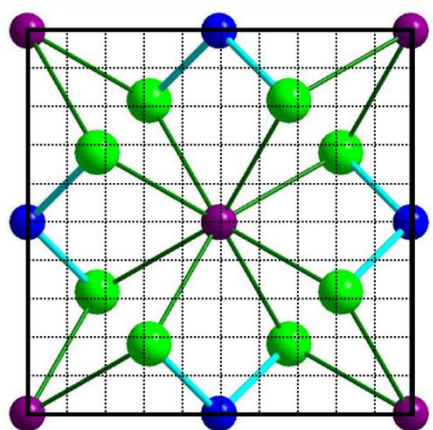


The unit cell of InSe contains 4 In atoms and 4 Se atoms, which form 2  $[\text{InSe}]_2$  bilayers. These bilayers consist of puckered honeycomb  $[\text{InSe}]$  nets connected by In–In bonds.

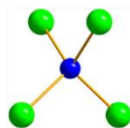
Since there are no Se–Se bonds, the oxidation state of Se is  $-2$  and the oxidation state of In is  $+2$ .

InSe, with 9 valence electrons per formula unit, is a non-octet compound. As a result, the extra electron per formula unit is used to form the In–In (“cation–cation”) bonds.

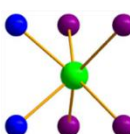
- (16) InTe adopts a tetragonal structure, with space group  $I4/mcm$  (#140) and lattice constants  $a = 8.454 \text{ \AA}$ , and  $c = 7.152 \text{ \AA}$ . The asymmetric unit contains In atoms at Wyckoff sites  $(0, 0, \frac{1}{4})$ , In atoms at Wyckoff sites  $(0, \frac{1}{2}, \frac{1}{4})$ , and Te atoms at Wyckoff sites  $(0.1823, 0.6823, 0)$ . Use the accompanying grid to draw a projection of one unit cell of the structure looking down along the  $[001]$  axis. From its structure, describe the coordination at each In site, at each Te site, and discuss its chemical formulation using oxidation states.



In1 Coordination



In2 Coordination



Te Coordination

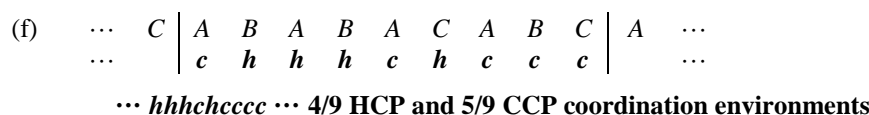
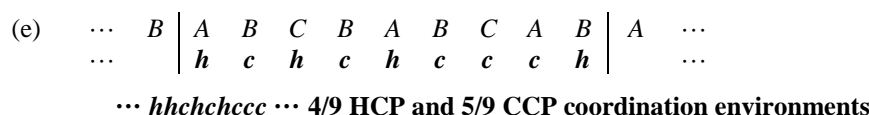
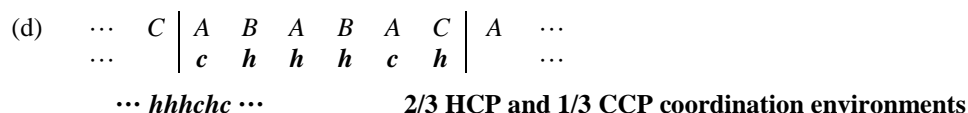
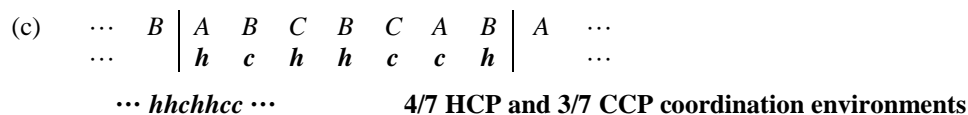
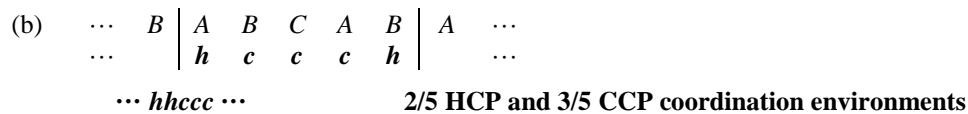
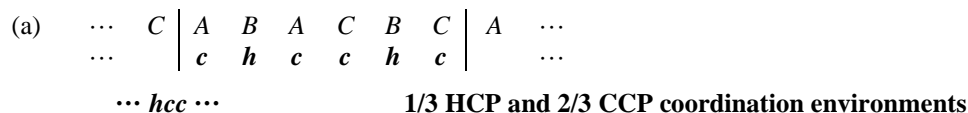
The unit cell of InTe contains 8 In atoms and 8 Te atoms, and there are two distinct types of In atoms: In1 site is 8-coordinate; In2 site is 4-coordinate by Te.

There are just In–Te bonds. Since there are no Te–Te bonds, the oxidation state of Te is  $-2$  and the average oxidation state of In is  $+2$ . In2 sites, which are tetrahedrally coordinated, are suitable for  $\text{In}^{3+}$ ; In1 sites are suitable for  $\text{In}^+$ .

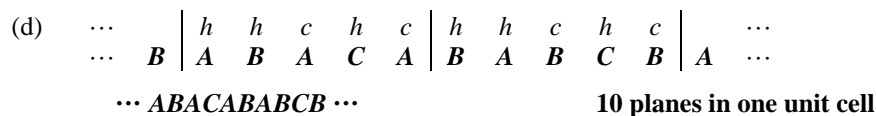
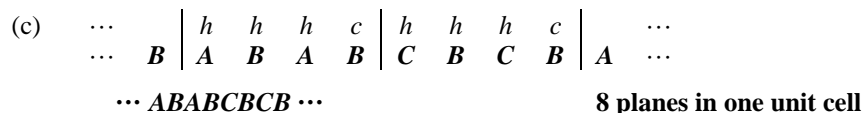
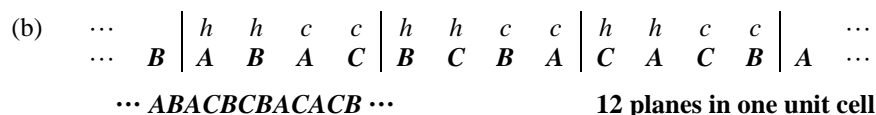
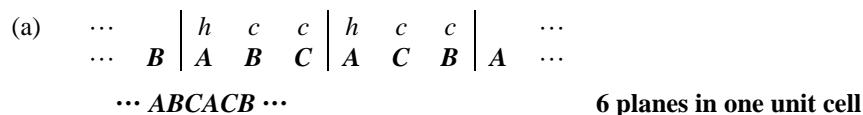
InTe is formulated as  $\text{In}^+\text{In}^{3+}\text{Te}_2$  with “ $\text{In}^{2+}$ ” disproportionating into  $\text{In}^+$  and  $\text{In}^{3+}$ .

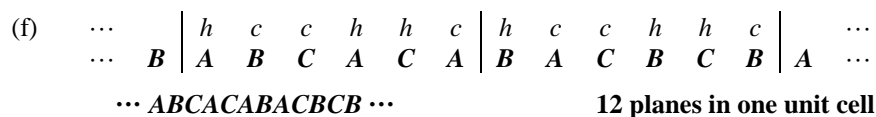
**Sphere Packings**

(17) Write the Jagodzinski symbol for each of the following progressions of close-packed planes of atoms. What are the fractions of local CCP and HCP coordination environments?



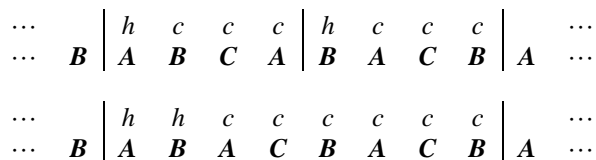
(18) Write the  $\dots ABC \dots$  notation for each of the following progressions of close-packed planes of atoms. How many planes constitute one unit cell?



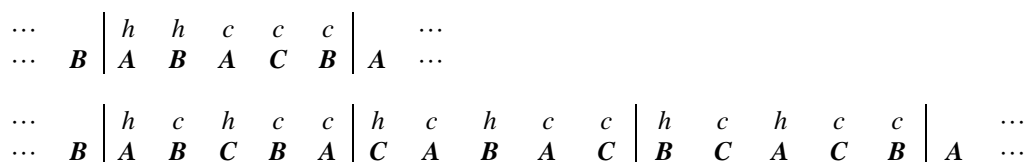


(19) Consider the following percent environments of close-packed planes of atoms. Write the Jagodzinski symbol and the corresponding  $\dots ABC \dots$  notation for two different solutions:

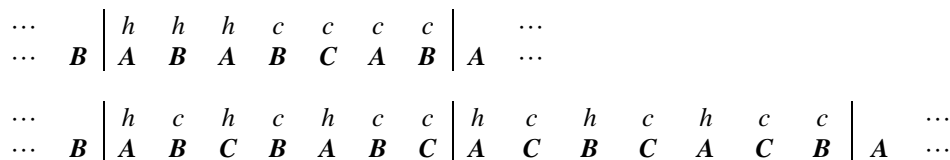
(a)  $25\% = 1/4 \text{ HCP}, 75\% = 3/4 \text{ CCP}$



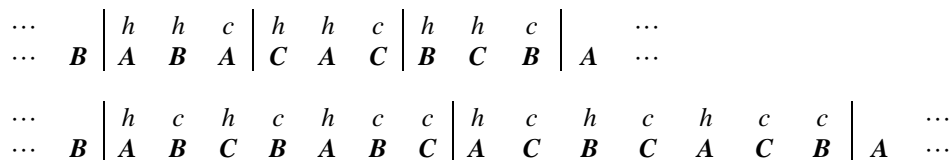
(b)  $40\% = 2/5 \text{ HCP}, 60\% = 3/5 \text{ CCP}$



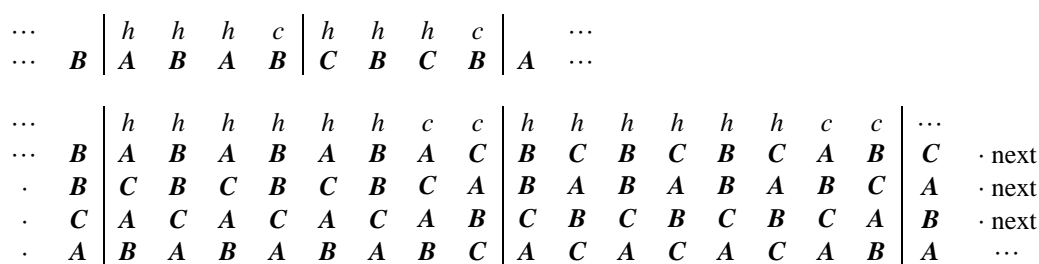
(c)  $43\% = 3/7 \text{ HCP}, 57\% = 4/7 \text{ CCP}$



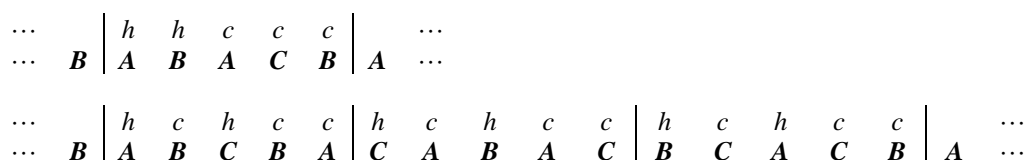
(d)  $67\% = 2/3 \text{ HCP}, 33\% = 1/3 \text{ CCP}$



(e)  $75\% = 3/4 \text{ HCP}, 25\% = 1/4 \text{ CCP}$



(f)  $55\% = 5/9 \text{ HCP}, 45\% = 4/9 \text{ CCP}$



- (20) Show that the fraction of space occupied by four equal spheres just touching in a tetrahedron is 77.96%.

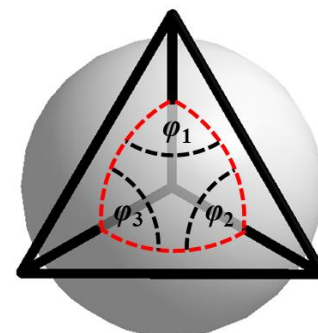
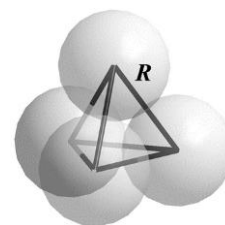
Helpful geometrical relations:

Volume of a Pyramid =  $\frac{1}{3}Ah$  ( $A$  = area of the base;  $h$  = height).

Volume of the sector of a sphere =  $\frac{1}{3}A'R$  ( $A'$  = area of the spherical triangle on the surface)

$A' = (\varphi_1 + \varphi_2 + \varphi_3 - \pi)R^2$ ;  $\varphi_1, \varphi_2, \varphi_3$  are the interior angles of the spherical triangle;  
 $R$  = radius of the sphere.

This figure shows the tetrahedron projected down a face. The sphere at the vertex intersects the tetrahedron by the spherical triangle shown by the dashed red lines.



**Volume of the tetrahedron in terms of R:**

$$\text{Area of the base} = \frac{1}{2}(2R) \left( \frac{\sqrt{3}}{2}(2R) \right) = \sqrt{3}R^2$$

$$\text{Height} = \sqrt{(2R)^2 - \frac{1}{3}(2R)^2} = \sqrt{\frac{8}{3}}R$$

$$\text{Volume} = \frac{1}{3}(\sqrt{3}R^2) \left( \sqrt{\frac{8}{3}}R \right) = \sqrt{\frac{8}{9}}R^3 = 0.9428 R^3$$

**Volume of a sphere sector inside the tetrahedron:**

$$\text{Dihedral angle of tetrahedron} = \varphi_1 = \varphi_2 = \varphi_3 = \pi - \arccos\left(-\frac{1}{3}\right) = 1.2310 (= 70.5288^\circ)$$

$$\text{Area of the spherical triangle of the sector} = (3(1.2310) - \pi)R^2 = 0.5513 R^2$$

$$\text{Volume of the sector} = \frac{1}{3}(0.5513 R^2)(R) = 0.1838 R^3$$

There are 4 sectors inside the tetrahedron. From this the fraction of space occupied by the spheres just touching in a tetrahedron is:

$$\frac{4 V_{\text{sector}}}{V_{\text{tetrahedron}}} = \frac{4(0.1838 R^3)}{0.9428 R^3} = 0.7796.$$

- (21) Evaluate the packing efficiencies using equally sized spheres for:

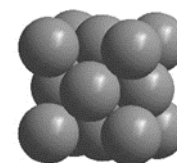
- (a) Face-centered cubic packing

Spheres (radius  $R$ ) touch along the face-diagonals of the cube, which contains 4 spheres.

Let  $a$  = edge of the cubic cell. Then,  $\sqrt{2}a = 4R$ , so that  $a = (4/\sqrt{2})R$ .

$$\text{Volume of 4 spheres} = 4 \frac{4\pi}{3} R^3 = \frac{16\pi}{3} R^3. \quad \text{Volume of cube} = a^3 = \frac{32}{\sqrt{2}} R^3$$

$$\text{Packing efficiency } \eta = \left( \frac{16\pi}{3} \right) / \frac{32}{\sqrt{2}} = \frac{\sqrt{2}\pi}{6} = 0.7405$$



- (b) Hexagonal close packing

Spheres (radius  $R$ ) touch along the  $a$ -,  $b$ -, and  $(a+b)$ -directions. For ideal sphere packing, the  $c/a$  ratio of the unit cell, which contains 2 spheres, is  $\sqrt{8/3}$ .

$$a = 2R, c = \sqrt{8/3}a = \sqrt{32/3}R.$$

$$\text{Volume of 2 spheres} = 2 \frac{4\pi}{3} R^3 = \frac{8\pi}{3} R^3. \quad \text{Volume of unit cell} = \frac{\sqrt{3}}{2} a^2 c = 8\sqrt{2}R^3$$

$$\text{Packing efficiency } \eta = \left( \frac{8\pi}{3} \right) / 8\sqrt{2} = \frac{\sqrt{2}\pi}{6} = 0.7405$$



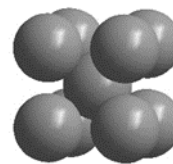
- (c) Body-centered cubic

Spheres (radius  $R$ ) touch along the body-diagonals of the cube, which contains 2 spheres.

Let  $a$  = edge of the cubic cell. Then,  $\sqrt{3}a = 4R$ , so that  $a = (4/\sqrt{3})R$ .

Volume of 2 spheres =  $2 \frac{4\pi}{3} R^3 = \frac{8\pi}{3} R^3$ .      Volume of cube =  $a^3 = \frac{64}{3\sqrt{3}} R^3$

Packing efficiency  $\eta = \left(\frac{8\pi}{3}\right) / \frac{64}{3\sqrt{3}} = \frac{\sqrt{3}\pi}{8} = 0.6802$



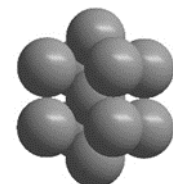
- (d) Body-centered tetragonal packing

Spheres (radius  $R$ ) touch along one direction as well as the body-diagonals of the tetragonally distorted cube, which contains 4 spheres.

Let  $c$  = vertical edge of the cell along which spheres touch. Then,  $c = 4R$ , so that  $a = \sqrt{6}R$ .

Volume of 4 spheres =  $4 \frac{4\pi}{3} R^3 = \frac{16\pi}{3} R^3$ .      Volume of cell =  $a^2 c = 24R^3$

Packing efficiency  $\eta = \left(\frac{16\pi}{3}\right) / 24 = \frac{2\pi}{9} = 0.6981$

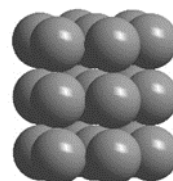


- (e) Simple hexagonal packing

Spheres (radius  $R$ ) touch along the  $a$ -,  $b$ -,  $(a+b)$ -, and  $c$ -directions. The unit cell contains 1 sphere. Therefore,  $a = 2R$ ,  $c = 2R$ .

Volume of 1 sphere =  $\frac{4\pi}{3} R^3$ .      Volume of unit cell =  $\frac{\sqrt{3}}{2} a^2 c = 4\sqrt{3} R^3$

Packing efficiency  $\eta = \left(\frac{4\pi}{3}\right) / 4\sqrt{3} = \frac{\sqrt{3}\pi}{9} = 0.6046$

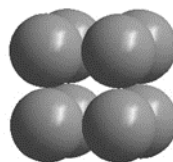


- (f) Simple cubic packing

Spheres (radius  $R$ ) touch along the axes of the cube, which contains 1 sphere. Let  $a$  = edge of the cubic cell. Then,  $a = 2R$ .

Volume of 1 sphere =  $\frac{4\pi}{3} R^3$ .      Volume of cube =  $a^3 = 8R^3$

Packing efficiency  $\eta = \left(\frac{4\pi}{3}\right) / 8 = \frac{\pi}{6} = 0.5236$



- (22) Consider the 3-d sphere packing sequence  $\dots A A B B \dots$ . What is the coordination number for each sphere in this packing? Evaluate the packing efficiency using equally sized spheres.

Consider an  $A$  layer: each sphere has 6 neighbors in the plane, 1 neighbor from the adjacent  $A$  layer, and 3 neighbors from the adjacent  $B$  layer. Therefore, the coordination number is 10.

The unit cell contains 4 spheres. Spheres touch along the  $a$ -,  $b$ -, and  $(a+b)$ -directions. Along the  $c$ -direction, there are 2 pairs of direct one-on-one contacts and 2 instances of close-packed contacts. Therefore,

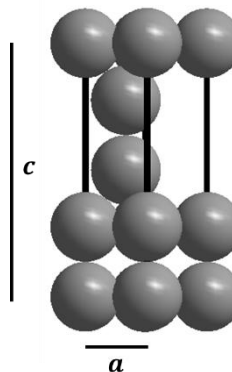
$$a = 2R, c = 4R + 4\sqrt{2/3}R = (4 + \sqrt{32/3})R.$$

Volume of 4 spheres =  $4 \frac{4\pi}{3} R^3 = \frac{16\pi}{3} R^3$ .

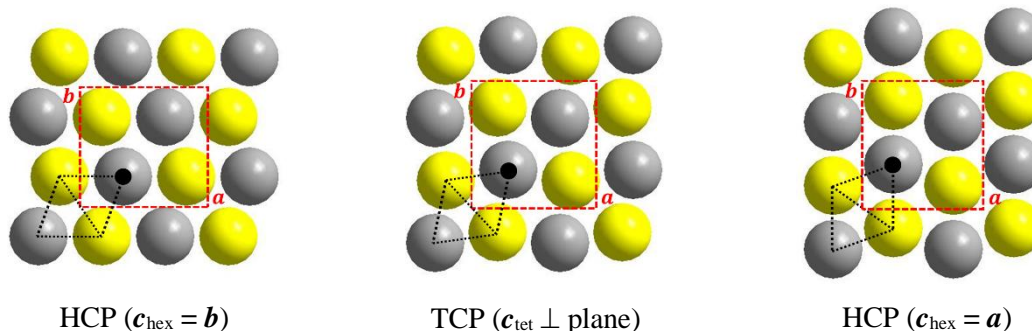
Volume of unit cell =  $\frac{\sqrt{3}}{2} a^2 c = 8(\sqrt{3} + \sqrt{2})R^3$

Packing efficiency  $\eta = \left(\frac{16\pi}{3}\right) / 8(\sqrt{3} + \sqrt{2}) = \frac{2\pi}{3(\sqrt{3} + \sqrt{2})} = 0.6657$

As anticipated, the packing efficiency is intermediate to that of HCP and simple hexagonal packing.



- (23) Tetragonal close packing (TCP), in which each sphere is 11-coordinate, can be derived from HCP as described in M. O’Keeffe, *Mat. Res. Bull.* **1984**, *19*, 1433-1438. To show this relationship, consider the projection of TCP down the  $c$ -axis (middle figure): the unit cell is the dotted red square ( $a = b$ ); spheres with  $z = 0$  are gray; spheres with  $z = \frac{1}{2}$  are yellow. The unit cell corners sit at the center of regular octahedra projected down an edge, shown by the dotted black lines. These octahedra actually form chains of edge-shared octahedra along the tetragonal  $c$ -axis. The direction from the octahedron center to a vertex (black dot) is along the face-diagonal.



HCP is achieved by keeping each octahedron rigid and rotating them by angle  $\varphi$  either clockwise (left figure) or counterclockwise (right figure).

- (a) The space group symmetry of the sphere packing between TCP (space group  $P4_2/mnm$ ) and the two orientations of HCP (space group  $P6_3/mmc$ ) is  $Pnmm$ , which is the highest-order subgroup of both  $P6_3/mmc$  and  $P4_2/mnm$ . Verify this feature of  $Pnmm$ .

$P6_3/mmc$  is hexagonal, and the full symbol is  $P6_3/m 2/m 2/c$ . Its point group is  $6/mmm$ , which has order 24.

$P4_2/mnm$  is tetragonal, and the full symbol is  $P4_2/m 2_1/n 2/m$ . Its point group is  $4/mmm$ , which has order 16.

The highest order point group common to both these hexagonal and tetragonal point groups has order 8 and is orthorhombic, with 3 mutually perpendicular 2-fold symmetry axes. This point group is  $mmm = 2/m 2/m 2/m$ , which is the point group of  $Pnmm$ .

The full symbol of  $Pnmm$  is  $P2_1/n 2_1/n 2/m$ . According to the diagrams,  $Pnmm$  is a maximal subgroup of  $P4_2/mnm$ . However, to achieve the orthorhombic cell from  $P6_3/mmc$ , the primitive hexagonal unit cell must be doubled.

- (b) Show that the octahedra in TCP are rotated by  $\pm\varphi = \pm\frac{1}{2} \arcsin \frac{1}{3} = \pm 9.7356^\circ$  to achieve the two different orientations of HCP.

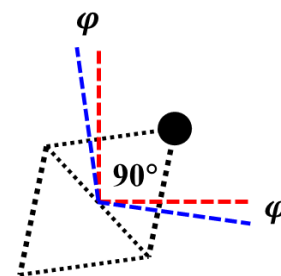
In TCP, the direction from the center of the octahedron to the vertex at the black dot is the face-diagonal of the square base, as shown here. The dashed red lines indicate the directions of the tetragonal  $a$ - and  $b$ -axes. In either of the HCP packings, the octahedron is rotated so that one of the orthogonal crystallographic axes  $a$  or  $b$  is perpendicular to a face of the octahedron. The directions perpendicular to these faces are  $[111]$  and  $[\bar{1}\bar{1}1]$ , which are given by the dashed blue lines, and the angle  $\theta$  between these directions is determined by:

$$[111] \cdot [\bar{1}\bar{1}1] = (-1)(1) + (-1)(1) + (1)(1) = -1 = (\sqrt{3})(\sqrt{3}) \cos \theta,$$

so that  $\cos \theta = -1/3$  and  $\theta = 109.4712^\circ$ .

Therefore, the octahedra are rotated by  $\pm\varphi = \pm\frac{1}{2} (109.4712^\circ - 90^\circ) = \pm 9.7356^\circ$ .

Since  $\sin(109.4712^\circ - 90^\circ) = -\cos 109.4712^\circ = 1/3$ ,  $\pm\varphi = \pm\frac{1}{2} \arcsin \frac{1}{3}$ .



- (c) Let  $R$  = radius of each sphere that just touch in these sphere packings. In terms of the angle  $\varphi$ , which can vary from  $-\frac{1}{2} \arcsin \frac{1}{3}$  to  $+\frac{1}{2} \arcsin \frac{1}{3}$ , show that the unit cell parameters are:

$$a = \left[ \left(1 + \frac{1}{\sqrt{2}}\right) \cos \varphi - \left(1 - \frac{1}{\sqrt{2}}\right) \sin \varphi \right] (2R);$$

$$b = \left[ \left(1 + \frac{1}{\sqrt{2}}\right) \cos \varphi + \left(1 - \frac{1}{\sqrt{2}}\right) \sin \varphi \right] (2R);$$

$$c = 2R.$$

The unit cell  $c$ -axis is the distance of two spheres in contact, i.e.,  $c = 2R$ .

By using the projection of the  $a$ - and  $b$ -axes with the edge-projected octahedra, we can conclude that:

$$a = 2 \left[ \sqrt{2}R \cos \left(\frac{\pi}{4} + \varphi\right) + R \cos \left(\frac{\pi}{4} - \varphi\right) \right]$$

$$= 2R \left[ \sqrt{2} \left( \frac{1}{\sqrt{2}} \cos \varphi - \frac{1}{\sqrt{2}} \sin \varphi \right) + \left( \frac{1}{\sqrt{2}} \cos \varphi + \frac{1}{\sqrt{2}} \sin \varphi \right) \right] = 2R \left[ \left(1 + \frac{1}{\sqrt{2}}\right) \cos \varphi - \left(1 - \frac{1}{\sqrt{2}}\right) \sin \varphi \right]$$

$$b = 2 \left[ \sqrt{2}R \sin \left(\frac{\pi}{4} + \varphi\right) + R \sin \left(\frac{\pi}{4} - \varphi\right) \right]$$

$$= 2R \left[ \sqrt{2} \left( \frac{1}{\sqrt{2}} \cos \varphi + \frac{1}{\sqrt{2}} \sin \varphi \right) + \left( \frac{1}{\sqrt{2}} \cos \varphi - \frac{1}{\sqrt{2}} \sin \varphi \right) \right] = 2R \left[ \left(1 + \frac{1}{\sqrt{2}}\right) \cos \varphi + \left(1 - \frac{1}{\sqrt{2}}\right) \sin \varphi \right]$$

To test these results, we evaluate the unit cell parameters for the different models illustrated above:

TCP ( $\varphi = 0$ ):  $a = 3.4142R$ ,  $b = 3.4142R$ ,  $c = 2R$   
 $a = b$

HCP ( $c_{hex} = b$ ;  $\varphi = -9.7356^\circ$ ):  $a = 3.4641R$ ,  $b = 3.2660R$ ,  $c = 2R$

$a = \sqrt{3}c$ ,  $b = \sqrt{8/3}c$ : this is the orthorhombic cell derived from a hexagonal cell.

HCP ( $c_{hex} = a$ ;  $\varphi = +9.7356^\circ$ ):  $a = 3.2660R$ ,  $b = 3.4641R$ ,  $c = 2R$

$a = \sqrt{8/3}c$ ,  $b = \sqrt{3}c$ : this is the orthorhombic cell derived from a hexagonal cell.

- (d) Evaluate the packing efficiency  $\eta$  as a function of  $\varphi$ . For which angle(s)  $\varphi$  is the packing efficiency the highest; the lowest?

The unit cell contains 4 spheres.

$$\text{Volume of 4 spheres} = 4 \frac{4\pi}{3} R^3 = \frac{16\pi}{3} R^3.$$

$$\text{Volume of unit cell} = abc = 8 \left[ \left(1 + \frac{1}{\sqrt{2}}\right)^2 \cos^2 \varphi - \left(1 - \frac{1}{\sqrt{2}}\right)^2 \sin^2 \varphi \right] R^3 = 8 \left[ \frac{3}{2} \cos 2\varphi + \sqrt{2} \right] R^3$$

$$\text{Packing efficiency } \eta = \frac{\left(\frac{16\pi}{3}\right)/4}{3 \cos 2\varphi + 2\sqrt{2}} = \frac{4\pi}{9 \cos 2\varphi + 6\sqrt{2}}$$

The lowest packing efficiency occurs when the denominator is largest:  $\varphi = 0$ , which is TCP.  $\eta = 0.7187$ .

The highest packing efficiency occurs when the denominator is smallest:  $\varphi = \pm 9.7356^\circ$ , which is HCP.  $\eta = 0.7405$ .

- (e) Determine the fractional coordinates of the sphere marked by the black dot in the figures above.

$$x = \sqrt{2}R \cos \left(\frac{\pi}{4} + \varphi\right) / a = (\cos \varphi - \sin \varphi) / [(2 + \sqrt{2}) \cos \varphi - (2 - \sqrt{2}) \sin \varphi]$$

$$y = \sqrt{2}R \sin \left(\frac{\pi}{4} + \varphi\right) / b = (\cos \varphi + \sin \varphi) / [(2 + \sqrt{2}) \cos \varphi + (2 - \sqrt{2}) \sin \varphi]$$

$$z = 0$$

Using these formulas, the coordinates for each case are:

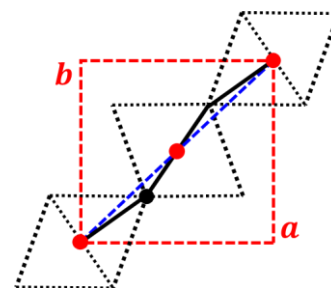
TCP ( $\varphi = 0$ ):  $x = 0.2929$ ,  $y = 0.2929$ ,  $z = 0$

HCP ( $c_{hex} = b$ ;  $\varphi = -9.7356^\circ$ ):  $x = 0.3333$ ,  $y = 0.25$ ,  $z = 0$

HCP ( $c_{hex} = a$ ;  $\varphi = +9.7356^\circ$ ):  $x = 0.25$ ,  $y = 0.3333$ ,  $z = 0$

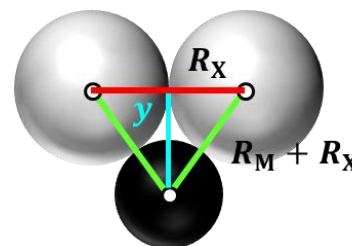
- (f) What is the polyhedron that surrounds the body-centered point  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  of the unit cell?

An octahedron, as shown by the various projections.



- (24) Evaluate the ideal radius ratios  $R_M/R_X$  for the polyhedral voids listed below.  $R_X$  = radius of spheres that form the polyhedron;  $R_M$  = radius of sphere that occupies the polyhedral void.

Ideal radius ratios are determined by the interstitial sphere  $M$  just touching the  $X$  spheres of the polyhedron. By geometry, one straightforward way to determine this ratio is to calculate the right triangle formed by the  $M$  sphere and two  $X$  spheres (see figure). The hypotenuse is  $R_M + R_X$ ; one edge of the right triangle is  $R_X$ , which is half the edge of the polyhedron; and the other edge of the right triangle is  $R_X/\tan(\theta/2)$  with  $\theta$  = angle between the two lines connecting the  $M$  sphere with two adjacent  $X$  spheres.



- (a) Tetrahedron

The  $M$  sphere fits at the center of a tetrahedron so that  $\theta = 109.4712^\circ$ :

$$(R_M + R_X)^2 = R_X^2 + (R_X/\tan(109.4712^\circ/2))^2 = R_X^2 + \frac{1}{2}R_X^2 = \frac{3}{2}R_X^2$$

$$\text{Therefore, } \frac{R_M}{R_X} = \sqrt{\frac{3}{2}} - 1 = 0.2247$$

- (b) Trigonal bipyramid

The 3 equatorial and 2 axial  $X$  spheres are inequivalent. If all  $X$  spheres touch each other, then the ideal  $M$  sphere fits snugly into the equatorial triangle and  $\theta = 120^\circ$ :

$$(R_M + R_X)^2 = R_X^2 + (R_X/\tan(120^\circ/2))^2 = R_X^2 + \frac{1}{3}R_X^2 = \frac{4}{3}R_X^2$$

$$\text{Therefore, } \frac{R_M}{R_X} = \sqrt{\frac{4}{3}} - 1 = 0.1547$$

- (c) Octahedron

The  $M$  sphere fits at the center of an octahedron so that  $\theta = 90^\circ$ :

$$(R_M + R_X)^2 = R_X^2 + (R_X/\tan(90^\circ/2))^2 = R_X^2 + R_X^2 = 2R_X^2$$

$$\text{Therefore, } \frac{R_M}{R_X} = \sqrt{2} - 1 = 0.4142$$

- (d) Trigonal prism

The  $M$  sphere fits snugly above and below the centers of the two triangular faces. According to the diagram,  $y = 2R_X/\sqrt{3}$  so that  $\theta = 81.7868^\circ$ :

$$(R_M + R_X)^2 = R_X^2 + (R_X/\tan(81.7868^\circ/2))^2 = R_X^2 + \frac{4}{3}R_X^2 = \frac{7}{3}R_X^2$$

$$\text{Therefore, } \frac{R_M}{R_X} = \sqrt{\frac{7}{3}} - 1 = 0.5275$$

- (e) Cube

The  $M$  sphere fits snugly above and below the centers of two square faces. According to the diagram,  $y = \sqrt{3}R_X$  so that  $\theta = 70.5288^\circ$ :

$$(R_M + R_X)^2 = R_X^2 + (R_X/\tan(70.5288^\circ/2))^2 = R_X^2 + 2R_X^2 = 3R_X^2$$

$$\text{Therefore, } \frac{R_M}{R_X} = \sqrt{3} - 1 = 0.7321$$

- (f) Icosahedron

The five-fold symmetry of the icosahedron means that the golden ratio  $\tau = \frac{\sqrt{5}+1}{2} \approx 1.6180$  plays an important role in its geometry. For the icosahedron,  $y = \tau - 1$  so that  $\theta = 63.4349^\circ$ :

$$(R_M + R_X)^2 = R_X^2 + (R_X/\tan(63.4349^\circ/2))^2 = \left(1 + \frac{1}{(\tau-1)^2}\right)R_X^2 = (\tau + 2)R_X^2$$

$$\text{Therefore, } \frac{R_M}{R_X} = \sqrt{\tau + 2} - 1 = 0.9021$$

- (25) Interstitial carbides are refractory materials that show metallic luster, good electrical conductivity, and extreme hardness. Their structures involve close packed arrangements of metal atoms M with carbon atoms in octahedral holes. For a given close packed layer sequence of M atoms, the maximum carbon content  $x$ , expressed as  $MC_x$ , is determined by the following rule:

*Only one of the two octahedral interstices on either side of an -h- layer of M atoms is ever occupied. Otherwise, all other octahedral interstices are occupied.*

- (a) Provide a rationale for this rule that couples stoichiometry and structure.

**With no C–C bonds and C being more electronegative than most metals, isolated carbide atoms will develop a formal negative charge. To minimize the electrostatic repulsion between these carbide species, they cannot occupy both octahedra surrounding an atom in an HCP local packing environment because these octahedra will share a common face and create a short C–C distance.**

Consider the following four close packed layer sequences (in Jagodzinski symbols) of the M atoms for four metal carbides: *hc*, *hcc*, *hhc*, *hhcc*. For each layer sequence, determine

- (b) the close packed layer sequence for one unit cell (repeating unit) using “A, B, C” for M atoms and “a, b, c” for C atoms, using the rule above;  
 (c) the value of “x” corresponding to the maximum carbon content in  $MC_x$ , and express the chemical formula using integer subscripts;  
 (d) the average coordination number of all metal atoms by carbon and the specific average coordination numbers for each M atom layer.

***hc*: ...ABC B... is the sequence of M atoms; ...cAcBaCaB... is the sequence with all octahedral holes filled. We must eliminate one “c” and one “a” layer of carbide atoms to give ...\_AcB\_CaB... (NOTE: another possibility is ...\_AcBaC\_B... in which the second B layer has no C atoms surrounding it, which would be unusual.)**

**The formula is  $M_4C_2 = M_2C = MC_{0.5}$ , so  $x = 0.5$   
 $2 \cdot \langle CN \rangle_M = 1 \cdot \langle CN \rangle_C = 6$ , so  $\langle CN \rangle_M = 3$**

***hcc*: ...ABCACB... is the sequence of M atoms; ...cAcBaCbAbCaB... is the sequence with all octahedral holes filled. We must eliminate one “c” and one “b” layer of carbide atoms to give ...\_AcBaC\_AbCaB... or ...\_AcBaCbA\_CaB...**

**The formula is  $M_6C_4 = M_3C_2 = MC_{0.67}$ , so  $x = 0.67$   
 $3 \cdot \langle CN \rangle_M = 2 \cdot \langle CN \rangle_C = 12$ , so  $\langle CN \rangle_M = 4$**

***hhc*: ...ABACACBCB... is the sequence of M atoms; ...cAcBcAbCbAbCaBaCaB... is the sequence with all octahedral holes filled. We must eliminate one “c,” one “b” and one “a” layer of carbide atoms to give ...\_cA\_BcAbC\_AbCaB\_CaB...**

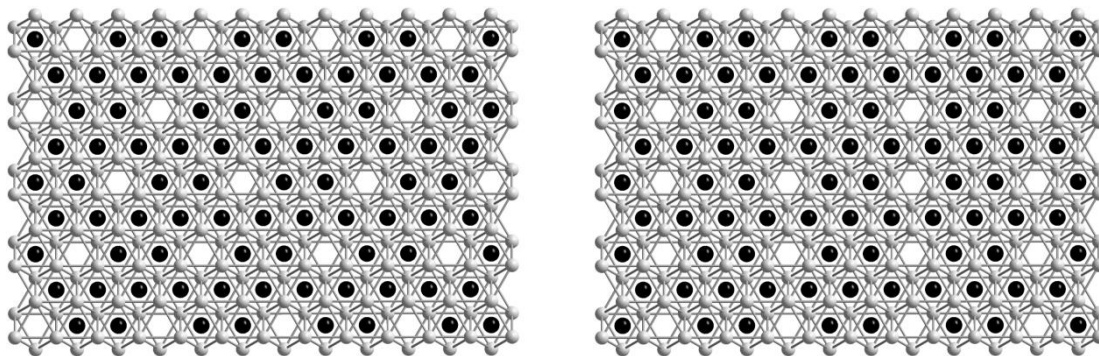
**The formula is  $M_9C_6 = M_3C_2 = MC_{0.67}$ , so  $x = 0.67$   
 $3 \cdot \langle CN \rangle_M = 2 \cdot \langle CN \rangle_C = 12$ , so  $\langle CN \rangle_M = 4$**

***hhcc*: ...ABACBCBACACB... is the sequence of M atoms; ...cAcBcAbCaBaCaBcAbCbAbCaB... is the sequence with all octahedral holes filled. We must eliminate one “c,” one “b” and one “a” layer of carbide atoms to give ...\_cA\_BcAbCaB\_CaBcAbC\_AbCaB...**

**The formula is  $M_{12}C_9 = M_4C_3 = MC_{0.75}$ , so  $x = 0.75$   
 $4 \cdot \langle CN \rangle_M = 3 \cdot \langle CN \rangle_C = 18$ , so  $\langle CN \rangle_M = 4.5$**

In  $V_6C_5$  and  $V_8C_7$ , the V atoms form a *ccp* arrangement and every layer of octahedral holes is uniformly, but not randomly occupied.

- (e) Draw two possible arrangements of carbon atoms for a single layer of octahedral holes of  $V_6C_5$ . What are the possible coordination numbers of V by carbon atoms?



If all octahedral holes are occupied, then the ideal formula is “ $V_6C_6$ .” In  $V_6C_5$ , the octahedral holes are 1/6 vacant. The two figures above represent structures such that every vacant site is completely surrounded by filled sites. Each V atom is 5-coordinate by C in a square-pyramidal environment.

- (f) For  $V_8C_7$ , what is the average coordination number of V by carbon atoms? Assuming the two closest whole integers, what is the concentration (in atomic percent V) of each coordination mode? Draw these two different coordination environments for V.

$8 \langle CN \rangle_V = 7 \cdot \langle CN \rangle_C = 42$ , so  $\langle CN \rangle_V = 5.25$  – the average coordination number is 5.25. Since this result is nonintegral, there must be at least two different coordination environments for the V atoms. With respect to the criterion of “randomly occupied” octahedral holes, there must be a mixture of six-coordinate and five-coordinate V atoms. To satisfy the topological equation, 1/4 of the V atoms must be six-coordinate (octahedral) and 3/4 of the V atoms must be five-coordinate (square pyramidal).

- (26) Aluminum carbonitrides  $Al_xC_yN_z$  have been studied for their possible refractory properties. They can be described as close packed arrangements of carbon and nitrogen atoms with aluminum atoms in tetrahedral voids. Four ternary compounds  $Al_xC_yN_z$  have been structurally characterized, in addition to aluminum carbide  $Al_xC_y$  and aluminum nitride  $Al_xN_z$ . The unit cells of the six compounds are either hexagonal or rhombohedral; for  $Al_xN_z$ ,  $c \sim 5.00 \text{ \AA}$ , and for  $Al_xC_y$ ,  $c \sim 25.00 \text{ \AA}$ . Below are listed the patterns of atomic sites for the 6 compounds (in no particular order) using the “ABC”-notation (capital letters are C sites, underlined capital letters are N sites, small letters are Al sites; all sites are fully occupied in the assigned layer). For each case,

- (a) Write down the Jagodzinski symbol for combined sequence of carbide and nitride layers;  
 (b) Identify the empirical formula of the compound, i.e., provide numbers for  $x$ ,  $y$ , and  $z$  in  $Al_xC_yN_z$ ;  
 (c) Estimate the value of the  $c$  lattice constant; and  
 (d) Describe the various coordination polyhedra surrounding the C and N atoms.

- (i) ... CaAc ...  
 (ii) ... AbBaAbBabAaBbAcCaAcCacAaCc ...  
 (iii) ... AbBabAaBbAcCacAaCc ...  
 (iv) ... AbBabAaBcCbcBbCaAcaCc ...  
 (v) ... AbBaAbBabAaBbAaBcCbBcCbcBbCcBbCaAcCaAcaCcAaCc ...  
 (vi) ... AbBaAbaBbAaBcCbBcbCcBbCaAcCacAaCc ...

(i) ... CaAc ...

... A|CA|C ... is ... |hh| ..., so the packing symbol is ...h...

Unit cell is Al<sub>2</sub>N<sub>2</sub>; empirical formula is AlN

c-parameter is 1×(c-AlN) + 0×(c-Al<sub>4</sub>C<sub>3</sub>) ~ 5.00 Å.

⟨CN⟩<sub>N</sub> = 4. Each N atom has 1 Al below and 3 Al above in a tetrahedral arrangement.

NOTE: (i) is AlN and there are two formula units (Al<sub>2</sub>N<sub>2</sub>) per unit cell (c ~ 5.00 Å).

(ii) ... AbBabAaBcCbcBbCaAcaCc ...

... C|ABABCBCAC|A ... is ... |hhchhchhc| ..., so the packing symbol is ...hhc...

Unit cell is Al<sub>12</sub>C<sub>9</sub>; empirical formula is Al<sub>4</sub>C<sub>3</sub> = (Al<sub>4</sub>C<sub>3</sub>)

c-parameter is 0×(c-Al<sub>2</sub>N<sub>2</sub>) + 1×(c-Al<sub>12</sub>C<sub>9</sub>) ~ 25.00 Å.

There are two types of C atoms, which we can see from solving

$$4(4) = \langle \text{CN} \rangle_{\text{C}}(3), \text{ so that } \langle \text{CN} \rangle_{\text{C}} = 5.33.$$

which suggests a mixture of 5- and 6-coordinate C. Of the 3 distinct C atoms, one-third are 6-coordinate (e.g., *bAc*), which is “octahedral” or trigonal antiprismatic, and two-thirds are 5-coordinate (e.g., *abAa*), which is close to a trigonal bipyramid (face-capped tetrahedron).

NOTE: (iv) is Al<sub>4</sub>C<sub>3</sub> and there are three formula units (Al<sub>12</sub>C<sub>9</sub>) per unit cell (c ~ 25.00 Å).

(iii) ... AbBaAbBabAaBbAcCaAcCacAaCc ...

... C|ABABABACAC|A ... is ... |hhhhhchhhhc| ..., so the packing symbol is ...hhhhhc...

Unit cell is Al<sub>14</sub>C<sub>6</sub>N<sub>6</sub>; empirical formula is Al<sub>7</sub>C<sub>3</sub>N<sub>3</sub>.

$$\text{Al}_{14}\text{C}_6\text{N}_6 = (\text{Al}_6\text{N}_6)(\text{Al}_8\text{C}_6) = (\text{Al}_2\text{N}_2)_3(\text{Al}_{12}\text{C}_9)_{2/3}$$

c-parameter is 3×(c-AlN) + (2/3)×(c-Al<sub>4</sub>C<sub>3</sub>) ~ 3(5.00 Å) + (2/3)(25.00 Å) = 31.67 Å.

Each layer of N atoms is surrounded by 2 layers of Al atoms in tetrahedral holes; therefore ⟨CN⟩<sub>N</sub> = 4. The coordination polyhedra (e.g., aAb) are tetrahedra.

There are two types of C atoms, which we can see from solving

$$4(7) = \langle \text{CN} \rangle_{\text{C}}(3) + 4(3), \text{ so that } \langle \text{CN} \rangle_{\text{C}} = 5.33,$$

which suggests a mixture of 5- and 6-coordinate C. Of the 3 distinct C atoms, one-third are 6-coordinate (e.g., *bAc*), which is “octahedral” or trigonal antiprismatic, and two-thirds are 5-coordinate (e.g., *abAa*), which is close to a trigonal bipyramid (face-capped tetrahedron).

(iv) ... AbBabAaBbAcCacAaCc ...

... C|ABABACAC|A ... is ... |hhhchhhc| ..., so the packing symbol is ...hhhc...

Unit cell is Al<sub>10</sub>C<sub>6</sub>N<sub>2</sub>; empirical formula is Al<sub>5</sub>C<sub>3</sub>N.

$$\text{Al}_{10}\text{C}_6\text{N}_2 = (\text{Al}_2\text{N}_2)(\text{Al}_8\text{C}_6) = (\text{Al}_2\text{N}_2)(\text{Al}_{12}\text{C}_9)_{2/3}$$

c-parameter is 1×(c-AlN) + (2/3)×(c-Al<sub>4</sub>C<sub>3</sub>) ~ 1(5.00 Å) + (2/3)(25.00 Å) = 21.67 Å.

Each layer of N atoms is surrounded by 2 layers of Al atoms in tetrahedral holes; therefore ⟨CN⟩<sub>N</sub> = 4. The coordination polyhedra (e.g., aAb) are tetrahedra.

There are two types of C atoms, which we can see from solving

$$4(5) = \langle \text{CN} \rangle_{\text{C}}(3) + 4(1), \text{ so that } \langle \text{CN} \rangle_{\text{C}} = 5.33.$$

Of the 3 distinct C atoms, one-third are 6-coordinate (e.g., *bAc*), which is “octahedral” or trigonal antiprismatic, and two-thirds are 5-coordinate (e.g., *abAa*), which is close to a trigonal bipyramid (face-capped tetrahedron).

(v) ...  $Ab\bar{B}a\bar{A}b\bar{B}ab\bar{A}a\bar{B}b\bar{A}a\bar{B}c\bar{C}b\bar{B}c\bar{C}bc\bar{B}b\bar{C}c\bar{B}b\bar{C}a\bar{A}c\bar{C}a\bar{A}c\bar{C}a\bar{A}c\bar{C}c\bar{A}a\bar{C}c$  ...

...  $C|ABABABABCBCBCBCACAC|A$  ... is ...  $|hhhhhchhhhhchhhhhc|$  ..., so the packing symbol is ... $hhhhhc$ ...

Unit cell is  $Al_{24}C_9N_{12}$ ; empirical formula is  $Al_8C_3N_4$ .

$$Al_{24}C_9N_{12} = (Al_2N_2)_6(Al_{12}C_9) = (Al_2N_2)_6(Al_{12}C_9)_1$$

$$c\text{-parameter is } 6 \times (c\text{-AlN}) + (1) \times (c\text{-Al}_4\text{C}_3) \sim 6(5.00 \text{ \AA}) + (1)(25.00 \text{ \AA}) = 55.00 \text{ \AA}.$$

Each layer of N atoms is surrounded by 2 layers of Al atoms in tetrahedral holes; therefore  $\langle CN \rangle_N = 4$ . The coordination polyhedra (e.g.,  $a\bar{A}b$ ) are tetrahedra.

There are two types of C atoms, which we can see from solving

$$4(8) = \langle CN \rangle_C(3) + 4(4), \text{ so that } \langle CN \rangle_C = 5.33.$$

Of the 3 distinct C atoms, one-third are 6-coordinate (e.g.,  $bAc$ ), which is "octahedral" or trigonal antiprismatic, and two-thirds are 5-coordinate (e.g.,  $abAa$ ), which is close to a trigonal bipyramid (face-capped tetrahedron).

(vi) ...  $Ab\bar{B}a\bar{A}ba\bar{B}b\bar{A}a\bar{B}c\bar{C}b\bar{B}cb\bar{C}c\bar{B}b\bar{C}a\bar{A}c\bar{C}ac\bar{A}a\bar{C}c$  ...

...  $C|ABABABABCBCBCACAC|A$  ... is ...  $|hhhchhhchhhc|$  ..., so the packing symbol is ... $hhhc$ ...

Unit cell is  $Al_{18}C_9N_6$ ; empirical formula is  $Al_6C_3N_2$ .

$$Al_{18}C_9N_6 = (Al_2N_2)_3(Al_{12}C_9) = (Al_2N_2)_3(Al_{12}C_9)_1$$

$$c\text{-parameter is } 3 \times (c\text{-AlN}) + (1) \times (c\text{-Al}_4\text{C}_3) \sim 3(5.00 \text{ \AA}) + (1)(25.00 \text{ \AA}) = 40.00 \text{ \AA}.$$

Each layer of N atoms is surrounded by 2 layers of Al atoms in tetrahedral holes; therefore  $\langle CN \rangle_N = 4$ . The coordination polyhedra (e.g.,  $a\bar{A}b$ ) are tetrahedra.

There are two types of C atoms, which we can see from solving

$$4(6) = \langle CN \rangle_C(3) + 4(2), \text{ so that } \langle CN \rangle_C = 5.33.$$

Of the 3 distinct C atoms, one-third are 6-coordinate (e.g.,  $bAc$ ), which is "octahedral" or trigonal antiprismatic, and two-thirds are 5-coordinate (e.g.,  $abAa$ ), which is close to a trigonal bipyramid (face-capped tetrahedron).

- (27) Silicon carbide SiC forms numerous polytypes, all of which are tetrahedral frameworks related to sphalerite, wurtzite, or some hybrid of these two. According to Wells, each SiC structure “can be considered as having planes of carbon atoms (or of silicon atoms), viewed either as packed ions or as centers of tetrahedra stacked one above another in different arrays.” In fact, these arrays are expressly the designations used for close packings of spheres in 3-dimensions. Below is a table listing 7 different SiC structures:

<i>ABC</i> Notation	Jagodzinski Notation	Estimated Repeating Length (Å)
... [AB] ...	... <i>h</i> ...	5.048 (2.524 / <i>h</i> layer)
... [ABC] ...	... <i>c</i> ...	7.604 (2.535 / <i>c</i> layer)
... [ABCACB] ...	... <i>hcc</i> ...	<b>15.188 (15.079)</b>
... [ABACBCACBABCBCAC] ...	... <i>hchcc</i> ...	<b>37.959 (37.70)</b>
... [ABCACBACABCBCACBACB] ...	... <i>hcchccc</i> ...	<b>53.169 (52.78)</b>
... [ABACABC] ...	... <i>hcccc</i> ...	<b>17.723 (17.637)</b>
... [ABCABACB] ...	... <i>hccc</i> ...	<b>20.258 (20.106)</b>

Fill in all (10) the blank entries. Explain how you estimated the repeating length.

There are various ways to estimate the repeating length. I have chosen to evaluate the average interplanar spacing for ... *h* ... and ... *c* ..., which are slightly different. Then, from the Jagodzinski Notation, use the fractions of -*h*- and -*c*- layers with the number of repeat layers determined from the *ABC* Notation. The specific calculations are:

$$15.188 \text{ \AA} = (6 \text{ layers}) \times [1/3 (2.524 \text{ \AA/layer}) + 2/3 (2.535 \text{ \AA/layer})]$$

$$37.959 \text{ \AA} = (15 \text{ layers}) \times [2/5 (2.524 \text{ \AA/layer}) + 3/5 (2.535 \text{ \AA/layer})]$$

$$53.169 \text{ \AA} = (21 \text{ layers}) \times [2/7 (2.524 \text{ \AA/layer}) + 5/7 (2.535 \text{ \AA/layer})]$$

$$17.723 \text{ \AA} = (7 \text{ layers}) \times [2/7 (2.524 \text{ \AA/layer}) + 5/7 (2.535 \text{ \AA/layer})]$$

$$20.258 \text{ \AA} = (8 \text{ layers}) \times [1/4 (2.524 \text{ \AA/layer}) + 3/4 (2.535 \text{ \AA/layer})]$$

See *Acta Cryst.* 1969, B25, 477-488. The values in parentheses and italics show experimental values.

**Atomic and Ionic Sizes**

(28)  $\beta$ -brass (CuZn) is a binary derivative of the BCC structure with Cu atoms at the corners and Zn atoms at the center of the unit cell.

(a) Use the crystal structure of Cu, which is cubic close-packed,  $a = 3.6149 \text{ \AA}$ , to estimate the metallic radius of 8-coordinate Cu.

**Cu is CCP:  $R_{12}(\text{Cu}) = (1/4)(\sqrt{2}a) = 1.2781 \text{ \AA}$ .**

**Using Goldschmidt's factor  $R_{12} = 1.029R_8$ ,  $R_8(\text{Cu}) = 1.242 \text{ \AA}$ .**

(b) Use the crystal structure of Zn, which is distorted hexagonally close-packed,  $a = 2.6649 \text{ \AA}$ ,  $c = 4.9468 \text{ \AA}$ , to estimate the metallic radius of 8-coordinate Zn.

**Zn is distorted HCP, with 6 shorter (2.6649  $\text{\AA}$ ) and 6 longer (2.9129  $\text{\AA}$ ) interatomic distances.**

**$R_{12}(\text{Zn}) = (1/2)[2.6649 \text{ \AA} + 2.9129 \text{ \AA}]/2 = 1.3945 \text{ \AA}$ .**

**Using Goldschmidt's factor  $R_{12} = 1.029R_8$ ,  $R_8(\text{Zn}) = 1.355 \text{ \AA}$ .**

(c) Use the following sequence of CCP Cu-Zn alloys,  $\alpha\text{-Cu}_{0.95}\text{Zn}_{0.05}$  ( $a = 3.6187 \text{ \AA}$ ),  $\alpha\text{-Cu}_{0.75}\text{Zn}_{0.25}$  ( $a = 3.6669 \text{ \AA}$ ), and  $\alpha\text{-Cu}_{0.64}\text{Zn}_{0.36}$  ( $a = 3.6982 \text{ \AA}$ ), to estimate a metallic radius of 12-coordinate Zn, and then estimate the metallic radius of 8-coordinate Zn. Compare your result with that of (b).

**Using the lattice constant of FCC Cu and the three values of  $\alpha$ -brasses, a linear regression analysis of lattice constant  $a$  vs. Zn content  $x$  gives:  $a \sim 0.2360x + 3.6107$ . Therefore, by extrapolating this line to  $x = 1$ , which is "FCC Zn", the predicted lattice constant is 3.8467  $\text{\AA}$ .**

**$R_{12}(\text{Zn}) = (1/4)(\sqrt{2}a) = 1.2781 \text{ \AA} = 1.3600 \text{ \AA}$ .**

**Using Goldschmidt's factor  $R_{12} = 1.029R_8$ ,  $R_8(\text{Zn}) = 1.322 \text{ \AA}$ .**

**This estimation procedure gives slightly smaller sizes to Zn than averaging distances in distorted HCP Zn. Nevertheless, they differ by  $\sim 2.5\%$ .**

(d) Use your answers to (a) and (b) as well as to (a) and (c) to estimate the lattice constant (in  $\text{\AA}$ ) of  $\beta$ -brass (CuZn).

**For a derivative of the BCC structure, atomic spheres touch along the body diagonal.**

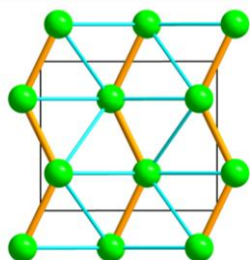
**The length of the body diagonal of  $\beta\text{-CuZn}$  is  $2R_8(\text{Cu}) + 2R_8(\text{Zn}) = \sqrt{3}a$ .**

**Using  $R_8(\text{Zn}) = 1.355 \text{ \AA}$ ,  $a \sim 2.999 \text{ \AA}$ ; using  $R_8(\text{Zn}) = 1.322 \text{ \AA}$ ,  $a \sim 2.961 \text{ \AA}$ .**

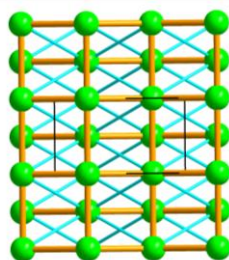
**The experimental value is 2.95  $\text{\AA}$ , which demonstrates that both methods provide decent estimates.**

(29)  $\alpha$ -U is orthorhombic, space group  $Cmcm$  with  $a = 2.854 \text{ \AA}$ ,  $b = 5.87 \text{ \AA}$ ,  $c = 4.955 \text{ \AA}$  and U atoms occupying the Wyckoff site  $(0, 0.1025, 1/4)$ .

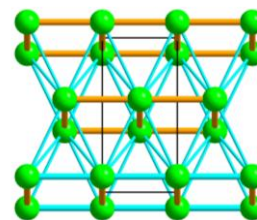
(a) Draw projections of the structure along the  $a$ -,  $b$ -, and  $c$ -directions. From these diagrams, identify the type of sphere packing the structure of  $\alpha$ -U most closely resembles.



Projection along  $a$   
 $c$ -axis is vertical



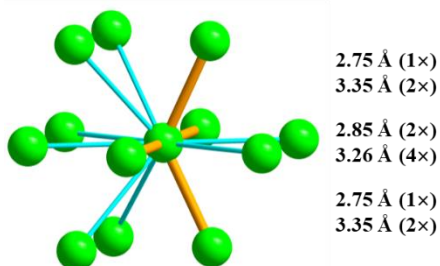
Projection along  $b$   
 $c$ -axis is horizontal



Projection along  $c$

**The projections along  $a$  and  $c$  show  $\dots AB\dots$  stacking of distorted close packed planes of U atoms. Therefore,  $\alpha$ -U is distorted HCP. The  $b/a$  ratio is 2.06, which is larger than the ideal value of 1.73; the  $c/a$  ratio is 1.74, which is also larger than the ideal value of 1.63.**

- (b) Determine the coordination environment for the U atom and evaluate the interatomic distances.



**In HCP, each atom is 12-coordinate with 6 atoms in the close packed plane, 3 atoms above and 3 atoms below this plane. For  $\alpha$ -U, the distortion creates 4 sets of distances – these were determined by the structure drawing program.**

- (c) Estimate the metallic radius of 12-coordinate U from this information.

**The average U–U distance is 3.14 Å, so  $R_{12}(\text{U}) \sim 1.57$  Å.**

- (d) Using your answer in (c), what is the packing efficiency?

**Unit cell volume =  $abc = 83.01$  Å<sup>3</sup>, which contains 4 atoms.**

**Volume of four U atom spheres =  $4(16.210 \text{ Å}^3) = 64.84 \text{ Å}^3$ .**

**Packing efficiency =  $(64.84 \text{ Å}^3) / (83.01 \text{ Å}^3) = 0.781$ . This value is slightly larger than the ideal value of 0.7405 for HCP and arises because an average sphere radius is used. As a result, the spheres must “overlap” in the unit cell.**

- (30) An ammonium halide,  $\text{NH}_4\text{X}$ , adopts the CsCl-type structure at room temperature,  $a = 4.059$  Å, and transforms to the NaCl-type structure at 138°C,  $a = 6.867$  Å. (From West)

- (a) The density of the room temperature polymorph is 2.431 g/cm<sup>3</sup>. Identify the substance.

**In the CsCl-type unit cell, there is one formula unit of  $\text{NH}_4\text{X}$ . Therefore,**

**Mass in unit cell (g) =  $(14.007 + 4(1.008) + \text{AW}(\text{X}))/6.022 \times 10^{23}$  (g)**

**Volume of unit cell (cm<sup>3</sup>) =  $(4.059 \text{ Å})^3 = 66.8740 \text{ Å}^3/10^{24} = 66.8740 \times 10^{-24}$  (cm<sup>3</sup>)**

**Density (g/cm<sup>3</sup>) = 2.431 = Mass in unit cell (g) / Volume of unit cell (cm<sup>3</sup>)**

**Therefore,  $\text{AW}(\text{X}) = 79.86$  g/mol, which corresponds to the halogen Br.**

**$\text{NH}_4\text{X} = \text{NH}_4\text{Br}$ .**

- (b) Calculate the percent difference in molar volume between the high-temperature NaCl-type and room-temperature CsCl-type polymorphs. Ignore any thermal expansion effects.

**We must compare the volumes of two structures for the same number of formula units. The volume of the room temperature CsCl-type structure corresponds to one formula unit of  $\text{NH}_4\text{Br}$ . The high temperature, NaCl-type structure contains 4 formula units in one unit cell. Therefore, the volume of one formula unit would be**

$$(6.867 \text{ Å})^3 / 4 = 80.955 \text{ Å}^3.$$

**The percent change from the room temperature form is**

$$[(80.955 \text{ Å}^3 - 66.874 \text{ Å}^3) / 66.874 \text{ Å}^3] \times 100\% = 21.1\%$$

**If the change is calculated with respect to the high temperature form, the percent change is 17.4 %.**

- (c) Assuming an effective radius of 1.50 Å for the ‘spherical’ ammonium cation and cations and anions are in contact, evaluate the radius of the anion in each polymorph. Are the anions in contact in the two structures using this model?

**Room temperature form: cation-anion contacts are along the body-diagonal of the cube, which is 7.0304 Å. The  $(\text{NH}_4)\text{–Br}$  distance would be 3.5152 Å. Therefore, the effective radius of the bromide**

ion in this structure is 2.02 Å. The bromide ions nearly touch in this structure, because the *a*-axis is 4.059 Å, which is very slightly larger than  $2 \times 2.02$  Å.

**High temperature form:** cation-anion contacts are along the unit cell edges, which are 6.867 Å. The (NH<sub>4</sub>)-Br distance is 3.434 Å. The effective radius of the bromide ion in this structure is 1.93 Å. In the NaCl-type structure, the bromide ions form CCP, so the nearest Br-Br distance is 4.856 Å. Therefore, the bromide ions with a radius of 1.93 Å will not touch in this polymorph.

Although these results seem somewhat counterintuitive, the high temperature structure will typically show a larger volume per formula unit. Such effects often occur most noticeably in second-nearest neighbor distances, which in these two cases, show a significant increase in distance, whereas the cation-anion distance actually decreases as the structure changes from 8-coordinate CsCl-type to 6-coordinate NaCl-type.

- (31) In crednerite CuMnO<sub>2</sub>, the Cu-O distance is 1.835 Å (2×) and the Mn-O distances are 1.928 Å (4×) and 2.260 Å (2×). Use the bond-valence method to determine the formulation of this compound.

Information:  $B = 0.37$  Å       $d_0(\text{Cu}^{\text{I}}-\text{O}) = 1.61$  Å       $d_0(\text{Mn}^{\text{II}}-\text{O}) = 1.790$  Å  
 $d_0(\text{Cu}^{\text{II}}-\text{O}) = 1.679$  Å       $d_0(\text{Mn}^{\text{III}}-\text{O}) = 1.760$  Å

Compare Cu<sup>I</sup>Mn<sup>III</sup>O<sub>2</sub> and Cu<sup>II</sup>Mn<sup>II</sup>O<sub>2</sub>:

$$\begin{aligned} v(\text{Cu}^{\text{I}}) &= 2 \exp(- (1.835 - 1.61) / 0.37) \\ &= 2(0.544) = 1.088 \\ v(\text{Mn}^{\text{III}}) &= 4 \exp(- (1.928 - 1.760) / 0.37) + 2 \exp(- (2.260 - 1.760) / 0.37) \\ &= 4(0.635) + 2(0.259) = 3.058 \\ v(\text{O}) &= (0.544) + 2(0.635) + (0.259) = 2.073 \\ v(\text{Cu}^{\text{II}}) &= 2 \exp(- (1.835 - 1.679) / 0.37) \\ &= 2(0.656) = 1.312 \\ v(\text{Mn}^{\text{II}}) &= 4 \exp(- (1.928 - 1.790) / 0.37) + 2 \exp(- (2.260 - 1.790) / 0.37) \\ &= 4(0.689) + 2(0.281) = 3.318 \\ v(\text{O}) &= (0.656) + 2(0.689) + (0.281) = 2.315 \end{aligned}$$

The better formulation is Cu<sup>I</sup>Mn<sup>III</sup>O<sub>2</sub>, which has  $d^{10}$  Cu<sup>I</sup> and  $d^4$  Mn<sup>III</sup>. The 6-coordinate Mn<sup>III</sup> sites are distorted driven by a Jahn-Teller instability. CuMnO<sub>2</sub> adopts a distorted (monoclinic) delafossite-type structure with linearly coordinated Cu<sup>I</sup> between [Mn<sup>III</sup>O<sub>6/3</sub>] layers.

- (32) Two different forms of CuVO<sub>3</sub> have been prepared at high pressure. In rhombohedral CuVO<sub>3</sub>, the Cu-O distances are 2.039 Å (3×) and 2.241 Å (3×) and the V-O distances are 1.788 Å (3×) and 2.073 Å (3×). In triclinic CuVO<sub>3</sub>, the different bond distances are:

$$\begin{aligned} \text{Cu-O: } & 1.984 \text{ Å, } 2.009 \text{ Å, } 2.103 \text{ Å, } 2.148 \text{ Å, } 2.161 \text{ Å, } 2.372 \text{ Å;} \\ \text{V-O: } & 1.776 \text{ Å, } 1.789 \text{ Å, } 1.814 \text{ Å, } 2.071 \text{ Å, } 2.079 \text{ Å, } 2.079 \text{ Å.} \end{aligned}$$

Use the bond-valence method to determine the formulations of each compound.

Information:  $B = 0.37$  Å       $d_0(\text{Cu}^{\text{I}}-\text{O}) = 1.61$  Å       $d_0(\text{V}^{\text{IV}}-\text{O}) = 1.784$  Å  
 $d_0(\text{Cu}^{\text{II}}-\text{O}) = 1.679$  Å       $d_0(\text{V}^{\text{V}}-\text{O}) = 1.803$  Å

Compare Cu<sup>I</sup>V<sup>V</sup>O<sub>3</sub> and Cu<sup>II</sup>V<sup>IV</sup>O<sub>3</sub> for each case.

**Rhombohedral:**

$$\begin{aligned} v(\text{Cu}^{\text{I}}) &= 3(0.314) + 3(0.182) = 1.488 \\ v(\text{V}^{\text{V}}) &= 3(1.041) + 3(0.482) = 4.569 \\ v(\text{O}) &= (0.314) + (0.182) + (1.041) + (0.482) = 2.019 \\ v(\text{Cu}^{\text{II}}) &= 3(0.378) + 3(0.219) = 1.791 \\ v(\text{V}^{\text{IV}}) &= 3(0.989) + 3(0.458) = 4.341 \\ v(\text{O}) &= (0.378) + (0.219) + (0.989) + (0.458) = 2.044 \end{aligned}$$

**Triclinic:**

$$v(\text{Cu}^{\text{I}}) = (0.364) + (0.340) + (0.264) + (0.234) + (0.226) + (0.128) = 1.556$$

$$v(\text{V}^{\text{V}}) = (1.076) + (1.039) + (0.971) + (0.485) + (0.474) + (0.474) = 4.519$$

$$v(\text{Cu}^{\text{II}}) = (0.438) + (0.410) + (0.318) + (0.282) + (0.267) + (0.154) = 1.869$$

$$v(\text{V}^{\text{IV}}) = (1.022) + (0.987) + (0.922) + (0.460) + (0.451) + (0.451) = 4.293$$

For both cases, the better formulation is  $\text{Cu}^{\text{II}}\text{V}^{\text{IV}}\text{O}_3$ , which has  $d^9$   $\text{Cu}^{\text{II}}$  and  $d^1$   $\text{V}^{\text{IV}}$ . The bond-valence values give atomic valence values that are somewhat different than the formal oxidation states in both models, which may suggest some degree of metal-metal bonding in these structures. Rhombohedral  $\text{CuVO}_3$  adopts an ilmenite-type structure, which involves HCP oxide and an ordering of Cu and V atoms each in 1/3 octahedral holes.

See J.R. Rea, E. Kostiner, *J. Solid State Chem.* 1973, 7, pp. 163-168. This paper proposes the formulation  $\text{Cu}^{\text{I}}\text{V}^{\text{V}}\text{O}_3$  for rhombohedral  $\text{CuVO}_3$  based on magnetic data and interatomic distances. Since  $\text{Cu}^{\text{I}}$  and  $\text{V}^{\text{V}}$  are both closed shell cations, diamagnetism or Van Vleck paramagnetism would be expected for this formulation.

See J.R. Rea, P.W. Bless, E. Kostiner, *J. Solid State Chem.* 1972, 5, pp. 446-451. This paper proposes the formulation  $\text{Cu}^{\text{II}}\text{V}^{\text{IV}}\text{O}_3$  for triclinic  $\text{CuVO}_3$  based on interatomic distances. An anomalous paramagnetic moment suggests metal-metal interactions.

- (33) A crystal structure determination of  $\text{MnO}(\text{OH})$  could not conclusively determine the H-atom positions. The asymmetric unit contains one Mn atom site and two different O atom sites. The O1–Mn distances are 1.977 Å, 1.982 Å, and 2.337 Å; the O2–Mn distances are 1.881 Å, 1.893 Å, and 2.213 Å. Use the bond-valence method to identify which O atom site is hydroxide.

Information:  $B = 0.37 \text{ \AA}$        $d_0(\text{Mn}^{\text{III}}-\text{O}) = 1.760 \text{ \AA}$ .

$$v(\text{O1}) = (0.556) + (0.549) + (0.210) = 1.315$$

$$v(\text{O2}) = (0.721) + (0.698) + (0.294) = 1.713$$

Since  $v(\text{O1})$  is much smaller than  $v(\text{O2})$ , the O1 site is likely the hydroxide.

**Structural Chemistry**

(34) The structure of  $\alpha\text{-Al}_2\text{O}_3$  consists of HCP oxide ions with Al ions in octahedral voids. There are 6 close packed layers of oxide ions in the unit cell. At room temperature, the unit cell is trigonal, Pearson symbol  $tR30$ :  $a = 4.764 \text{ \AA}$ ,  $c = 13.009 \text{ \AA}$ ,  $\gamma = 120^\circ$ .

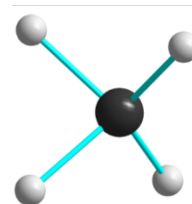
(a) What is the fraction of octahedral holes occupied by Al ions in  $\alpha\text{-Al}_2\text{O}_3$ ?

$\text{Al}_2\text{O}_3 = \text{Al}_{2/3}\text{O}$ . For HCP, # octahedral holes = # HCP atoms. Therefore, 2/3 of the octahedral holes are occupied by Al.

(b) In the asymmetric unit, all oxide ions are equivalent, and every layer of octahedral holes is equally filled. What is the local coordination of oxide ions by Al ions?

$\langle \text{CN} \rangle_{\text{Al}} = 6$ :  $(2)(6) = (3) \cdot \langle \text{CN} \rangle_{\text{O}}$  so that  $\langle \text{CN} \rangle_{\text{O}} = 4$  (4-coordinate).

In HCP O atoms, which we can designate as  $\cdots BC \cdots$  stacking of close-packed planes, the octahedral holes project onto the A sites. When all octahedral holes are occupied, each close packed atom would be surrounded by a trigonal prism (see discussion of the NiAs-type structure). The 4-coordinate environment arises by removing two vertices from the trigonal prism leading to a severely distorted tetrahedron. According to Wells, the tetrahedron and the octahedron are incompatible in this structure.



(c) What is the density (in  $\text{g/cm}^3$ ) of  $\alpha\text{-Al}_2\text{O}_3$  at room temperature?

There are 6 “ $\text{Al}_2\text{O}_3$ ” formula units per unit cell:

Mass in unit cell =  $6[2(26.981) + 3(15.999)] = 6[101.959] = 611.754 / 6.022 \times 10^{23} = 1.016 \times 10^{-21} \text{ g}$

Unit cell volume =  $(4.764 \text{ \AA})^2(13.009 \text{ \AA}) \cdot \sin 120^\circ = 255.693 \text{ \AA}^3 = 255.693 \times 10^{-24} \text{ cm}^3$

Density =  $1.016 \times 10^{-21} \text{ g} / 255.693 \times 10^{-24} \text{ cm}^3 = 3.973 \text{ g/cm}^3$ .

Another polymorph of alumina,  $\gamma\text{-Al}_2\text{O}_3$ , is described as a “defect spinel”. Spinel has the general formula  $AB_2O_4$  with A atoms in tetrahedral holes and B atoms in octahedral holes. The unit cell is cubic with 32 close packed oxide ions in one unit cell and a unit cell parameter of  $a = 7.9382(1) \text{ \AA}$ .

(d) What is the density (in  $\text{g/cm}^3$ ) of  $\gamma\text{-Al}_2\text{O}_3$  at room temperature?

The number of “ $\text{Al}_2\text{O}_3$ ” formula units per unit cell is 10.667 because  $32/3 = 10.667$ .

Mass in unit cell =  $10.667 (101.959) / 6.022 \times 10^{23} = 1.806 \times 10^{-21} \text{ g}$

Unit cell volume =  $(7.9382 \text{ \AA})^3 = 500.226 \text{ \AA}^3 = 500.226 \times 10^{-24} \text{ cm}^3$

Density =  $1.806 \times 10^{-21} \text{ g} / 500.226 \times 10^{-24} \text{ cm}^3 = 3.610 \text{ g/cm}^3$ .

(e) An X-ray diffraction study gives the Al ion distribution as completely random among tetrahedral and octahedral holes. How many octahedral and tetrahedral voids, on average, are occupied by Al ions in one unit cell of  $\gamma\text{-Al}_2\text{O}_3$ ? What is the average coordination number of oxide ions by Al ions?

The spinel-type structure is CCP oxide with 1/2 octahedral holes and 1/8 tetrahedral holes occupied, which gives the formula  $M^{(\text{tet})}M^{(\text{oct})}_2\text{O}_4$  or “ $M_3\text{O}_4$ ”. Using the spinel-type formulation,  $\gamma\text{-Al}_2\text{O}_3$  becomes  $\text{Al}_{8/3}\text{O}_4$  because we need to multiply each subscript of  $\text{Al}_2\text{O}_3$  by “4/3”. To emphasize the vacancies at the metal sites, the formula is  $(\text{Al}_{8/3}\square_{1/3})\text{O}_4$  or  $(\text{Al}_{8/9}\square_{1/9})_3\text{O}_4$ . Therefore, for randomly distributed vacancies, every metal site in the spinel-type structure is occupied by Al with a probability of 88.9% (8/9). With respect to tetrahedral and octahedral holes, we can rewrite the formula as  $(\text{Al}_{8/9}\square_{1/9})^{(\text{tet})}(\text{Al}_{8/9}\square_{1/9})^{(\text{oct})}_2\text{O}_4$ .

In one unit cell, which contains 32 O atoms, there are 64 tetrahedral holes and 32 octahedral holes. Therefore, in one unit cell:

# occupied tetrahedral voids =  $(8/9) \times (64/8) = 7.11$ ;

# occupied octahedral voids =  $(8/9) \times (32/2) = 14.22$ .

Therefore, one unit cell is formulated as  $(\text{Al}^{(\text{tet})})_{7.11}(\text{Al}^{(\text{oct})})_{14.22}\text{O}_{32}$  or, using the spinel formulation,  $(\text{Al}^{(\text{tet})})_{0.89}(\text{Al}^{(\text{oct})})_{1.77}\text{O}_4$ . Then, the average CN of oxide ions by Al,  $\langle \text{CN} \rangle_{\text{O}}$ , is

$$4(0.89) + 6(1.77) = 4\langle \text{CN} \rangle_{\text{O}}, \text{ so that } \langle \text{CN} \rangle_{\text{O}} = 3.56.$$

Thus, ca. 55% of the O atoms are 4-coordinate and ca. 45% are 3-coordinate to Al.

- (f) A theoretical study gives the tetrahedral holes fully occupied by Al ions and some vacancies on the octahedral holes. Again, how many octahedral and tetrahedral voids, on average, are occupied by Al ions in one unit cell of  $\gamma\text{-Al}_2\text{O}_3$ ? What is the average coordination number of oxide ions by Al ions?

Using the spinel-type formulation  $\text{M}^{(\text{tet})}\text{M}^{(\text{oct})}_2\text{O}_4$  for " $\text{Al}_2\text{O}_3$ ", the sum of Al ions in tetrahedral and octahedral holes must be 2.67. If all tetrahedral holes in the spinel-type structure are occupied, then the number of Al ions remaining, per formula unit, must be 1.67. The formulation becomes  $(\text{Al}_1\Box_0)^{(\text{tet})}(\text{Al}_{5/6}\Box_{1/6})^{(\text{oct})}_2\text{O}_4$ , or in one unit cell:

$$\# \text{ occupied tetrahedral voids} = (1) \times (64/8) = 8;$$

$$\# \text{ occupied octahedral voids} = (5/6) \times (32/2) = 13.33.$$

Using the spinel-type formulation,  $(\text{Al}^{(\text{tet})})_1(\text{Al}^{(\text{oct})})_{1.67}\text{O}_4$ . Then, the average CN of oxide ions by Al,  $\langle \text{CN} \rangle_{\text{O}}$ , is

$$4(1) + 6(1.67) = 4\langle \text{CN} \rangle_{\text{O}}, \text{ so that } \langle \text{CN} \rangle_{\text{O}} = 3.5.$$

Thus, 50% of the O atoms are 4-coordinate and 50% are 3-coordinate to Al as a result of cation ordering in the spinel-type structure.

On the other hand, the structure of  $\alpha\text{-Al}_2\text{S}_3$  consists of HCP sulfide ions with Al ions in tetrahedral voids. Like  $\alpha\text{-Al}_2\text{O}_3$ , there are 6 close packed layers of sulfide ions in the unit cell. At room temperature, the unit cell is hexagonal, Pearson symbol  $hP30$ :  $a = 6.438 \text{ \AA}$ ,  $c = 17.898 \text{ \AA}$ ,  $\gamma = 120^\circ$ .

- (g) What is the fraction of tetrahedral holes occupied by Al ions in the HCP array of sulfide ions?  
 $\text{Al}_2\text{S}_3 = \text{Al}_{2/3}\text{S}$ . For HCP, # tetrahedral holes =  $2 \times \# \text{ HCP atoms}$ . Therefore, 1/3 of the tetrahedral holes are occupied by Al.
- (h) There are three inequivalent sets of sulfide ions in this structure. What is the coordination number and local coordination geometry of each sulfide ion by Al ions?  
 Since each Al atom is tetrahedrally 4-coordinate, each S atom is, on average, 8/3- or 2.67-coordinate. This means that 2/3 S atoms are 3-coordinate and 1/3 S atoms are 2-coordinate. The likely local environments at these S atoms are trigonal pyramidal (3-coordinate) and bent (2-coordinate).
- (i) What is the density (in  $\text{g/cm}^3$ ) of  $\alpha\text{-Al}_2\text{S}_3$  at room temperature?

There are 6 " $\text{Al}_2\text{S}_3$ " formula units per unit cell:

$$\text{Mass in unit cell} = 6[2(26.981) + 3(32.06)] = 6[150.142] = 900.852 / 6.022 \times 10^{23} = 1.496 \times 10^{-21} \text{ g}$$

$$\text{Unit cell volume} = (6.438 \text{ \AA})^2(17.898 \text{ \AA}) \cdot \sin 120^\circ = 642.447 \text{ \AA}^3 = 642.447 \times 10^{-24} \text{ cm}^3$$

$$\text{Density} = 1.496 \times 10^{-21} \text{ g} / 642.447 \times 10^{-24} \text{ cm}^3 = 2.329 \text{ g/cm}^3.$$

$\text{MgSiO}_3$  can be prepared under high pressure in the ilmenite-type structure, which is a ternary variant of  $\alpha\text{-Al}_2\text{O}_3$ . This crystal structure is metastable at ambient conditions and adopts a trigonal unit cell, Pearson symbol  $tR30$ :  $a = 4.728 \text{ \AA}$ ,  $c = 13.559 \text{ \AA}$ ,  $\gamma = 120^\circ$ .

- (j) What is the density (in  $\text{g/cm}^3$ ) of ilmenite-type  $\text{MgSiO}_3$  at room temperature and pressure?

There are 6 " $\text{MgSiO}_3$ " formula units per unit cell:

$$\text{Mass in unit cell} = 6[(24.305) + (28.085) + 3(15.999)]$$

$$= 6[100.387] = 602.322 / 6.022 \times 10^{23} = 1.001 \times 10^{-21} \text{ g}$$

$$\text{Unit cell volume} = (4.728 \text{ \AA})^2(13.559 \text{ \AA}) \cdot \sin 120^\circ = 262.490 \text{ \AA}^3 = 262.490 \times 10^{-24} \text{ cm}^3$$

$$\text{Density} = 1.001 \times 10^{-21} \text{ g} / 262.490 \times 10^{-24} \text{ cm}^3 = 3.810 \text{ g/cm}^3.$$

The preferred structure of  $\text{MgSiO}_3$  under ambient conditions involves a close packing of O atoms with Mg atoms in octahedral holes and Si atoms in tetrahedral holes. The unit cell is orthorhombic containing 8 nearly close packed layers of oxygen atoms and 16 formula units.

(k) How many octahedral and tetrahedral holes are occupied in one unit cell?

**16 formula units means there are 48 O atoms, 16 Mg atoms and 16 Si atoms per unit cell. Therefore, one unit cell contains 96 tetrahedral holes and 48 octahedral holes.**

$$\# \text{ occupied octahedral voids by Mg atoms} = (1/3) \times (48) = 16$$

$$\# \text{ occupied tetrahedral voids by Si atoms} = (1/6) \times (96) = 16$$

(l) What is the average coordination number at the O atoms by Mg and Si atoms?

**$4(1) + 6(1) = 3 \cdot \langle \text{CN} \rangle_{\text{O}}$ , so that  $\langle \text{CN} \rangle_{\text{O}} = 3.33$ . Thus, the most likely scenario is that 2/3 O atoms are 3-coordinate and 1/3 O atoms are 4-coordinate.**

(m) One diffraction study reports the unit cell volume to be  $834.76 \text{ \AA}^3$ . What is the density (in  $\text{g/cm}^3$ ) of this crystal and how does it compare to the density of the ilmenite-type structure? Provide a rationale for the difference.

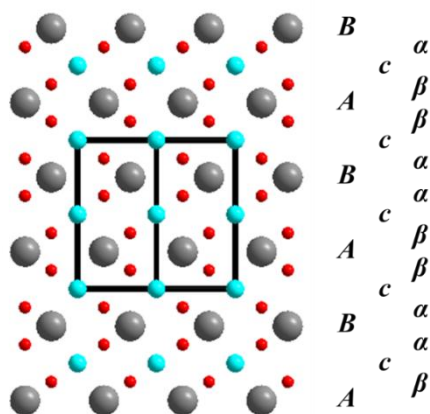
$$\text{Mass in unit cell} = 16[100.387] = 1606.192 / 6.022 \times 10^{23} = 2.667 \times 10^{-21} \text{ g}$$

$$\text{Unit cell volume} = 834.76 \text{ \AA}^3 = 834.76 \times 10^{-24} \text{ cm}^3$$

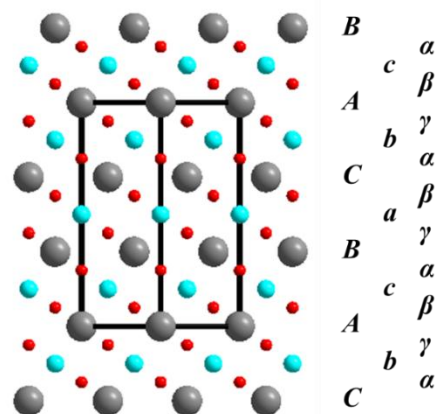
$$\text{Density} = 2.667 \times 10^{-21} \text{ g} / 834.76 \times 10^{-24} \text{ cm}^3 = 3.195 \text{ g/cm}^3.$$

**The density of  $\text{MgSiO}_3$  at high pressure is ca. 19% higher than that at ambient pressure, which suggests a significantly smaller volume/formula unit as pressure increases.**

(35) Important classes of metal(III) oxides  $\text{M}_2\text{O}_3$  involve eutactic arrays of M(III) atoms with O atoms in octahedral and/or tetrahedral holes. The two limiting eutactic arrays of M(III) atoms are HCP and CCP, and the sequence of octahedral (lower case) and tetrahedral (Greek lower case) holes for each of these arrays are shown as (110) projections below with the corresponding  $\dots ABC \dots$  notation:



**HCP:  $\dots A \beta c \alpha B \alpha c \beta \dots$**



**CCP:  $\dots A \beta c \alpha B \gamma a \beta C a b \gamma \dots$**

Consider the following three scenarios leading to  $\text{M}_2\text{O}_3$  structures:

- Uniform occupation of tetrahedral holes with 100% octahedral holes occupied by O atoms;
- Uniform occupation of tetrahedral holes with 50% octahedral holes occupied by O atoms; and
- Uniform occupation of tetrahedral holes with 0% octahedral holes occupied by O atoms.

(a) Determine the average coordination numbers in each scenario.

**For the formula  $\text{M}_2\text{O}_3$ , there are 2 octahedral and 4 tetrahedral holes in the eutactic array for every 2 M(III) atoms. Therefore,**

If 100% octahedral holes are occupied by O atoms, then 2 (of 3) O atoms are in octahedra and 1 (of 3) O atoms are in tetrahedral holes. The average coordination number of M(III) by O is:

$$6(2) + 4(1) = 2 \cdot \langle \text{CN} \rangle_{\text{M}}, \text{ or } \langle \text{CN} \rangle_{\text{M}} = 16/2 = 8.$$

If 50% octahedral holes are occupied by O atoms, then 1 (of 3) O atoms are in octahedra and 2 (of 3) O atoms are in tetrahedral holes. The average coordination number of M(III) by O is:

$$6(1) + 4(2) = 2 \cdot \langle \text{CN} \rangle_{\text{M}}, \text{ or } \langle \text{CN} \rangle_{\text{M}} = 14/2 = 7.$$

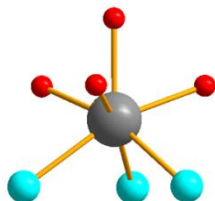
If 0% octahedral holes are occupied by O atoms, then 0 (of 3) O atoms are in octahedra and 3 (of 3) O atoms are in tetrahedral holes. The average coordination number of M(III) by O is:

$$6(0) + 4(3) = 2 \cdot \langle \text{CN} \rangle_{\text{M}}, \text{ or } \langle \text{CN} \rangle_{\text{M}} = 12/2 = 6.$$

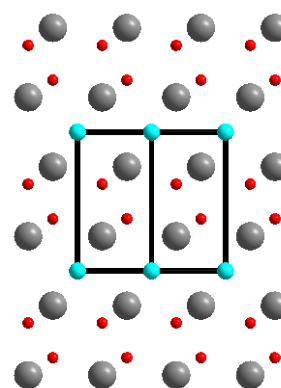
An important structure-building principle for filling octahedral and tetrahedral holes in eutactic arrays is that the atoms filling these holes avoid occupying adjacent sites that share faces. Using this principle,

- (b) For each of the HCP and CCP eutactic arrays of M(III) atoms, which of the three scenarios above is preferred? Explain your choice.

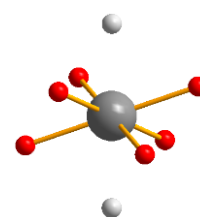
**HCP:** If 100% octahedral holes are occupied, then [OM<sub>6</sub>] share faces along the *c*-direction. If 0% octahedral holes are occupied, then 75% of all tetrahedral holes are occupied so that some [OM<sub>4</sub>] tetrahedra share faces along the *c*-direction. As a result, the only viable option is for 50% octahedral holes to be occupied, so that 50% of all tetrahedral holes are also occupied. If each layer of octahedral holes is 50% occupied, then occupied tetrahedral holes must necessarily share a common face with these octahedra. On the other hand, if alternate layers of octahedral holes are fully occupied, then



a viable solution, shown here, can be achieved. In this structure, bilayers of M(III) atoms alternate occupation of all octahedral and all tetrahedral holes. Each M(III) atom is 7-coordinate by a mono-capped, distorted octahedron (trigonal antiprism). This type of structure is observed for La<sub>2</sub>O<sub>3</sub>.



**CCP:** If any octahedral holes are occupied, then [OM<sub>6</sub>] share faces with [OM<sub>4</sub>] tetrahedra. As a result, the only viable option is for 0% octahedral holes to be occupied, so that 75% of all tetrahedral holes are occupied. In CCP M(III) atoms, each M(III) atom is surrounded by a cube of 8 tetrahedral voids, 6 of which will be occupied by O atoms. To minimize the electrostatic repulsions between oxides, the optimal filling pattern is for 2 opposite tetrahedra to be vacant, leading to a distorted octahedral (trigonal antiprismatic) coordination environment, shown here.



- (36) An important class of complex oxides is based on a quaternary compound in the Mg-Al-Si-O system that contains 24 separated [SiO<sub>4</sub>]<sup>4-</sup> molecular ions in a cubic unit cell with *a* = 11.459 Å. The structure has four inequivalent sites in the asymmetric unit, one site for each element, and every O atom is 4-coordinate. The three cationic species show different coordination numbers. From this information,
- Determine the empirical formula of the compound.
  - Determine the coordination numbers of Mg and Al atoms by oxide ions.
  - Determine the density (in g/cm<sup>3</sup>) of the compound.

The general formula is Mg<sub>*u*</sub>Al<sub>*v*</sub>Si<sub>24</sub>O<sub>96</sub>.

To obey electroneutrality:  $2u + 3v + 4(24) = 2(96)$ , or  $2u + 3v = 96$

To obey connectivity:  $mu + nv + 4(24) = 4(96)$ , or  $mu + nv = 288$ .

In this equation,  $m$  = coordination number of Mg by O and  $n$  = coordination number of Al by O. Si is 4-coordinate by O.

Let's solve this problem empirically rather than analytically. Since Al is larger than Si and Mg is larger than Al, we can assume that Al will be 6-coordinate octahedral in this silicate. Then, we obtain the following equation for Mg:  $(m-4)u = 96$ .

If  $m = 7$ , then  $u = 32$  and  $v = 10.67$ , which is not acceptable.

If  $m = 8$ , then  $u = 24$  and  $v = 16$ , which is acceptable.

Then, the formula is  $Mg_{24}Al_{16}Si_{24}O_{96}$ , which gives the empirical formula  $Mg_3Al_2Si_3O_{12}$ . Si is 4-coordinate; Al is 6-coordinate; and Mg is 8-coordinate. FW = 403.122 g/mol and there are 8 formula units in one unit cell.

Mass in unit cell (g) =  $8(403.122 \text{ g/mol})/6.022 \times 10^{23} = 5.355 \times 10^{-21} \text{ g}$

Volume of unit cell ( $\text{\AA}^3$ ) =  $(11.459 \text{ \AA})^3 = 1504.666 \text{ \AA}^3$

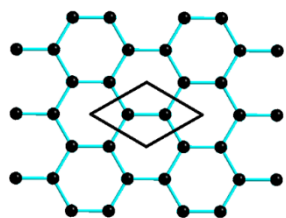
Volume of unit cell ( $\text{cm}^3$ ) =  $(1504.666 \text{ \AA}^3)(1 \text{ cm} / 10^8 \text{ \AA})^3 = 1504.666 \times 10^{-24} \text{ cm}^3$

Density ( $\text{g/cm}^3$ ) =  $5.355 \times 10^{-21} \text{ g} / 1.505 \times 10^{-21} \text{ cm}^3 = 3.559 \text{ g/cm}^3$ .

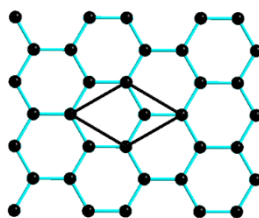
(37) Describe the different polymorphs that can occur for honeycomb ( $6^3$ ) planar nets when four such layers are needed to create a periodic structure. Treat the two cases:

(a) every atom is the same (as in graphite), or

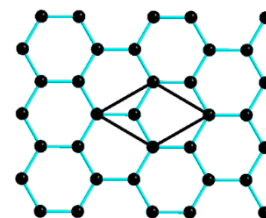
The 2-d honeycomb network in which every atom is the same has sixfold rotational symmetry and can be derived from the close-packed plane by ordered vacancies in three different ways:



A-site



B-site



C-site

We can symbolize various stacking variants by using the vacant site designator:

... AAA ... : eclipsed stacking of the planes; in every AAA (underlined) plane, each atom has 3 nearest neighbors in the plane and 2 next nearest neighbors between planes = 3+2-coordinate

... AAAB ... : in AAA planes, each atom is 3+2-coordinate  
 in AAB planes, one atom is 3+2-coordinate, one atom is 3+1-coordinate  
 in ABA planes, one atom is 3+2-coordinate, one atom is 3-coordinate

... AABB ... : in AAB and ABB planes, one atom is 3+2-coordinate, one atom is 3+1-coordinate

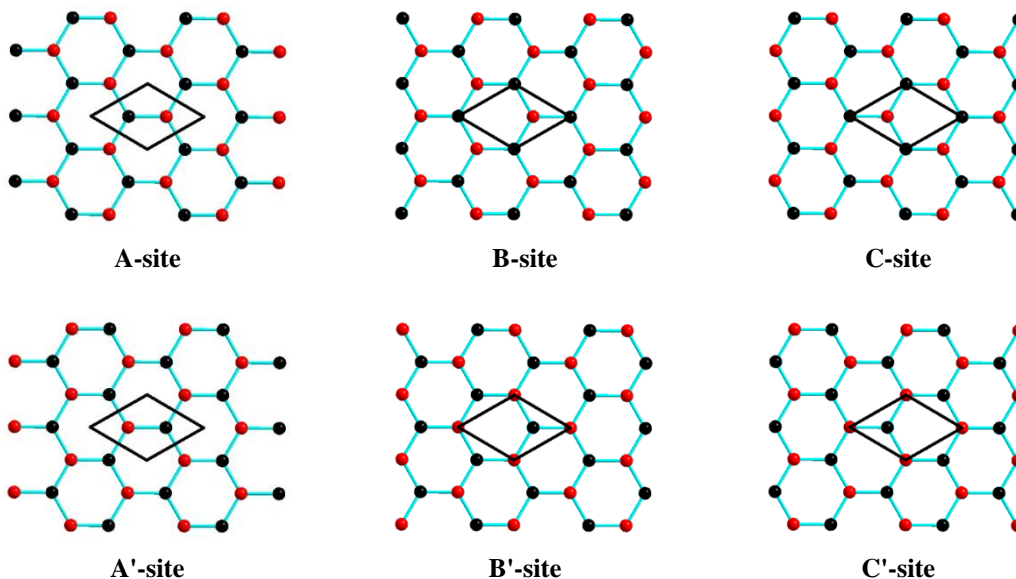
... AABC ... : in AAB and CAA planes, one atom is 3+2-coordinate, one atom is 3+1-coordinate  
 in ABC and BCA planes, each atom is 3+1-coordinate

... ABAB ... : in ABA and BAB planes, one atom is 3+2-coordinate, one atom is 3-coordinate

... ABAC ... : in ABA and ACA planes, one atom is 3+2-coordinate, one atom is 3-coordinate  
 in BAC planes, each atom is 3+1-coordinate

(b) there are two different atoms, which alternate in the honeycomb net, e.g., BN. In addition, there will only be heteroatomic contacts along the stacking direction.

The 2-d alternating honeycomb network has threefold rotational symmetry and there are two different possibilities for each honeycomb net above:



We can symbolize various stacking variants by using the vacant site designator:

- ... AA'AA' ... : in every plane, each atom is 3+2-coordinate
- ... AA'AB' ... : in AA'A planes, every atom is 3+2-coordinate  
in A'AB' planes, one atom is 3+2-coordinate, one atom is 3+1-coordinate  
in AB'A planes, one atom is 3+2-coordinate, one atom is 3-coordinate
- ... AA'BB' ... : in every plane, one atom is 3+2-coordinate, one atom is 3+1-coordinate
- ... AA'BC' ... : in AA'B and C'AA' planes, one atom is 3+2-coordinate, one atom is 3+1-coordinate  
in A'BC' and BC'A planes, every atom is 3+1-coordinate
- ... AB'AB' ... : in every plane, one atom is 3+2-coordinate, one atom is 3-coordinate
- ... AB'AC' ... : in AB'A and AC'A planes, one atom is 3+2-coordinate, one atom is 3-coordinate  
in B'AC' planes, every atom is 3+1-coordinate

(38)  $\text{CrVO}_4$  is a complex oxide that crystallizes in an orthorhombic structure. The oxide ions form a distorted CCP array with one metal occupying octahedral and the other metal occupying tetrahedral holes. The metal–oxygen distances are:  $M(\text{tet})\text{--O} = 1.6334 \text{ \AA} (2\times)$  and  $1.7098 \text{ \AA} (2\times)$ ;  $M(\text{oct})\text{--O} = 1.9842 \text{ \AA} (2\times)$  and  $2.0487 \text{ \AA} (4\times)$ .

(a) What fractions of octahedral and tetrahedral holes are occupied in the CCP oxide array?

**For the formula  $\text{CrVO}_4$ , there are 4 octahedral and 8 tetrahedral holes in the eutactic array for every 4 O atoms. Therefore, 1/4 of all octahedral holes and 1/8 of all tetrahedral holes are occupied by metal atoms.**

(b) What are likely coordination geometries at the oxide ions?

**According to the connectivity,  $6(1) + 4(1) = 4 \cdot \langle \text{CN} \rangle_{\text{O}}$ , or  $\langle \text{CN} \rangle_{\text{O}} = 10/4 = 2.5$ . Therefore, there must be more than one kind of O atom in the structure. Most likely, one set of O atoms will be 3-coordinate in a trigonal pyramidal environment, and a second set of O atoms will be 2-coordinate in a bent configuration.**

(c) Common oxidation states for vanadium include +2, +3, +4, and +5; common oxidation states for chromium include +2, +3, +4, +6. Using this information, write down the possible formulations of  $\text{CrVO}_4$ . By considering the brief structural description, identify the likelihood of each formulation. Explain your assignments.

**The oxidation states of the metal atoms must sum to 8, which allows three possible formulations:**

**Cr<sup>III</sup>V<sup>V</sup>O<sub>4</sub>:** Cr<sup>III</sup> is  $d^3$  and V<sup>V</sup> is  $d^0$ ; the  $d^3$  configuration prefers octahedral coordination with half-filled  $t_{2g}$  orbitals; the  $d^0$  configuration could be tetrahedral or octahedral. This formulation is possible with Cr in octahedral holes and V in tetrahedral holes.

**Cr<sup>IV</sup>V<sup>IV</sup>O<sub>4</sub>:** Cr<sup>IV</sup> is  $d^2$  and V<sup>IV</sup> is  $d^1$ ; neither the  $d^1$  nor  $d^2$  configurations has strong preference for tetrahedral coordination. This formulation is not very likely for this compound.

**Cr<sup>VI</sup>V<sup>II</sup>O<sub>4</sub>:** Cr<sup>VI</sup> is  $d^0$  and V<sup>II</sup> is  $d^3$ ; the  $d^3$  configuration prefers octahedral coordination with half-filled  $t_{2g}$  orbitals; the  $d^0$  configuration could be tetrahedral or octahedral. This formulation is possible with Cr in tetrahedral holes and V in octahedral holes.

The two most probable formulations, therefore, are Cr<sup>III</sup>V<sup>V</sup>O<sub>4</sub> and Cr<sup>VI</sup>V<sup>II</sup>O<sub>4</sub>. Although it is challenging, a priori, to evaluate one formulation over the other,  $d^3$  Cr<sup>III</sup> is more commonly observed in oxides than V<sup>II</sup>. Furthermore, the higher oxidation state is generally preferred for the more electropositive metal, which would be V vs. Cr. As a result, the most likely formulation is Cr<sup>III</sup>V<sup>V</sup>O<sub>4</sub>.

(d) Use the Bond-Valence Method to assess which formulation is the best choice for CrVO<sub>4</sub>.

Information:  $B = 0.37 \text{ \AA}$

$d_0(\text{V}^{\text{II}}-\text{O}) = 1.70 \text{ \AA}$	$d_0(\text{Cr}^{\text{II}}-\text{O}) = 1.73 \text{ \AA}$
$d_0(\text{V}^{\text{III}}-\text{O}) = 1.743 \text{ \AA}$	$d_0(\text{Cr}^{\text{III}}-\text{O}) = 1.724 \text{ \AA}$
$d_0(\text{V}^{\text{IV}}-\text{O}) = 1.784 \text{ \AA}$	$d_0(\text{Cr}^{\text{IV}}-\text{O}) = 1.81 \text{ \AA}$
$d_0(\text{V}^{\text{V}}-\text{O}) = 1.803 \text{ \AA}$	$d_0(\text{Cr}^{\text{VI}}-\text{O}) = 1.794 \text{ \AA}$

<b>Cr<sup>III</sup>V<sup>V</sup>O<sub>4</sub>:</b>	Cr <sup>III</sup> -O tetrahedral:	$2(1.003) + 2(0.803) = 3.612$	$\Delta = +0.612$
	V <sup>V</sup> -O octahedral:	$2(0.660) + 4(0.528) = 2.774$	$\Delta = -2.226$
	V <sup>V</sup> -O tetrahedral:	$2(1.241) + 2(0.995) = 4.472$	$\Delta = -0.528$
	Cr <sup>III</sup> -O octahedral:	$2(0.533) + 4(0.427) = 2.774$	$\Delta = -0.226$
<b>Cr<sup>IV</sup>V<sup>IV</sup>O<sub>4</sub>:</b>	Cr <sup>IV</sup> -O tetrahedral:	$2(1.265) + 2(1.014) = 4.558$	$\Delta = +0.558$
	V <sup>IV</sup> -O octahedral:	$2(0.627) + 4(0.502) = 3.262$	$\Delta = -0.738$
	V <sup>IV</sup> -O tetrahedral:	$2(1.179) + 2(0.945) = 4.248$	$\Delta = -0.248$
	Cr <sup>IV</sup> -O octahedral:	$2(0.672) + 4(0.539) = 3.500$	$\Delta = -0.500$
<b>Cr<sup>VI</sup>V<sup>II</sup>O<sub>4</sub>:</b>	Cr <sup>VI</sup> -O tetrahedral:	$2(1.212) + 2(0.971) = 4.366$	$\Delta = -1.634$
	V <sup>II</sup> -O octahedral:	$2(0.499) + 4(0.400) = 2.598$	$\Delta = +0.598$
	V <sup>II</sup> -O tetrahedral:	$2(0.940) + 2(0.753) = 3.386$	$\Delta = +1.386$
	Cr <sup>VI</sup> -O octahedral:	$2(0.644) + 4(0.516) = 3.352$	$\Delta = -2.648$

The Bond-Valence Method achieves two reasonable outcomes: Cr<sup>III</sup>V<sup>V</sup>O<sub>4</sub> with Cr in octahedral and V in tetrahedral holes; and Cr<sup>IV</sup>V<sup>IV</sup>O<sub>4</sub> with Cr in octahedral and V in tetrahedral holes. Therefore, both reasonable formulations coincide in their preferences for V in tetrahedra and Cr in octahedra. By combining ideas from ligand field theory for transition metal atoms and the Bond-Valence Method, the preferred formulation of CrVO<sub>4</sub> is Cr<sup>III</sup>V<sup>V</sup>O<sub>4</sub>.

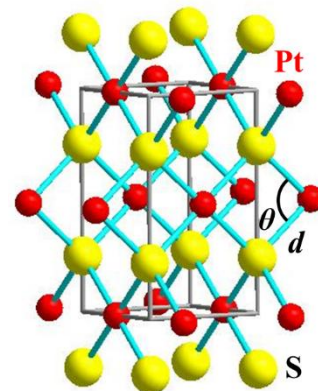
(e) Read the papers *Mat. Res. Bull.* **1988**, 23, pp. 595-601 and *Acta Cryst.* **1967**, 22, p. 321, which describe a synthesis and study of the metal atom positions in CrVO<sub>4</sub>. How do these results compare with your conclusions in parts (c) and (d)?

According to the 1988 paper, CrVO<sub>4</sub> is prepared by fusing Cr<sub>2</sub>O<sub>3</sub> and V<sub>2</sub>O<sub>5</sub> at 723 K. These starting binary oxides involve Cr<sup>III</sup> and V<sup>V</sup>.

According to the 1967, which applies X-ray absorption fine structure, identify a low-energy maximum associated with V, which is apparently characteristic for metal atoms in tetrahedral coordination.

Therefore, CrVO<sub>4</sub> is best formulated as Cr<sup>III</sup>V<sup>V</sup>O<sub>4</sub>.

- (39) The PtS structure represents a compromise between covalent and ionic forces. The space group is  $P4_2/mmc$  (#131) and the asymmetric unit has Pt at  $2c$  (0,  $\frac{1}{2}$ , 0) and S at  $2e$  (0, 0,  $\frac{1}{4}$ ). Consider two structural parameters: (i) the Pt–S distance  $d$ ; and (ii) the S–Pt–S angle  $\theta$ .



- (a) Express the lattice constants  $a$  and  $c$  and unit cell volume in terms of the parameters  $d$  and  $\theta$ .

$$a = 2d \sin\left(\frac{\pi-\theta}{2}\right) = 2d \cos\frac{\theta}{2} \quad c = 4d \sin\frac{\theta}{2}$$

$$V = a^2c = 16d^3 \sin^2\frac{\theta}{2} \cos^2\frac{\theta}{2}$$

- (b) Determine the maximum and minimum unit cell volume for fixed  $d$ . What is the significance of these two extreme volumes?

To calculate the extremum of the unit cell volume for fixed  $d$ , it is better to rewrite the volume as

$$V = 16d^3 \sin^2\frac{\theta}{2} \left(1 - \sin^2\frac{\theta}{2}\right) = 16d^3 \left(\sin^2\frac{\theta}{2} - \sin^4\frac{\theta}{2}\right)$$

Then,

$$\frac{dV}{d\theta} = 16d^3 \left(\frac{1}{2} \cos\frac{\theta}{2} - \frac{3}{2} \sin^2\frac{\theta}{2} \cos\frac{\theta}{2}\right) = 8d^3 \cos\frac{\theta}{2} \left(1 - 3\sin^2\frac{\theta}{2}\right) \text{ and}$$

$$\frac{d^2V}{d\theta^2} = \frac{d}{d\theta} \left[8d^3 \left(3 \cos^3\frac{\theta}{2} - 2 \cos\frac{\theta}{2}\right)\right] = 8d^3 \left(\sin\frac{\theta}{2} - \frac{9}{2} \cos^2\frac{\theta}{2} \sin\frac{\theta}{2}\right)$$

Extremum occur for  $\theta = \pi$ , at which  $\frac{d^2V}{d\theta^2} > 0$ , and  $\theta = 2 \arcsin\left(\frac{1}{\sqrt{3}}\right)$ , at which  $\frac{d^2V}{d\theta^2} < 0$ . Therefore,

**Maximum:**  $\theta = 2 \arcsin\left(\frac{1}{\sqrt{3}}\right) = 70.5288^\circ$ .  $\pi - \theta = 109.4712^\circ$  is the tetrahedral angle at a central atom. The maximum volume represents the minimum electrostatic energy by maximizing the distances between anions.

**Minimum:**  $\theta = 180^\circ$ . As a result, the volume of the unit cell is 0 because  $a = 0$ , and is not possible.

- (c) The observed values of the lattice constants for PtS are  $a = 3.2660 \text{ \AA}$ , and  $c = 5.7508 \text{ \AA}$ . What are the values of  $d$  and  $\theta$  for PtS.

According to the formulas for  $a$  and  $c$ , eliminate  $d$  by taking ratio  $c/2a$ :

$$\frac{c}{2a} = \frac{4d \sin(\theta/2)}{4d \cos(\theta/2)} = \tan(\theta/2) = \frac{5.7508}{2(3.2660)} = 0.8804; \quad \theta = 82.72^\circ, \quad \pi - \theta = 97.28^\circ$$

Therefore,

$$d = \frac{a}{2 \cos(\theta/2)} = \frac{3.2660 \text{ \AA}}{2(0.7506)} = 2.1757 \text{ \AA} \text{ or } d = \frac{c}{4 \sin(\theta/2)} = \frac{5.7508 \text{ \AA}}{4(0.6608)} = 2.1757 \text{ \AA}$$

- (d) Using  $d(\text{Pt–S})$  from (c), evaluate the lattice constants for the case of square planar coordinated Pt; for ideally tetrahedrally coordinated S.

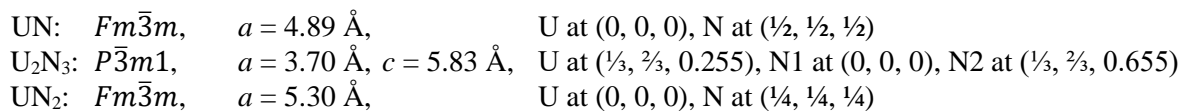
**Square planar coordinated Pt:**  $\theta = 90^\circ$ ;  $a = 2d \cos\frac{\theta}{2} = 2(2.1757 \text{ \AA})(0.7071) = 3.0769 \text{ \AA}$   
 $c = 4d \sin\frac{\theta}{2} = 4(2.1757 \text{ \AA})(0.7071) = 6.1538 \text{ \AA}$

**Tetrahedrally coordinated S:**  $\theta = 70.5288^\circ$ ;  $a = 2d \cos\frac{\theta}{2} = 2(2.1757 \text{ \AA})(0.8165) = 3.5529 \text{ \AA}$   
 $c = 4d \sin\frac{\theta}{2} = 4(2.1757 \text{ \AA})(0.5774) = 5.0246 \text{ \AA}$

The observed lattice constants are intermediate between these two scenarios. Therefore, the arrangement around each S atom distorts from ideal tetrahedral; the arrangement around each Pt atom distorts from ideal square planar. This result explains the interpretation of this structure as being a compromise between ionic and covalent bonding forces.

- (40) Uranium carbides and nitrides are classes of metallic compounds useful as nuclear fuels and showing similar chemical compositions. The structural data for the known stoichiometric solids are:

UC:  $Fm\bar{3}m$ ,  $a = 4.96 \text{ \AA}$ , U at (0, 0, 0), C at ( $\frac{1}{2}$ ,  $\frac{1}{2}$ ,  $\frac{1}{2}$ )  
 $U_2C_3$ :  $I\bar{4}3d$ ,  $a = 8.09 \text{ \AA}$ , U at (0.05, 0.05, 0.05), C at (0.289, 0,  $\frac{1}{4}$ )  
 $UC_2$ :  $I4/mmm$ ,  $a = 3.52 \text{ \AA}$ ,  $c = 6.00 \text{ \AA}$ , U at (0, 0, 0), C at (0, 0, 0.390)



(a) Describe each structure in terms of U atom packing, the nature of the carbide or nitride species, and the formal oxidation states of U.

UC: NaCl-type structure. U forms a CCP eutactic packing with C atoms in octahedral holes. Since C atoms are well separated from each other, the formal charge at C is  $-4$ . Therefore, uranium is U(IV).

U<sub>2</sub>C<sub>3</sub>: Pu<sub>2</sub>C<sub>3</sub>-type structure. U forms a distorted BCC packing with C atoms in adjacent octahedral holes and form dimers with C–C distances of  $1.39 \text{ \AA}$ , which is consistent with C=C double bonds. Therefore, the formal charge on each dimer is  $-4$ , or  $-2$  for each C atom, and the oxidation state of uranium is formally U(III).

UC<sub>2</sub>: CaC<sub>2</sub>-type structure. U forms an elongated BCC packing with C<sub>2</sub> dimers in octahedral holes and oriented along the *c*-axis. The distance of the dicarbide unit is  $1.32 \text{ \AA}$ , which is consistent with C=C double bonds, so the formal charge on each dimer is  $-4$ . As a result, the oxidation state of uranium is U(IV).

UN: NaCl-type structure. U forms a CCP eutactic packing with N atoms in octahedral holes. Since N atoms are well separated from each other, the formal charge at N is  $-3$ . Therefore, uranium is U(III).

U<sub>2</sub>N<sub>3</sub>: La<sub>2</sub>O<sub>3</sub>-type structure. U forms a distorted HCP packing with  $\frac{1}{3}$  N atoms in alternating layers of octahedral holes and  $\frac{2}{3}$  N atoms in alternating bilayers of tetrahedral holes. There are no N–N bonds, so the formal charge at N is  $-3$ . As a result, uranium is either mixed valent or intermediate valent with an average oxidation state of  $+4.5$ .

UN<sub>2</sub>: CaF<sub>2</sub>-type structure. U forms a CCP eutactic packing with N atoms in all tetrahedral holes. Since N atoms are well separated from each other, the formal charge at N is  $-3$ . Therefore, uranium is U(VI).

(b) Calculate the densities (in g/cm<sup>3</sup>) of each compound. Uranium metal has a density of  $\sim 19.1 \text{ g/cm}^3$ . Discuss variations of the values within the carbide and nitride families, as well as for identical compositions.

UC: # Formula units per unit cell = 4  
 Mass in unit cell (g) =  $4(250.040 \text{ g/mol})/6.022 \times 10^{23} = 1.661 \times 10^{-21} \text{ g}$   
 Volume of unit cell (cm<sup>3</sup>) =  $(4.96 \text{ \AA})^3(1 \text{ cm} / 10^8 \text{ \AA})^3 = 1.220 \times 10^{-22} \text{ cm}^3$   
 Density (g/cm<sup>3</sup>) =  $1.661 \times 10^{-21} \text{ g} / 1.220 \times 10^{-22} \text{ cm}^3 = 13.61 \text{ g/cm}^3$

U<sub>2</sub>C<sub>3</sub>: # Formula units per unit cell = 8  
 Mass in unit cell (g) =  $8(512.091 \text{ g/mol})/6.022 \times 10^{23} = 6.803 \times 10^{-21} \text{ g}$   
 Volume of unit cell (cm<sup>3</sup>) =  $(8.09 \text{ \AA})^3(1 \text{ cm} / 10^8 \text{ \AA})^3 = 5.295 \times 10^{-22} \text{ cm}^3$   
 Density (g/cm<sup>3</sup>) =  $6.803 \times 10^{-21} \text{ g} / 5.295 \times 10^{-22} \text{ cm}^3 = 12.85 \text{ g/cm}^3$

UC<sub>2</sub>: # Formula units per unit cell = 2  
 Mass in unit cell (g) =  $2(262.051 \text{ g/mol})/6.022 \times 10^{23} = 8.703 \times 10^{-22} \text{ g}$   
 Volume of unit cell (cm<sup>3</sup>) =  $(3.52 \text{ \AA})^2(6.00 \text{ \AA})(1 \text{ cm} / 10^8 \text{ \AA})^3 = 7.434 \times 10^{-23} \text{ cm}^3$   
 Density (g/cm<sup>3</sup>) =  $8.703 \times 10^{-22} \text{ g} / 7.434 \times 10^{-23} \text{ cm}^3 = 11.71 \text{ g/cm}^3$

UN: # Formula units per unit cell = 4  
 Mass in unit cell (g) =  $4(252.036 \text{ g/mol})/6.022 \times 10^{23} = 1.674 \times 10^{-21} \text{ g}$   
 Volume of unit cell (cm<sup>3</sup>) =  $(4.89 \text{ \AA})^3(1 \text{ cm} / 10^8 \text{ \AA})^3 = 1.169 \times 10^{-22} \text{ cm}^3$   
 Density (g/cm<sup>3</sup>) =  $1.674 \times 10^{-21} \text{ g} / 1.169 \times 10^{-22} \text{ cm}^3 = 14.32 \text{ g/cm}^3$

U<sub>2</sub>N<sub>3</sub>: # Formula units per unit cell = 1  
 Mass in unit cell (g) =  $1(518.078 \text{ g/mol})/6.022 \times 10^{23} = 8.603 \times 10^{-22} \text{ g}$   
 Volume of unit cell (cm<sup>3</sup>) =  $(3.70 \text{ \AA})^2(5.83 \text{ \AA}) \sin 120^\circ (1 \text{ cm} / 10^8 \text{ \AA})^3 = 6.912 \times 10^{-23} \text{ cm}^3$

$$\text{Density (g/cm}^3\text{)} = 8.603 \times 10^{-22} \text{ g} / 6.912 \times 10^{-23} \text{ cm}^3 = 12.45 \text{ g/cm}^3$$

UN<sub>2</sub>: # Formula units per unit cell = 4

$$\text{Mass in unit cell (g)} = 4(266.043 \text{ g/mol})/6.022 \times 10^{23} = 1.767 \times 10^{-21} \text{ g}$$

$$\text{Volume of unit cell (cm}^3\text{)} = (5.30 \text{ \AA})^3(1 \text{ cm} / 10^8 \text{ \AA})^3 = 1.489 \times 10^{-22} \text{ cm}^3$$

$$\text{Density (g/cm}^3\text{)} = 1.767 \times 10^{-21} \text{ g} / 1.489 \times 10^{-22} \text{ cm}^3 = 11.87 \text{ g/cm}^3$$

All densities of these uranium carbides and nitrides are lower than the pure metal, which is expected by “diluting” uranium with much lighter elements. Within each class, i.e., carbides and nitrides separately, the densities decrease with increasing mole fraction of the lighter element. If the carbide and nitride compounds with similar compositions are compared, UN and UN<sub>2</sub> are denser, respectively, than UC and UC<sub>2</sub>. However, U<sub>2</sub>N<sub>3</sub> is less dense than U<sub>2</sub>C<sub>3</sub>, which suggests a volume effect. The volume of the sesquinitride is impacted by filling octahedral and tetrahedral holes by nitride units, whereas the sesquicarbide involves singular dicarbide units filling voids in distorted BCC packing of uranium.

- (c) UC<sub>2</sub> is C deficient, i.e., ~UC<sub>1.8</sub>. What are the types and fractions of the different carbide units in this structure? What can you conclude about the oxidation state of U in this compound?

The structure of stoichiometric UC<sub>2</sub> is tetragonal CaC<sub>2</sub>-type with C–C distances of 1.32 Å, which is consistent with C=C double bonds. There is a 1:1 ratio of U atoms to C<sub>2</sub> units. Carbon deficiency will create a random mixture of *u* carbide and *v* dicarbide units such that *u* + *v* = 1. Therefore, UC<sub>2-x</sub> = UC<sub>*u*</sub>(C<sub>2</sub>)<sub>*v*</sub> = UC<sub>*x*</sub>(C<sub>2</sub>)<sub>1-x</sub>. For UC<sub>1.8</sub>, *x* = 0.2 so that 20% carbon occurs as carbide and 80% carbon occurs as dicarbide. Since both the carbide and the dicarbide unit with C=C double bond have formal charges of -4, the oxidation state of U is +4.

- (d) N-rich uranium sesquinitride U<sub>2</sub>N<sub>3+x</sub> adopts a cubic structure, space group *Ia* $\bar{3}$ , *a* = 10.628 Å. The asymmetric unit is U1 at (0, 0, 0), U2 at (0.271, 0, ¼), N at (0.105, 0.367, 0.131), and the extra N atoms partially occupy the Wyckoff sites (0.133, 0.133, 0.133). How does this structure for *x* = 0 compare to trigonal U<sub>2</sub>N<sub>3</sub>? Why do you think the structure type changes upon nitrogen doping? Discuss possible changes in oxidation state at U atoms from U<sub>2</sub>N<sub>3</sub> to U<sub>2</sub>N<sub>3+x</sub>.

The U atoms form a distorted CCP arrangement with N atoms in tetrahedral holes. As a result, the U atoms are 6-coordinate. In trigonal U<sub>2</sub>N<sub>3</sub>, the U atoms adopt a distorted HCP arrangement with 1/3 N atoms in octahedral holes and 2/3 N atoms in tetrahedral holes. These U atoms are 7-coordinate.

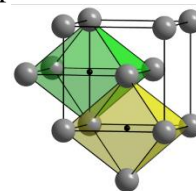
To include additional N atoms in trigonal U<sub>2</sub>N<sub>3</sub> to realize U<sub>2</sub>N<sub>3+x</sub>, N atoms must occupy voids that share common faces, which is destabilizing. The transition to CCP U atoms allows occupation of tetrahedral holes without sharing faces.

As mentioned above, the average oxidation state of U in U<sub>2</sub>N<sub>3</sub> is +4.5. With additional N atoms in tetrahedral holes, U will be formally oxidized approaching an average oxidation state of +5. The +5 oxidation state can be achieved when *x* = 1/3 in U<sub>2</sub>N<sub>3+x</sub>.

- (41) The BCC packing of atoms involves a cubic unit cell of side *a* with atoms at (0,0,0) and (½, ½, ½). The space group is *Im* $\bar{3}m$ .

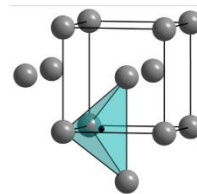
- (a) Identify the fractional coordinates and point group symmetry of the “octahedral” holes in this packing. The octahedra are not regular. How many octahedral holes are there per atom?

Octahedral holes are located at the centers of the cubic cell edges (green) (0, 0, ½), (½, 0, 0), (0, ½, 0) and faces (yellow) (½, ½, 0), (0, ½, ½), (½, 0, ½). As the picture shows, these octahedra are compressed along one of their axes and their point group symmetry is 4/*mmm* = *D*<sub>4h</sub>. Per unit cell, there are 3 distinct edges and 3 distinct faces, so there are 6 octahedral holes for every 2 BCC atoms or 3 octahedral holes per BCC atom.



- (b) Identify the fractional coordinates and point group symmetry of the “tetrahedral” holes in this packing. The tetrahedra are not regular. How many tetrahedral holes are there per atom?

Tetrahedral holes are located in the faces (light blue)  $(\frac{1}{2}, \frac{1}{4}, 0)$ ,  $(\frac{1}{4}, \frac{1}{2}, 0)$ ,  $(\frac{1}{2}, \frac{3}{4}, 0)$ ,  $(\frac{3}{4}, \frac{1}{2}, 0)$  and then in the equivalent faces at  $(\frac{1}{4}, 0, \frac{1}{2})$ ,  $(\frac{1}{2}, 0, \frac{1}{4})$ ,  $(\frac{3}{4}, 0, \frac{1}{2})$ ,  $(\frac{1}{2}, 0, \frac{3}{4})$ ,  $(0, \frac{1}{4}, \frac{1}{2})$ ,  $(0, \frac{1}{2}, \frac{1}{4})$ ,  $(0, \frac{3}{4}, \frac{1}{2})$ ,  $(0, \frac{1}{2}, \frac{3}{4})$ . These tetrahedra are stretched along two opposite edges and their point group symmetry is  $42m = \mathcal{D}_{2d}$ . Per unit cell, there are 12 tetrahedral holes for every 2 BCC atoms or 6 tetrahedral holes per BCC atom.



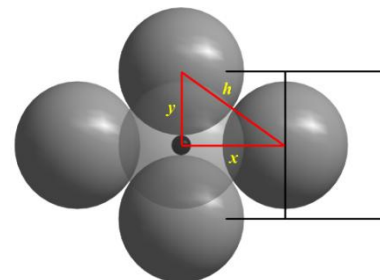
- (c) For ideal BCC packing, what is the optimal radius ratio for spheres filling an “octahedral” hole?

Use the accompanying diagram, viewing down  $[1\bar{1}0]$ :

$h = \frac{\sqrt{3}}{2}a = 2R$  is along the body-diagonal of the cube of side  $a$   
 where spheres touch and provides the relationship between  $R$  and  $a$ ;

$y = \frac{1}{2}a$  is along the edge of the cube of side  $a$ ;

$x = \frac{1}{\sqrt{2}}a$  is along face-diagonal of the cube of side  $a$ .



The shorter distance between the center of a BCC packed atom and the center of the octahedral hole is

$$y = R + r = \frac{1}{2}a = \frac{1}{2} \cdot \frac{4}{\sqrt{3}}R = \sqrt{\frac{4}{3}}R$$

Therefore,  $\frac{r}{R} = \sqrt{\frac{4}{3}} - 1 = 0.1547$

- (d) For ideal BCC packing, what is the optimal radius ratio for spheres filling an “tetrahedral” hole?

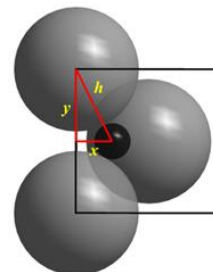
Use the accompanying diagram, viewing down  $[100]$ :

$y = \frac{1}{2}a$  is along the edge of the cube of side  $a$ ;

$x = \frac{1}{4}a$  is also along the edge of the cube of side  $a$ .

$$h = \sqrt{x^2 + y^2} = \frac{\sqrt{5}}{4}a = \frac{\sqrt{5}}{4} \cdot \frac{4}{\sqrt{3}}R = \sqrt{\frac{5}{3}}R = R + r.$$

Therefore,  $\frac{r}{R} = \sqrt{\frac{5}{3}} - 1 = 0.2910$ .

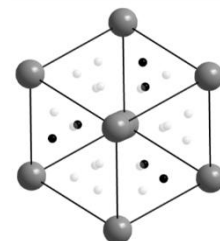
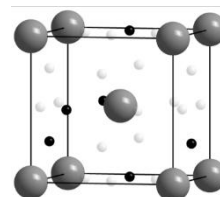


Notice that the “size” of the tetrahedral hole is larger than the “size” of the octahedral hole in BCC packing.

- (e) What fraction of “tetrahedral” holes are occupied by M atoms in BCC packing of X atoms to give the formula  $M_3X_2$ ? From your answer to (b), suggest the arrangement of M atoms that will minimize electrostatic repulsions between M atoms. What is the resulting space group?

Since there are 6 tetrahedral holes per BCC atom X, there are 12 tetrahedral holes per 2 BCC atoms. For  $M_3X_2$ , 3/12 or 1/4 of all tetrahedral holes are occupied.

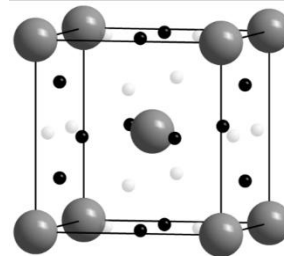
To minimize electrostatic repulsions, the distance(s) between M atoms must be maximized. The centers of the tetrahedral holes are located on each face of the cubic unit cell and there are 4 centers per face. Therefore, one site per face is occupied and the same occupied site occurs via translational periodicity. For the  $z = 0$  plane, let the occupied position be  $(\frac{1}{4}, \frac{1}{2}, 0)$ . Then, maximum distances to adjacent faces with  $x = 0$  and  $y = 0$  are, respectively,  $(0, \frac{1}{4}, \frac{1}{2})$  and  $(\frac{1}{2}, 0, \frac{1}{4})$ . These three sites are related to each other by a 3-fold rotation along the  $[111]$  direction, i.e., one of the body-diagonals of the cubic cell. Looking down this direction suggests 2-fold rotations orthogonal to this axis, but no mirror planes. Therefore, the point group of the space group is  $32 = \mathcal{D}_3$  and would be rhombohedral because  $a_1 = a_2 = a_3 = a$  and  $\alpha_1 = \alpha_2 = \alpha_3 \sim 90^\circ$ . This space group is  $R32$ .  $Ni_3S_2$  is one example.



- (f) What fraction of “tetrahedral” holes are occupied by M atoms in BCC packing of X atoms to give the formula  $M_3X$ ? From your answer to (b), suggest the arrangement of M atoms that will minimize electrostatic repulsions between M atoms. What is the resulting space group?

Since there are 6 tetrahedral holes per BCC atom X, for  $M_3X$ , 3/6 or 1/2 of all tetrahedral holes are occupied.

To minimize electrostatic repulsions, the distance(s) between M atoms must be maximized. The centers of the tetrahedral holes are located on each face of the cubic unit cell and there are 4 centers per face. Therefore, two sites per face are occupied and the same occupied sites occur via translational periodicity. For the  $z = 0$  plane, the occupied positions can be  $(\frac{1}{4}, \frac{1}{2}, 0)$  and  $(\frac{3}{4}, \frac{1}{2}, 0)$ . Then, maximum distances to adjacent faces with  $x = 0$  and  $y = 0$  are, respectively,  $(0, \frac{1}{4}, \frac{1}{2})$ ,  $(0, \frac{3}{4}, \frac{1}{2})$  and  $(\frac{1}{2}, 0, \frac{1}{4})$ ,  $(\frac{1}{2}, 0, \frac{3}{4})$ . These six sites, along with all translationally equivalent sites, are related to each other by 3-fold rotations along the body-diagonals of the cubic cell. Furthermore, mirror planes perpendicular to the sides of the cube remain. However, the mirror planes perpendicular to the face-diagonals are lost. The coordination around each X atom of the BCC packing is a distorted icosahedron of 12 M atoms, but the orientations for these icosahedra around  $(0, 0, 0)$  and  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  are related by a glide reflection. Therefore, the point group of the space group is  $m\bar{3} = \mathcal{T}_h$  and would remain cubic but with body-centering removed. This space group is  $Pm\bar{3}n$ .  $Ti_3Sb$  and  $Nb_3Ge$  are two examples.



An ordered derivative of BCC packing is the CsCl-type structure with space group  $Pm\bar{3}m$ . One example is TiFe with  $a \sim 2.98 \text{ \AA}$ , which is an effective hydrogen storage material.

- (g) Identify the numbers per unit cell, atomic environments, and point group symmetry for the various “octahedral” and “tetrahedral” holes in TiFe.

**Octahedral holes are located at the centers of the cubic cell edges and faces, but the environments are different in CsCl-type TiFe. Let Ti atoms occupy cell corners and Fe atoms occupy cell centers. Then, there are 3  $[Ti_2Fe_4]$  octahedral holes per unit cell at the cell edges  $(0, 0, \frac{1}{2})$ ,  $(\frac{1}{2}, 0, 0)$ ,  $(0, \frac{1}{2}, 0)$  and 3  $[Fe_2Ti_4]$  octahedral holes per unit cell at the cell faces  $(\frac{1}{2}, \frac{1}{2}, 0)$ ,  $(0, \frac{1}{2}, \frac{1}{2})$ ,  $(\frac{1}{2}, 0, \frac{1}{2})$ . The point group symmetry of both sites is  $4/mmm = \mathcal{D}_{4h}$ .**

**Tetrahedral holes are located in the faces at  $(\frac{1}{2}, \frac{1}{4}, 0)$ ,  $(\frac{1}{4}, \frac{1}{2}, 0)$ ,  $(\frac{1}{2}, \frac{3}{4}, 0)$ ,  $(\frac{3}{4}, \frac{1}{2}, 0)$ ,  $(\frac{1}{4}, 0, \frac{1}{2})$ ,  $(\frac{1}{2}, 0, \frac{1}{4})$ ,  $(\frac{3}{4}, 0, \frac{1}{2})$ ,  $(\frac{1}{2}, 0, \frac{3}{4})$ ,  $(0, \frac{1}{4}, \frac{1}{2})$ ,  $(0, \frac{1}{2}, \frac{1}{4})$ ,  $(0, \frac{3}{4}, \frac{1}{2})$ ,  $(0, \frac{1}{2}, \frac{3}{4})$ . All tetrahedral holes have the same environment  $[Ti_2Fe_2]$  and their point group symmetry is  $mm2 = \mathcal{C}_{2v}$ .**

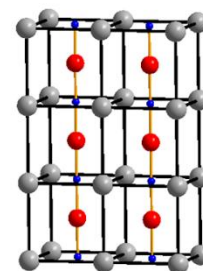
- (h) H atoms occupy “octahedral” voids in TiFeH. Given that more electronegative metals prefer lower coordination numbers with nonmetal atoms, which and what fraction of “octahedral” voids in TiFe are occupied by H atoms?

**Fe is more electronegative than Ti. To ensure that Fe has a lower coordination number to H than Ti, H atoms occupy the  $[Fe_2Ti_4]$  “octahedral” voids.**

**There are 3  $[Fe_2Ti_4]$  “octahedral” holes per TiFe unit cell, so one-third of these holes are occupied in TiFeH.**

- (i) Using your answer to (h), there are two possible arrangements of H atoms so that all Ti atoms are equivalent, and all Fe atoms are equivalent. What are these two arrangements? What are the local coordination environments at the metals by H atoms? Identify the space groups and approximate unit cell parameters of these two structures.

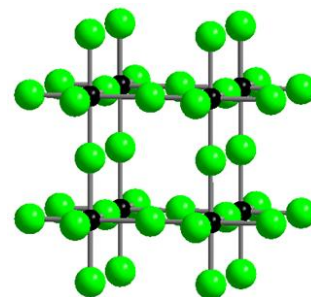
**The simplest structure involves a single TiFe unit cell with one set of  $[Fe_2Ti_4]$  “octahedral” holes occupied by H atoms, the structure shown to the right (Ti = gray atoms; Fe = red atoms; H = small blue atoms). Each Fe atom is linearly coordinated by 2 H atoms; each Ti atom is square planar coordinated by 4 H atoms. As a result, there are parallel linear  $[FeH]$  chains. By occupying one set of “octahedral” holes, cubic symmetry**



is destroyed. The resulting space group is  $P4/mmm$  and the unit cell is  $a = b \sim c \sim 2.98 \text{ \AA}$ , assuming negligible changes to lattice constants by inserting H atoms. The  $c$ -axis is parallel to the [FeH] chains. A second structure can be deduced by focusing on the Fe coordination. A reasonable alternative is for the coordination at Fe atoms to be 2-coordinate *bent*, which is shown here. In this case, there are [FeH] zigzag chains and the unit cell must contain at least 2 TiFeH formula units. The simplest unit cell is  $a \sim \sqrt{2}b \sim c \sim 4.2 \text{ \AA}$ ; the structure is shown in projection down the  $b$ -axis. There are mirror planes in the plane of the [FeH] chains (perpendicular to  $b$ ); there are mirror planes intersecting the Fe atoms (perpendicular and to  $a$ ); and there are glide reflections intersecting H atoms in the [FeH] zigzag chains (perpendicular to  $c$ ). The resulting space group is  $Pmma$ , which belongs to the orthorhombic crystal class.

NOTE: The structure of TiFeH is reported to adopt the orthorhombic space group  $P222_1$  with lattice constants  $a = 2.97 \text{ \AA}$ ,  $b = 4.53 \text{ \AA}$ ,  $c = 4.38 \text{ \AA}$ . See *J. Less-Common Met.* 1987, 130, pp. 69-78.

- (42) An early report of “NbF<sub>3</sub>” was, in fact, a range of oxyfluorides with variable proportions of anions, NbO<sub>x</sub>F<sub>y</sub>. The structural framework closely resembles the cubic ReO<sub>3</sub>-type structure, but with disordered arrangements of O and F atoms. The ReO<sub>3</sub>-type structure has space group  $Pm\bar{3}m$  with Re atoms at  $1a$  sites (0,0,0) and O atoms at  $3d$  sites ( $\frac{1}{2},0,0$ ).



In the ReO<sub>3</sub>-type structure, each metal is octahedrally coordinated and each anion is linearly coordinated. We can describe it as a 3D network of vertex-sharing octahedra.

Assume NbO<sub>x</sub>F<sub>y</sub> adopts a *defect-free* ReO<sub>3</sub>-type structure, i.e., no anion or cation vacancies.

- (a) Write the chemical formula of NbO<sub>x</sub>F<sub>y</sub> using the single stoichiometric variable  $x$ . What is the allowed range of  $x$ ?

In a defect-free structure,  $y = 3 - x$ , so that we can write the formula NbO<sub>x</sub>F<sub>3-x</sub>.

The *highest* oxidation state for Nb is +5, so the condition on  $x$  is

$$5 - 2x - (3 - x) = 2 - x \geq 0. \text{ Therefore, } 0 \leq x \leq 2.$$

- (b) Which of these formulations in part (a) give integral oxidation states for Nb?

$x = 0$ : NbF<sub>3</sub> (Nb<sup>3+</sup>)

$x = 1$ : NbOF<sub>2</sub> (Nb<sup>4+</sup>)

$x = 2$ : NbO<sub>2</sub>F (Nb<sup>5+</sup>)

- (c) For each of the formulations in part (b), what are the most probable coordination environments at the Nb atoms? Be specific concerning arrangement of ligands.

Since there are no vacancies, Nb is surrounded by an octahedron of 6 ligands.

For NbO<sub>x</sub>F<sub>3-x</sub>, then, on average,  $(x/3) \cdot 6 = 2x$  ligands are O atoms and  $(1 - x/3) \cdot 6 = 6 - 2x$  ligands are F atoms. Therefore,

NbF<sub>3</sub> ( $x = 0$ ): all Nb atoms are [NbF<sub>6</sub>] environments.

NbOF<sub>2</sub> ( $x = 1$ ): most probable are [NbO<sub>2</sub>F<sub>4</sub>], which could be either *cis*- or *trans*- for O.

NbO<sub>2</sub>F ( $x = 2$ ): most probable are [NbO<sub>4</sub>F<sub>2</sub>], which could be either *cis*- or *trans*- for F.

Now, assume NbO<sub>x</sub>F<sub>y</sub> allows defects at just at the anion sites, but all cation sites are fully occupied and the oxidation state of Nb remains fixed at Nb(III).

- (d) Write the chemical formula of NbO<sub>x</sub>F<sub>y</sub> using just the single stoichiometric variable  $x$ . What is the allowed range of  $x$ ?

For the +3 oxidation state for Nb, then  $3 - 2x - y = 0$ , or  $y = 3 - 2x$ . Therefore, NbO<sub>x</sub>F<sub>3-2x</sub>.

The limitation on  $x$  is dictated by stoichiometry:  $0 \leq 3 - 2x$ , or  $x \leq 3/2$ .

- (e) Which of these formulations in (d) give integral average coordination numbers at Nb atoms?

$$(1) \cdot \langle \text{CN} \rangle_{\text{Nb}} = 2x + 2(3 - 2x) = 6 - 2x, \text{ so that } \langle \text{CN} \rangle_{\text{Nb}} = 6 - 2x.$$

- $x = 0$ :  $\text{NbF}_3$ , Nb is 6-coordinate (octahedral)  
 $x = 0.5$ :  $\text{NbO}_{0.5}\text{F}_2$ , Nb is 5-coordinate on average (square pyramidal)  
 $x = 1$ :  $\text{NbOF}$ , Nb is 4-coordinate on average (square planar or sawhorse)  
 $x = 1.5$ :  $\text{NbO}_{1.5}$ , Nb is 3-coordinate on average (T-shaped or trigonal pyramid)

- (f) For each of the formulations in part (e), what are the most probable coordination environments at the Nb atoms? Be specific concerning arrangement of ligands.

$\text{NbF}_3$ : all Nb atoms are  $[\text{NbF}_6]$  environments

$\text{NbO}_{0.5}\text{F}_2$ , most probable are  $[\text{NbOF}_4]$ , with O atom either in axial or equatorial sites

$\text{NbOF}$ , most probable are  $[\text{NbO}_2\text{F}_2]$ . For square planar, the two different ligands could be *cis*- or *trans*-; for sawhorse, there are two equatorial and two axial positions, which provides three different configurations: O on equatorial; O on axial; O + F on both sites

$\text{NbO}_{1.5}$ , Nb atoms are  $[\text{NbO}_3]$  T-shaped or trigonal pyramid environments

- (g) To maintain its structural stability, the  $\text{ReO}_3$ -type structure must have the metal atoms at least five-coordinate on average. Using this rule, what is the limiting composition of this model of  $\text{NbO}_x\text{F}_y$ ? For this composition, what are the most probable coordination environments at the Nb atoms? (Be specific concerning arrangement of ligands.)

In a defect structure with Nb(III), then  $3 - 2x - y = 0$ , or  $y = 3 - 2x$ . Thus, we can write the formula  $\text{Nb}_{1-x}\text{O}_x\text{F}_{3-2x}$ . Therefore,  $0 < x \leq 1.5$ .

Nb is surrounded by 6 ligand sites, but some of these sites are vacant. For  $\text{Nb}_{1-x}\text{O}_x\text{F}_{3-2x}$ ,  $x/3$  ligands are O,  $x/3$  ligands are vacancies;  $1 - 2x/3$  ligands are F. Therefore, on average, surrounding Nb would be  $2x$  ( $= 6 - x/3$ ) O atoms,  $2x$  vacancies, and  $6 - 4x$  F atoms. Therefore, we could have 6-coordinate octahedra, 5-coordinate square pyramids, 4-coordinate square planar or *cis*-divacant octahedra (sawhorse), and, least probable, 3-coordinate T-shaped or trigonal pyramids.

If the average coordination number of Nb must be at least 5, then  $5 \leq 2x + 2(3 - 2x) = 6 - 2x$ . Therefore,  $x \leq 1/2$ . The limiting composition is  $\text{NbO}_{0.5}\text{F}_2$ .

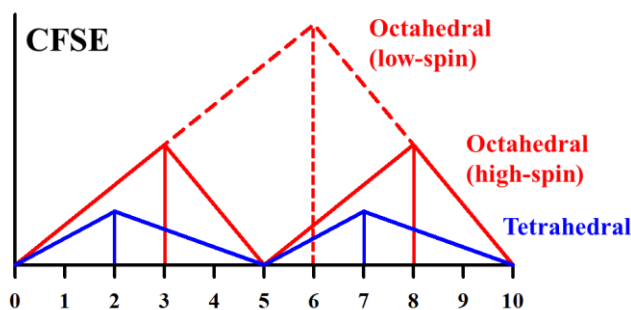
In this formulation, 1/5 of ligands at Nb are O atoms, 4/5 are F atoms. Therefore, two types of square pyramids are possible: (i) O in the apex; (ii) O in the equatorial plane.

“ $\text{BiF}_3$ ” (in the anti- $\text{Li}_3\text{Bi}$  structure) also involves oxyfluorides  $\text{BiO}_x\text{F}_y$ .

- (h) Which of the two models described above for  $\text{NbO}_x\text{F}_y$ , i.e., defect-free or anion defects, is *better suited* for  $\text{BiO}_x\text{F}_y$ ? Explain your selection. What types of environments surround Bi in this anti- $\text{Li}_3\text{Bi}$ -type structure for your choice of model?

$\text{Bi}^{3+}$  and  $\text{Bi}^{5+}$  are common oxidation states for Bi with electronegative ligands like oxide and fluoride. Therefore,  $\text{BiO}_x\text{F}_y$  will follow the second model above with just  $\text{Bi}^{3+}$ , which means a formulation as  $\text{Bi}_{1-x}\text{O}_x\text{F}_{3-2x}$ . The number of vacancies will increase if both  $\text{Bi}^{3+}$  and  $\text{Bi}^{5+}$  are involved.

- (43) The spinel-type structure occurs for numerous oxides formulated as  $\text{A}^{\text{II}}\text{B}^{\text{III}}_2\text{O}_4$  in which the cations A and B occupy tetrahedral and octahedral voids of a CCP array of oxide ions. “Normal” spinels have the divalent metal in tetrahedral holes and the trivalent metals in octahedral holes. “Inverse” spinels have one-half of the trivalent metals in tetrahedral holes and the remaining one-half of the trivalent metals plus the divalent metal in octahedral holes. The graph illustrates crystal field stabilization energies (CFSEs) for metal atoms in octahedral and tetrahedral fields relative to isolated atoms as a function of *d*-electron configurations. The higher the value of CFSE, the greater the stabilization. Using this information, determine the preferred spinel-type structure, *normal* or *inverse*, for  $\text{Mn}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4$ , and  $\text{Co}_3\text{O}_4$ .



O atom ligands to transition metals serve as  $\pi$ -donor ligands, so the metals will be expected to adopt high-spin configurations. Then, using the CFSE information in the curves:

$\text{Mn}_3\text{O}_4 = \text{Mn}^{\text{II}}\text{Mn}^{\text{III}}_2\text{O}_4$ :  $\text{Mn}^{\text{II}}$  is  $d^5$ , which shows no preference to either octahedral or tetrahedral when high-spin.

$\text{Mn}^{\text{III}}$  is  $d^4$ , which shows modest preference for octahedral when high-spin. However, since the  $e_g$  orbital is half-occupied, it is susceptible to a first-order Jahn-Teller distortion and lowering from cubic symmetry.

Normal spinel is anticipated:  $\text{Mn}^{\text{II}}(\text{Mn}^{\text{III}})_2\text{O}_4$ , but lower crystalline symmetry than cubic.

$\text{Fe}_3\text{O}_4 = \text{Fe}^{\text{II}}\text{Fe}^{\text{III}}_2\text{O}_4$ :  $\text{Fe}^{\text{II}}$  is  $d^6$ , which modestly prefers an octahedral environment when high-spin.

$\text{Fe}^{\text{III}}$  is  $d^5$ , which shows no preference to either octahedral or tetrahedral when high-spin.

Inverse spinel is anticipated:  $\text{Fe}^{\text{III}}(\text{Fe}^{\text{II}}\text{Fe}^{\text{III}})\text{O}_4$

$\text{Co}_3\text{O}_4 = \text{Co}^{\text{II}}\text{Co}^{\text{III}}_2\text{O}_4$ :  $\text{Co}^{\text{II}}$  is  $d^7$ , which very modestly prefers an octahedral environment when high-spin, although this has the highest CFSE for tetrahedral.

$\text{Co}^{\text{III}}$  is  $d^6$ , which modestly prefers an octahedral environment when high-spin.

Normal spinel is anticipated:  $\text{Co}^{\text{II}}(\text{Co}^{\text{III}})_2\text{O}_4$

(44) The structure of wüstite, iron(II) oxide, is halite-type ( $cF8$ ) but iron deficient  $\text{Fe}_{1-x}\text{O}$ . In the crystal structure, iron deficiency can be realized simply by either vacancies at the Fe sites or additional O atoms at interstitial sites. More complex options involve combinations of these possibilities.

(a) Determine an expression for the density (in  $\text{g/cm}^3$ ) of  $\text{Fe}_{1-x}\text{O}$  in terms of  $x$  and  $a$  (in  $\text{\AA}$ ), the length of an edge of the halite-type unit cell, assuming there are vacancies on Fe sites only.

In the NaCl-type unit cell, there are 4 formula units of  $\text{Fe}_{1-x}\text{O}$ :

$$\text{Mass (4 Fe}_{1-x}\text{O)} = 4 (55.845(1-x) + 15.999) = (287.376 - 223.38x) \text{ g/mol}$$

$$\text{Mass (4 Fe}_{1-x}\text{O)} = (287.376 - 223.38x) / 6.022 \times 10^{23} = (47.721 - 37.094x) \times 10^{-23} \text{ g}$$

$$\text{Volume (4 Fe}_{1-x}\text{O)} = a^3 \times 10^{-24} \text{ cm}^3$$

$$\text{Density} = (47.721 - 37.094x) \times 10^{-23} \text{ g} / a^3 \times 10^{-24} \text{ cm}^3 = (477.21 - 370.94x) / a^3 \text{ (g/cm}^3\text{)}$$

(b) Determine an expression for the density (in  $\text{g/cm}^3$ ) of  $\text{FeO}_{1+y}$  in terms of  $y$  and  $a$  (in  $\text{\AA}$ ), the length of an edge of the halide-type unit cell, assuming complete occupation of Fe and O sites plus O atoms in interstitial sites.

$$\text{Mass (4 FeO}_{1+y}\text{)} = 4 (55.845 + 15.999(1+y)) = (287.376 + 63.996y) \text{ g/mol}$$

$$\text{Mass (4 FeO}_{1+y}\text{)} = (287.376 + 63.996y) / 6.022 \times 10^{23} = (47.721 + 10.627y) \times 10^{-23} \text{ g}$$

$$\text{Volume (4 FeO}_{1+y}) = a^3 \times 10^{-24} \text{ cm}^3$$

$$\text{Density} = (47.721 + 10.627y) \times 10^{-23} \text{ g} / a^3 \times 10^{-24} \text{ cm}^3 = (477.21 + 106.27y) / a^3 \text{ (g/cm}^3)$$

- (c) For a wüstite sample analyzed to be  $\text{Fe}_{0.93}\text{O}$  with  $a = 4.312 \text{ \AA}$ , calculate the densities (in  $\text{g/cm}^3$ ) for each model in (a) and (b).

$$x = 0.07:$$

$$\text{Density} = (477.21 - 370.94(0.07)) / (4.312)^3 = 451.2442 / 80.1745 = 5.628 \text{ g/cm}^3$$

$$\text{Fe}_{0.93}\text{O} = \text{FeO}_{1/0.93} = \text{FeO}_{1.0753}$$

$$y = 0.0753:$$

$$\text{Density} = (477.21 + 106.27(0.0753)) / (4.312)^3 = 485.2121 / 80.1745 = 6.052 \text{ g/cm}^3$$

- (d) Assuming that  $a = 4.312 \text{ \AA}$  and a density difference of  $0.1 \text{ g/cm}^3$  can be detected with confidence, what is the smallest value of  $x$  that measurement of density will be able to distinguish between the two models of  $\text{FeO}$ ?

$$\text{For small } x, \text{ then Fe}_{1-x}\text{O} \sim \text{FeO}_{1+x}$$

$$\Delta(\text{density}) = [(477.21 + 106.27x) / 80.1745] - [(477.21 - 370.94x) / 80.1745] > 0.1$$

$$\text{Therefore, } 477.21x > 8.01745 \quad \text{or } x > 0.017.$$

- (e) Mössbauer spectroscopy indicates the presence of Fe(II) and Fe(III) in  $\text{Fe}_{1-x}\text{O}$ . What are the molar fractions of Fe(II) and Fe(III) relative to O in this system?

Use conservation of atoms and charge for 1 mole  $\text{Fe}_{1-x}\text{O}$ :

Let  $u = \# \text{ moles Fe(II)}$  and  $v = \# \text{ moles Fe(III)}$ .

$$\text{From mass balance: } u + v = 1 - x; \quad \text{From charge balance: } 2u + 3v = 2$$

$$\text{Therefore, } u = \text{fraction of Fe(II)} = 1 - 3x \text{ and } v = \text{fraction of Fe(III)} = 2x.$$

- (f) Fe(III) can occupy tetrahedral holes rather than octahedral holes in oxide close packings. In  $\text{Fe}_{1-x}\text{O}$ , if an Fe(III) atom is in a tetrahedral hole, then the surrounding octahedral holes must be vacant because the Fe-Fe distance would be too short. Assuming only Fe(III) occupy tetrahedral holes, then what fraction of Fe(III) of all Fe(III) atoms in  $\text{Fe}_{1-x}\text{O}$  occupy tetrahedral holes?

In the NaCl-type structure, the tetrahedral holes of the O atom cubic close packing are surrounded by 4 octahedral void sites. Therefore, if a tetrahedral hole is occupied by Fe(III), then the 4 surrounding octahedral holes must be vacant. Let  $w = \# \text{ Fe(III) atoms in tetrahedral holes for every O atom}$ . Then, the structural formula for  $\text{Fe}_{1-x}\text{O}$  becomes:

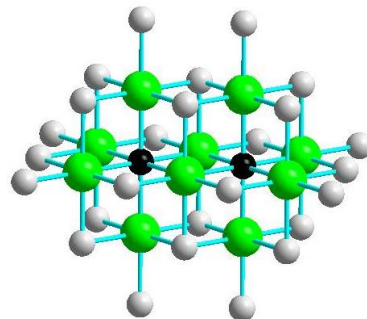
$$\text{Fe}_w^{\text{III}}\text{Fe}_{1-4w}\text{O} \cong \text{Fe}_{1-3w}\text{O}. \text{ Therefore, } w = x/3.$$

Therefore, the fraction of Fe(III) occupying tetrahedral holes is:

$$(x/3) / (2x) = 1/6.$$

For further details about the structure and properties of wüstite, see R.M. Hazen and R. Jeanloz, *Rev. Geophys. Space Phys.* (1984) 22, 37-46.

- (45) ScS is one composition of a broad homogeneity range with S/Sc ratio ranging from  $\sim 0.9$  to  $\sim 1.24$ . Although the exact vacancy distribution is not known for these halite-type structures, calculations suggest two types of behavior:
- for the S-rich region, vacancies at the Sc sites tend to be adjacent to each other so that there will be a mixture of 5-coordinate and 4-coordinate S atoms in addition to 6-coordinate (octahedral) S atoms;
  - for the Sc-rich region, single site vacancies at S atom sites create  $\text{Sc}_6$  octahedra clusters embedded in the halite-type crystal, so that there is a mixture of 6-coordinate and 5-coordinate Sc atoms.



- (a) Consider a fragment of NaCl-type ScS shown here. The large green spheres are S atoms; the gray and black spheres are Sc atoms. If the two black Sc atoms are removed, creating the type of vacancy described for the S-rich  $\text{Sc}_{1-x}\text{S}$  phases and assuming the S atoms have no other vacancies around them, what is the ratio of 5-coordinate to 4-coordinate S in this model?

**According to the diagram, there are 2 S atoms that bridge the two black spheres, whereas the remaining 8 S atoms do not. Therefore, upon creating vacancies at the two black sphere sites, there will be 8 5-coordinate S atoms and 2 4-coordinate S atoms, giving a ratio 8:2 = 4:1.**

- (b) Using your answer to (a), determine the fractions of 6-coordinate, 5-coordinate, and 4-coordinate S atoms in S-rich  $\text{Sc}_{1-x}\text{S}$  phases in terms of  $x$ . What is the maximum value of  $x$  allowed by this vacancy model?

**Let  $u$  = fraction of 4-coordinate S atoms,  $v$  = fraction of 5-coordinate S atoms, and  $w$  = fraction of 6-coordinate S atoms.**

**Then,  $u + v + w = 1$  and  $6(1-x) = 4u + 5v + 6w$ .**

**From (a),  $v = 4u$ , which gives the following two linear equations:  $5u + w = 1$  and  $6-6x = 24u + 6w$ .**

**Therefore,  $u = x$ ,  $v = 4x$ , and  $w = 1 - 5x$ .**

**The maximum value of  $x$  is  $1/5 = 20\%$ .**

- (c) Using the vacancy model described above for Sc-rich  $\text{ScS}_{1-y}$  phases, determine the fraction of 6-coordinate and 5-coordinate Sc atoms in  $\text{ScS}_{1-y}$ . What is the maximum value of  $y$  allowed by this vacancy model?

**Let  $u$  = fraction of 5-coordinate Sc atoms,  $v$  = fraction of 6-coordinate Sc atoms.**

**Then,  $u + v = 1$  and  $5u + 6v = 6(1-y)$ .**

**Therefore,  $u = 6y$ ,  $v = 1 - 6y$ .**

**The maximum value of  $y$  is  $1/6 = 16.7\%$ .**

- (d) If the 6 Sc atoms surrounding each S vacancy in the Sc-rich phases hold 14 valence electrons, what is the average oxidation state of the 6-coordinate Sc atoms? What is the maximum value of  $y$  allowed by this vacancy model?

**Since there are no S-S bonds in the structure, every S atom is assigned a formal oxidation state  $-2$ .**

**From (c), the fraction of 5-coordinate Sc atoms is  $6y$ . Six 5-coordinate Sc atoms form the cluster with 14 valence electrons, so that each of these Sc atoms has  $14/6 = 7/3$  valence electrons. Therefore, the oxidation state of the 5-coordinate Sc atoms is  $3 - (7/3) = +2/3$ .**

**By using charge balance:  $v_6(1 - 6y) + (2/3)(6y) = 2 - 2y$ , in which  $v_6$  = average oxidation state of the 6-coordinate Sc atoms.**

**Therefore,  $v_6 = \frac{2-4y}{1-6y}$ , so that as the S deficiency  $y$  increases, the average oxidation state of 6-coordinate Sc atoms increases. Now, since the maximum allowed oxidation state of Sc is  $+3$ , the upper limit of  $y$  set by this model is  $1/14 = 7.14\%$ .**

- (46) Gamma brasses are members of Hume-Rothery intermetallic phases that tend to follow the valence electron counting rule of having an average value of  $21/13$  valence  $s$  and  $p$  electrons per atom. Many gamma brass structures adopt the space group  $I\bar{4}3m$  (#217) and four sites in the asymmetric unit:

- (A)  $8c$  (0.11, 0.11, 0.11);      (C)  $12e$  (0.36, 0, 0);  
 (B)  $8c$  (0.33, 0.33, 0.33);      (D)  $24g$  (0.31, 0.31, 0.04).

- (a) What is the point group of the space group?

**The space group  $I\bar{4}3m$  is symmorphic. Therefore, the point group of the space group is  $\bar{4}3m = T_d$ , which has order = 24.**

- (b) What are the point group symmetries of each site in the asymmetric unit?

(A) **Sites are along one three-fold axis and mirror planes:  $3m = C_{3v}$  with order 6.**

- (B) Sites are also along one three-fold axis and mirror planes:  $3m = C_{3v}$  with order 6.  
 (C) Sites are along one  $\bar{4}$ -axis and mirror planes; the only rotation is two-fold:  $2mm = C_{2v}$  with order 6.  
 (D) Sites lie on a mirror plane:  $m = C_s$  with order 2.

**NOTE:** The product of the multiplicity of the site with the order of its point group is  $48 = 2 \times 24$ .

- (c) Gamma brass structures can be described as BCC packings of metal atom clusters. How many atoms constitute these clusters? How many atoms from each site in the asymmetric unit contribute to one cluster?

**In BCC packing, there will be 2 clusters per unit cell. Each cluster must consist of atoms corresponding to each site in the asymmetric unit. Therefore, the number of atoms in one gamma brass cluster is  $4 + 4 + 6 + 12 = 26$  atoms. Each member of the sum identifies the number of atoms from each site A, B, C, and D, respectively.**

Gamma brass structures can form in each of the following binary systems:

Ag-Cd, Au-Sn, Cu-Al, Cu-Hg, Cu-Zn, Ni-Zn, Pd-In

- (d) For each pair of elements, determine a possible gamma brass composition.

**For a given binary composition  $A_xB_y$ , and for the average valence electron composition of 21/13, there are two constraints on  $x$  and  $y$ :  $x + y = 13$  and  $v_Ax + v_By = 21$ , in which  $v_A, v_B$  are the numbers of valence  $s$  and  $p$  electrons for elements A and B, respectively.**

<b>Ag-Cd:</b>	$v_{Ag} = 1; v_{Cd} = 2 \rightarrow x = 5; y = 8.$	<b>Ag<sub>5</sub>Cd<sub>8</sub></b>
<b>Au-Sn:</b>	$v_{Au} = 1; v_{Sn} = 4 \rightarrow x = 10.33; y = 2.67.$	<b>Au<sub>10.33</sub>Sn<sub>2.67</sub> = Ag<sub>31</sub>Cd<sub>8</sub></b>
<b>Cu-Al:</b>	$v_{Cu} = 1; v_{Al} = 3 \rightarrow x = 9; y = 4.$	<b>Cu<sub>9</sub>Al<sub>4</sub></b>
<b>Cu-Hg:</b>	$v_{Cu} = 1; v_{Hg} = 2 \rightarrow x = 5; y = 8.$	<b>Cu<sub>5</sub>Hg<sub>8</sub></b>
<b>Cu-Zn:</b>	$v_{Cu} = 1; v_{Zn} = 2 \rightarrow x = 5; y = 8.$	<b>Cu<sub>5</sub>Zn<sub>8</sub></b>
<b>Ni-Zn:</b>	$v_{Ni} = 0; v_{Zn} = 2 \rightarrow x = 2.5; y = 10.5.$	<b>Ni<sub>2.5</sub>Zn<sub>10.5</sub> = Ni<sub>5</sub>Zn<sub>21</sub></b>
<b>Pd-In:</b>	$v_{Pd} = 0; v_{In} = 3 \rightarrow x = 6; y = 7.$	<b>Pd<sub>6</sub>In<sub>7</sub></b>

- (e) Assuming their crystal structures adopt the space group  $I\bar{4}3m$ , what is the composition of the gamma brass cluster in each binary system? According to your answer, can the elements be ordered or not in the cluster for each binary system?

<b>Ag<sub>5</sub>Cd<sub>8</sub>:</b>	<b>Ag<sub>10</sub>Cd<sub>16</sub>,</b>	<b>Ordered: Ag on one 8c and 12e sites; Cd on other 8c and 24g sites</b>
<b>Ag<sub>31</sub>Cd<sub>8</sub>:</b>	<b>Au<sub>20.67</sub>Sn<sub>5.33</sub>,</b>	<b>Disordered</b>
<b>Cu<sub>9</sub>Al<sub>4</sub>:</b>	<b>Cu<sub>18</sub>Al<sub>8</sub>,</b>	<b>Ordered: Cu on 12e and 24g sites; Al on both 8c sites</b>
<b>Cu<sub>5</sub>Hg<sub>8</sub>:</b>	<b>Cu<sub>10</sub>Hg<sub>16</sub>,</b>	<b>Ordered: Cu on one 8c and 12e sites; Hg on other 8c and 24g sites</b>
<b>Cu<sub>5</sub>Zn<sub>8</sub>:</b>	<b>Cu<sub>10</sub>Zn<sub>16</sub>,</b>	<b>Ordered: Cu on one 8c and 12e sites; Zn on other 8c and 24g sites</b>
<b>Ni<sub>5</sub>Zn<sub>21</sub>:</b>	<b>Ni<sub>5</sub>Zn<sub>21</sub>,</b>	<b>Disordered</b>
<b>Pd<sub>6</sub>In<sub>7</sub>:</b>	<b>Pd<sub>12</sub>In<sub>14</sub>,</b>	<b>Ordered: Pd on 24g sites; In on both 8c and 12e sites</b>

- (f) The gamma brass in the Cu-Al system adopts the space group  $P\bar{4}3m$ . What is the consequence of this change in space group regarding the composition of the gamma brass clusters in this structure?

**The space group  $P\bar{4}3m$  no longer keeps the body-centering translations. Therefore, the gamma brass clusters located at  $(0, 0, 0)$  are different from those at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ . As a result, the compositions of the two clusters must be different, because there is just one possible arrangement for a cluster composition "Cu<sub>18</sub>Al<sub>8</sub>", as given in (e). There are two ordered possibilities: (1) Cu<sub>16</sub>Al<sub>10</sub> and Cu<sub>20</sub>Al<sub>6</sub>; or (2) Cu<sub>14</sub>Al<sub>12</sub> and Cu<sub>22</sub>Al<sub>4</sub>. From experimental work, option (2) is found.**

(47)  $\text{Re}_3\text{As}_7$  adopts a cubic structure ( $cI40$ ) with space group  $Im\bar{3}m$  (#229) and  $a = 8.716 \text{ \AA}$ . There are three sites in the asymmetric unit: Re atoms at  $12e$  (0.34, 0, 0); As atoms at  $12d$  ( $\frac{1}{4}$ , 0,  $\frac{1}{2}$ ); and As atoms at  $16f$  (0.168, 0.168, 0.168).

- (a) Without knowing any details about the crystal structure of  $\text{Re}_3\text{As}_7$  while considering relative electronegativities and possible oxidation states of the components,  $\text{Re}_3\text{As}_7$  could be semiconducting. Explain why this statement is true. What does this statement imply about the nature of homoatomic and heteroatomic bonding in the compound?

**As is more electronegative than Re; the highest positive oxidation state of Re is +7, the highest negative oxidation state of As is -3. The formulation  $(\text{Re}^{7+})_3(\text{As}^{3-})_7$  is electrically neutral. Since both elements have formal closed shell configurations, this formulation of  $\text{Re}_3\text{As}_7$  could be semiconducting, i.e., nonmetallic. Furthermore, the corresponding structure should not have any homoatomic Re-Re or As-As bonds but only heteroatomic Re-As bonds.**

- (b) The crystal structure of  $\text{Re}_3\text{As}_7$  reveals that the  $12e$  and  $16f$  sites each form homoatomic dimers and every Re atom is 7-coordinate by As. What are the Re-Re and As-As distances of these dimers? What are the coordination numbers for each As atom site?

**Re atoms occupy the  $12e$  sites, which are**

$$(\pm x, 0, 0), (0, \pm x, 0), (0, 0, \pm x), (\frac{1}{2} \pm x, 0, 0), (0, \frac{1}{2} \pm x, 0), (0, 0, \frac{1}{2} \pm x).$$

**From these coordinates a Re-Re dimer is given by Re atoms at  $(x, 0, 0)$  and  $(1 - x, 0, 0)$ . Therefore, the Re-Re distance is  $(1 - 2x)a = 0.32(8.716 \text{ \AA}) = 2.79 \text{ \AA}$ .**

**As atoms in dimers occupy the  $16f$  sites, which are**

$$(\pm x, \pm x, \pm x), (\frac{1}{2} \pm x, \frac{1}{2} \pm x, \frac{1}{2} \pm x).$$

**From these coordinates an As-As dimer is given by As atoms at  $(x, x, x)$  and  $(\frac{1}{2} - x, \frac{1}{2} - x, \frac{1}{2} - x)$ . Therefore, the As-As distance is  $\sqrt{3}(\frac{1}{2} - 2x)a = 0.284(8.716 \text{ \AA}) = 2.476 \text{ \AA}$ .**

**Since each Re atom is 7-coordinate by As, then, using  $\text{Re}_3\text{As}_7$ , As is 3-coordinate by Re. The  $12d$  As sites are 3-coordinate (trigonal pyramidal), only to Re; the  $16f$  As sites are 4-coordinate (tetrahedral), 3 to Re and 1 to As.**

- (c) Consider the generic composition  $\text{M}_3\text{X}_7$  with transition metal M occupying the  $12e$  sites and main group element X occupying the  $12d$  and  $16f$  sites. If each dimer in  $\text{M}_3\text{X}_7$  is held together by one electron pair, how many valence electrons per  $\text{M}_3\text{X}_7$  formula unit may give semiconducting behavior?

**M atom in  $12e$  sites have 1 valence electron, used to form one two-center, two-electron bond.**

**X atom in  $12d$  sites have 8 valence electrons because it only shows heteroatomic M-X interactions.**

**X atom in  $16f$  sites have 7 valence electrons to form dimers isoelectronic with halogens.**

**There are  $3 \text{ } 1e^-$  M atoms,  $3 \text{ } 8e^-$  X atoms, and  $4 \text{ } 7e^-$  X atoms in  $\text{M}_3\text{X}_7$  for a total of 55 valence electrons per  $\text{M}_3\text{X}_7$  formula unit that may give semiconducting behavior because this electron count would be electron precise for the atomic structure.**

- (d)  $\text{Re}_3\text{As}_7$  is metallic. Explain this observation based upon your answer to (c). Discuss the nature of bonding in this compound.

**$\text{Re}_3\text{As}_7$  has  $3(7e^-) + 7(5e^-) = 56$  valence electrons per formula unit, which exceeds the value expected for semiconducting behavior. Therefore,  $\text{Re}_3\text{As}_7$  is metallic.**

**Most of the bonding holding this compound together is heteroatomic, polar-covalent Re-As interactions. However, due to electronegativity differences and numbers of valence electrons per atom, charge transfer from the cationic Re atoms to the anionic As atoms is not complete. If one electron pair is necessary for the Re-Re bond, then the formal oxidation state of Re is 6+. If one net bonding electron pair is necessary for the As-As bond, then the formal oxidation of As in the dimer is 2-. We can now formulate the compound as  $(\text{Re}^{6+})_3(\text{As}^{3-})_3(\text{As}^{2-})_4e^-$ , which gives one extra valence electron.**

- (e) The  $\text{Re}_3\text{As}_7$ -type structure ( $I40$ ) occurs for several transition metal tetrelides and pnictides (groups 14 and 15 elements). Semiconducting behavior has been predicted and studied for the ternary examples  $\text{Mo}_3\text{Sb}_{7-x}\text{X}_x$  and  $\text{Nb}_3\text{Sb}_{7-x}\text{X}_x$ . For each example, identify an element X in the same period of the components and the composition that should be semiconducting. Formulate the ternary compounds using relevant oxidation states.

$\text{M}_3\text{X}_7$  requires a total of 55 valence electrons for semiconducting behavior.

$\text{Mo}_3\text{Sb}_{7-x}\text{X}_x$ :  $3(6e^-) + (7-x)(5e^-) + x(v_X e^-) = 53e^- + (v_X - 5e^-)x$ .  
Therefore, X must be more electron-rich than Sb, e.g., Te or I.  
If Te, then  $x = 2$ :  $\text{Mo}_3\text{Sb}_5\text{Te}_2$ ; If I, then  $x = 1$ :  $\text{Mo}_3\text{Sb}_6\text{I}$

$\text{Nb}_3\text{Sb}_{7-x}\text{X}_x$ :  $3(5e^-) + (7-x)(5e^-) + x(v_X e^-) = 50e^- + (v_X - 5e^-)x$ .  
Therefore, X must be more electron-rich than Sb, e.g., Te or I.  
If Te, then  $x = 5$ :  $\text{Nb}_3\text{Sb}_2\text{Te}_5$ ; If I, then  $x = 2.5$ :  $\text{Nb}_3\text{Sb}_{4.5}\text{I}_{2.5}$

- (48) Isostructural compounds in both the La-Te and La-Sb systems have been studied for their potential thermoelectric properties. The two structures are cubic with space group  $I\bar{4}3d$  (#220) and there are two sites in the asymmetric unit:  $12a$  ( $\frac{3}{8}, 0, \frac{1}{4}$ ) and  $16c$  ( $\sim 0.08, \sim 0.08, \sim 0.08$ ). The lattice constants are  $a = 9.649 \text{ \AA}$  for the La-Sb compound and  $a = 9.628 \text{ \AA}$  for the La-Te compound. Neither structure shows significant homoatomic bonding.

- (a) Determine the empirical formulas for each compound. Explain your reasoning.

Binary compounds are formulated as  $\text{A}_{12}\text{B}_{16}$ , which gives the general empirical formula  $\text{A}_3\text{B}_4$ . To determine how to assign the elements to A and B, we must consider that these structures do not have significant homoatomic bonding. This statement implies that the valence electron count per formula unit is nearly closed shell.

La-Te: Compare  $\text{La}_3\text{Te}_4$  and  $\text{La}_4\text{Te}_3$ .  $\text{La}_3\text{Te}_4$  has  $3(3e^-) + 4(6e^-) = 33e^-$ , which has 1 extra valence electron beyond 4 closed shell  $\text{Te}^{2-}$ .  $\text{La}_4\text{Te}_3$  has  $4(3e^-) + 3(6e^-) = 30e^-$ , which has 6 extra valence electrons beyond 3 closed shell  $\text{Te}^{2-}$ . Therefore, the La-Te compound is  $\text{La}_3\text{Te}_4$ .

La-Sb: Compare  $\text{La}_3\text{Sb}_4$  and  $\text{La}_4\text{Sb}_3$ .  $\text{La}_3\text{Sb}_4$  has  $3(3e^-) + 4(5e^-) = 29e^-$ , which is 3 extra valence electrons short for 4 closed shell  $\text{Sb}^{3-}$ .  $\text{La}_4\text{Sb}_3$  has  $4(3e^-) + 3(5e^-) = 27e^-$ , which has 3 extra valence electrons beyond 3 closed shell  $\text{Sb}^{3-}$ .  $\text{La}_3\text{Sb}_4$  would expectedly give Sb-Sb bonds to satisfy the octet rule;  $\text{La}_4\text{Sb}_3$  distributes 3 valence electrons among 4 La atoms, which provides relatively weak La-La bonding. Therefore, the La-Sb compound is  $\text{La}_4\text{Sb}_3$ .

- (b) Determine the densities (in  $\text{g/cm}^3$ ) of each compound. Discuss their differences.

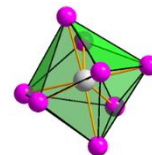
$\text{La}_3\text{Te}_4$ : Mass in one unit cell =  $[12(138.905) + 16(127.60)] / 6.022 \times 10^{23} = 6.158 \times 10^{-21} \text{ g}$   
Volume of unit cell =  $(9.628)^3 / 10^{24} = 8.925 \times 10^{-22} \text{ cm}^3$   
Density =  $6.90 \text{ g/cm}^3$

$\text{La}_4\text{Sb}_3$ : Mass in one unit cell =  $[16(138.905) + 12(121.760)] / 6.022 \times 10^{23} = 6.117 \times 10^{-21} \text{ g}$   
Volume of unit cell =  $(9.649)^3 / 10^{24} = 8.984 \times 10^{-22} \text{ cm}^3$   
Density =  $6.81 \text{ g/cm}^3$

$\text{La}_3\text{Te}_4$  is slightly denser than  $\text{La}_4\text{Sb}_3$ , which is observed by the differences in unit cell volumes because formula weights are rather close to each other. The difference in unit cell volumes reflects differences in atomic sizes and bonding strengths. Any weak La-La bonding that may occur in  $\text{La}_4\text{Sb}_3$  does not compress the structural volume significantly.

- (c) Atoms in the  $16c$  sites are 6-coordinate (distorted octahedral) to atoms in the  $12a$  sites. What is the coordination number and geometry for atoms in the  $12a$  sites?

$12\langle\text{CN}\rangle_{12a} = 16(6) = 96$ . Therefore,  $\langle\text{CN}\rangle_{12a} = 8$ -coordinate. The polyhedron is best assigned to be a bisdisphenoid.



- (d) For the space group  $I\bar{4}3d$  (#220), the  $16c$  Wyckoff sites are designated  $(x, x, x)$ , which include the origin  $(0, 0, 0)$ . What is the sphere packing obtained by placing atoms at  $(0, 0, 0)$  in this space group? What kinds of holes and what fraction are occupied by atoms in the  $12a$  sites? Determine

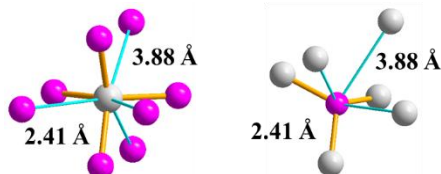
the numbers, distances (in terms of the lattice constant  $a$ ), and geometry of the 1<sup>st</sup> and 2<sup>nd</sup> nearest 16c neighbors surrounding each 12a site; also for the 12a sites surrounding each 16c site.

If the 16c sites were (0, 0, 0), then these atoms form a BCC packing.

The 12a sites occupy tetrahedral holes in the BCC packing. Because there are 12 tetrahedral holes per cubic unit cell in BCC packing, i.e., per 2 BCC atoms, 16 BCC sites generate 96 tetrahedral holes. The 12a sites occupy  $12/96 = 1/8$  of all tetrahedral holes in BCC packing.

Each 12a site has 4 nearest neighbors at 2.41 Å, forming a distorted tetrahedron, and 4 2<sup>nd</sup> nearest neighbors at 3.88 Å that sit over each face of the tetrahedron (see left-side figure).

Each 16c sites has 3 nearest neighbors at 2.41 Å and 3 2<sup>nd</sup> nearest neighbors at 3.88 Å. All 6 neighbors form a distorted trigonal antiprism (see right-side figure).



- (e) What is accomplished in the structure by shifting the atoms in site 16c from (0, 0, 0) to ( $\sim 0.08$ ,  $\sim 0.08$ ,  $\sim 0.08$ )? (See *J. Appl. Phys.* **1966**, 37, 1433-1435.)

The shift is along the body-diagonal (three-fold axis) of the cubic unit cell. As a result, the 1<sup>st</sup> and 2<sup>nd</sup> nearest neighbor distances move towards being equal. When the fractional coordinate reaches  $1/12 = 0.0833$ , then the two sets of distances are equal. Thus, the local coordination environments tend to become more regular in their shapes.

- (f) The La-Te compound is metallic and corresponds to one end of a homogeneity range. The other end is a semiconducting compound with  $a = 9.619$  Å. What chemical formula is this semiconducting La-Te compound likely to have? Discuss the coordination geometries at La and Te in this compound. What is its density (in g/cm<sup>3</sup>)?

In the La-Te system, La<sub>2</sub>Te<sub>3</sub> should be the semiconducting compound of this homogeneity range because La is a trivalent metallic element and Te is a divalent semimetallic element.

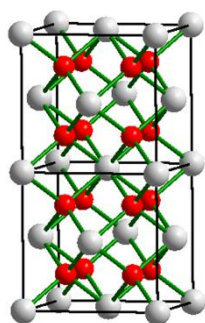
To achieve La<sub>2</sub>Te<sub>3</sub> from La<sub>3</sub>Te<sub>4</sub> with both sites fully occupied, there will be vacancies at the La (12a) sites, i.e., La<sub>3-x</sub>Te<sub>4</sub>, where  $x = 0.333$  (1/3): La<sub>2.67</sub>Te<sub>4</sub>. As a result, while the La atoms remain 8-coordinate, the Te atoms become, on average  $(8/3)(8) / 4 = 5.33$ -coordinate. For the greatest separation of vacancies in the structure, 2/3 Te will be 5-coordinate and 1/3 Te will be 6-coordinate (distorted octahedral).

La<sub>2</sub>Te<sub>3</sub>: Mass in one unit cell =  $[12(138.905) + 16(127.60)] / 6.022 \times 10^{23} = 6.158 \times 10^{-21}$  g

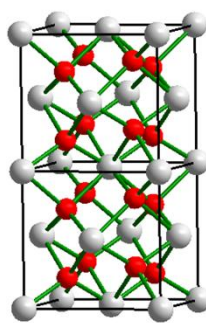
Volume of unit cell =  $(9.628)^3 / 10^{24} = 8.925 \times 10^{-22}$  cm<sup>3</sup>

Density = 6.90 g/cm<sup>3</sup>

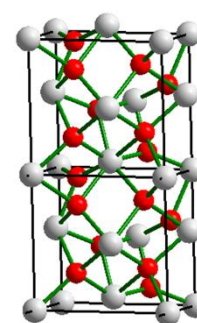
- (49) Zirconium dioxide adopts three different crystal structures with increasing temperature: (i) monoclinic baddeleyite; (ii) tetragonal zirconia; and (iii) cubic zirconia. High-temperature cubic zirconia can be stabilized by replacing some Zr atoms with Y (yttria-stabilized cubic zirconia). These figures illustrate the three crystal structures; each structure image contains 23 Zr atoms (light gray) and 16 O atoms (red). Zr–O bonds are shown in green.



**Cubic**  
 $a = 5.15 \text{ \AA}$



**Tetragonal**  
 $a = 3.72 \text{ \AA}; c = 5.12 \text{ \AA}$



**Monoclinic**  
 $a = 5.15 \text{ \AA}; b = 5.20 \text{ \AA}$   
 $c = 5.32 \text{ \AA}; \beta = 99.2^\circ$

- (a) According to these figures, what is the structure type of cubic zirconia? Identify the coordination number and geometry at Zr and O. What is the volume (in  $\text{\AA}^3$ ) of one formula unit?  
**Zr atoms form CCP arrangement with O atoms in tetrahedral holes. This form of  $\text{ZrO}_2$  is the fluorite ( $\text{CaF}_2$ ) type. Each O is 4-coordinate by Zr in a tetrahedron; each Zr is 8-coordinate by O in a cube.**

**1 unit cell is  $136.59 \text{ \AA}^3$  and contains 4 formula units. The volume of one formula unit is  $34.15 \text{ \AA}^3$ .**

- (b) How is tetragonal zirconia related to cubic zirconia? Identify the coordination number and geometry at Zr and O. What is the volume (in  $\text{\AA}^3$ ) of one formula unit?

**Tetragonal  $\text{ZrO}_2$  is closely related to cubic  $\text{ZrO}_2$ . The Zr atoms form a distorted CCP arrangement. According to the lattice constants, the cubic cell is compressed along the  $c$ -direction of the tetragonal cell ( $\sqrt{2}a = 5.26 \text{ \AA}$ ). The O atoms are shifted away from the centers of the distorted tetrahedra. Again, each O is 4-coordinate by Zr in a distorted tetrahedron; each Zr is 8-coordinate by O in a distorted cube.**

**1 unit cell is  $70.85 \text{ \AA}^3$  and contains 2 formula units. The volume of one formula unit is  $35.43 \text{ \AA}^3$ .**

- (c) How is monoclinic baddeleyite related to cubic zirconia? Identify the coordination number and geometry at Zr and O. What is the volume (in  $\text{\AA}^3$ ) of one formula unit?

**Monoclinic  $\text{ZrO}_2$  is a further distortion in which 50% of the O atoms shift away from the tetrahedron centers toward a face to become 3-coordinate. Zr atoms continue to adopt a distorted CCP arrangement. Since the other 50% of the O atoms are 4-coordinate by Zr in a distorted tetrahedron, then each Zr is 7-coordinate by O.**

**1 unit cell is  $140.64 \text{ \AA}^3$  and contains 2 formula units. The volume of one formula unit is  $35.16 \text{ \AA}^3$ .**

- (d) Cubic zirconia can be stabilized by substituting Y atoms for Zr atoms. If  $x$  = fraction of Zr atoms that are replaced by Y atoms, what is the resulting chemical formula of the compound using just the variable  $x$ ? What are the average coordination numbers of the O and the metal atoms?

**Since Y is a trivalent metal, substituting Y for tetravalent Zr will lower the O content to ensure electroneutrality:  $\text{Y}_x\text{Zr}_{1-x}\text{O}_{2-y}$ . Therefore,  $3x + 4(1-x) = 2(2-y)$ , so that  $y = x/2$ . Yttria-stabilized zirconia is formulated as  $\text{Y}_x\text{Zr}_{1-x}\text{O}_{2-x/2}$ .**

**This formulation means that the CCP arrangement contains no vacancies. Therefore, every O atom is 4-coordinate tetrahedral by metal atoms. The average coordination number of each metal atom is  $4(2-x/2) = 8-2x$ .**

- (e) Yttria ( $\text{Y}_2\text{O}_3$ ) is cubic with a density of  $\sim 5.01 \text{ g/cm}^3$ . From this information, conclude whether yttria is better described as “defect NaCl-type” or “defect  $\text{CaF}_2$ -type”. Explain your selection.

**Defect NaCl-type means that the O sites, which would adopt a CCP arrangement, are fully occupied while vacancies occur at the Y sites. One cubic unit cell contains “ $\text{Y}_{8/3}\text{O}_4$ ”, i.e., 4 O atoms with the requisite number of Y atoms. The mass of atoms in one unit cell is  $(2.67 \cdot 88.906 + 4 \cdot 15.999) / 6.022 \times 10^{23} = 5.00 \times 10^{-22} \text{ g}$ . Therefore, the volume of one unit cell is  $\sim 99.79 \text{ \AA}^3$ . The resulting lattice constant is  $\sim 4.64 \text{ \AA}$ .**

**Defect  $\text{CaF}_2$ -type means that the metal sites are fully occupied while vacancies occur at the O sites. One cubic unit cell contains “ $\text{Y}_4\text{O}_6$ ”, i.e., 4 metal atoms with the requisite number of O atoms. The mass of atoms in one unit cell is  $(4 \cdot 88.906 + 6 \cdot 15.999) / 6.022 \times 10^{23} = 7.50 \times 10^{-22} \text{ g}$ . Therefore, the volume of one unit cell is  $\sim 149.69 \text{ \AA}^3$ . The resulting lattice constant is  $\sim 5.30 \text{ \AA}$ .**

**Using the estimated lattice constants, O··O distances in the defect  $\text{CaF}_2$ - and NaCl-types are, respectively,  $2.65 \text{ \AA}$  and  $3.28 \text{ \AA}$ . These distances imply  $\text{O}^{2-}$  radii to be  $1.33 \text{ \AA}$  or  $1.64 \text{ \AA}$ . The radius estimated from the defect  $\text{CaF}_2$ -type is closer to the tabulated values of  $\text{O}^{2-}$  radii. Therefore,  $\text{Y}_2\text{O}_3$  with necessary vacancies is better described as defect  $\text{CaF}_2$ -type; it adopts the bixbyite structure.**

- (f) Yttrium oxyfluoride (YOF) adopts a distorted cubic zirconia-type structure that is rhombohedral with  $a \sim 3.80 \text{ \AA}$ ,  $c \sim 18.89 \text{ \AA}$ . What is the volume (in  $\text{\AA}^3$ ) of one formula unit? How does it compare with that of cubic zirconia?

**The volume of the unit cell is  $236.23 \text{ \AA}^3$ . Since the volume of one formula unit of  $\text{ZrO}_2$  is  $\sim 35 \text{ \AA}^3$ , then we can expect  $\sim 6$  formula units of YOF in the rhombohedral unit cell. This number makes sense because it must be a multiple of 3. Then, the volume of each YOF formula unit is  $39.37 \text{ \AA}^3$ , which is about 10% larger than that of  $\text{ZrO}_2$ . The increased size of Y as compared to Zr and changes in electrostatic interactions result in this change.**

The eight Y-anion (X) distances are  $\text{Y-X1} = 2.414 \text{ \AA}$  (3 $\times$ ),  $2.471 \text{ \AA}$  (1 $\times$ );  $\text{Y-X2} = 2.242 \text{ \AA}$  (3 $\times$ ),  $2.346 \text{ \AA}$  (1 $\times$ ). Using the bond-valence method, propose how O and F atoms are distributed on the X1 and X2 sites.

Information:  $B = 0.37 \text{ \AA}$   $d_0(\text{Y}^{\text{III}}-\text{O}) = 2.014 \text{ \AA}$   $d_0(\text{Y}^{\text{III}}-\text{F}) = 1.875 \text{ \AA}$

**Each anion is 4-coordinate to Y. Compare F on X1 and O on X2 with F on X2 and O on X1:**

$$\begin{aligned} v(\text{F} = \text{X1}) &= 3 \exp(-2.414 - 1.875/0.37) + \exp(-2.471 - 1.875/0.37) \\ &= 3(0.233) + (0.200) = 0.899 \end{aligned}$$

$$\begin{aligned} v(\text{O} = \text{X2}) &= 3 \exp(-2.242 - 2.014/0.37) + \exp(-2.346 - 2.014/0.37) \\ &= 3(0.540) + (0.408) = 2.028 \end{aligned}$$

$$\begin{aligned} v(\text{F} = \text{X2}) &= 3 \exp(-2.242 - 1.875/0.37) + \exp(-2.346 - 1.875/0.37) \\ &= 3(0.371) + (0.280) = 1.393 \end{aligned}$$

$$\begin{aligned} v(\text{O} = \text{X1}) &= 3 \exp(-2.414 - 2.014/0.37) + \exp(-2.471 - 2.014/0.37) \\ &= 3(0.339) + (0.291) = 1.308 \end{aligned}$$

**The arrangement with F on X1 and O on X2 gives atomic valences that are closer to the proper valences of F (1) and O (2) than the alternative.**

- (g) Niobium oxynitride ( $\text{NbON}$ ) is a ternary derivative of the monoclinic baddeleyite structure with lattice constants  $a = 4.98 \text{ \AA}$ ,  $b = 5.02 \text{ \AA}$ ,  $c = 5.21 \text{ \AA}$ ;  $\beta = 100.8^\circ$ . What is the volume (in  $\text{\AA}^3$ ) of one formula unit? How does it compare with that of monoclinic baddeleyite?

**The volume of the unit cell is  $127.94 \text{ \AA}^3$  and it contains 4 formula units. Then, the volume of each  $\text{NbON}$  formula unit is  $31.99 \text{ \AA}^3$ , which is about 10% smaller than that of monoclinic  $\text{ZrO}_2$ . The smaller size of Nb as compared to Zr and changes in electrostatic interactions result in this change.**

The Nb-anion (X) distances are  $\text{Nb-X1} = 2.055 \text{ \AA}$ ,  $2.087 \text{ \AA}$ ,  $2.135 \text{ \AA}$ ,  $2.167 \text{ \AA}$ ;  $\text{Nb-X2} = 1.994 \text{ \AA}$ ,  $2.066 \text{ \AA}$ ,  $2.138 \text{ \AA}$ . Using the bond-valence method, propose how N and O atoms are distributed on the X1 and X2 sites.

Information:  $B = 0.37 \text{ \AA}$   $d_0(\text{Nb}^{\text{V}}-\text{O}) = 1.911 \text{ \AA}$   $d_0(\text{Nb}^{\text{V}}-\text{N}) = 2.06 \text{ \AA}$

The X1 anion is 4-coordinate to Nb; the X2 anion is 3-coordinate to Nb. Compare O on X1 and N on X2 with O on X2 and N on X1:

$$v(\text{O} = \text{X1}) = (0.678) + (0.621) + (0.546) + (0.501) = 2.346$$

$$v(\text{N} = \text{X2}) = (1.195) + (0.984) + (0.810) = 2.989$$

$$v(\text{O} = \text{X2}) = (0.799) + (0.658) + (0.541) = 1.998$$

$$v(\text{N} = \text{X1}) = (1.014) + (0.930) + (0.817) + (0.749) = 3.51$$

The results of the bond-valence calculations give excellent agreement for the atomic valences of the 3-coordinate anion sites X2, but larger atomic valences for the 4-coordinate anion sites X1. The agreement is better for O on X1 and N on X2.

- (h) Provide a rationale for the structural differences between YOF and NbON.

The effective nuclear charges felt by the valence electrons and, thereby, electronegativities increase along the triad Y-Zr-Nb. As a result, covalency of metal-nonmetal bonding increases. Likewise, electronegativities of the anions increase along the triad N-O-F. Therefore, YOF adopts a structure with higher averaged coordination numbers at the anions and cations due to larger ionic contributions to the heteroatomic bonding than in NbON.

- (50) Clathrates are structures based upon 3-d 4-connected (tetrahedral) networks of atoms or molecules forming large cages that encapsulate atoms or small molecules. Methane hydrate is an example of a clathrate structure with O atoms of water molecules building the 3-d network and encapsulated methane molecules. The composition for the fully saturated methane hydrate solid has 1 mole methane for every 5.75 moles of water.

- (a) Write a chemical formula for fully saturated methane hydrate in the form  $(\text{CH}_4)_m(\text{H}_2\text{O})_n$ .

$$\frac{m}{n} = \frac{1}{5.75} = \frac{4}{23} : \quad (\text{CH}_4)_4(\text{H}_2\text{O})_{23}$$

- (b) What is the mass percent of methane in fully saturated methane hydrate?

$$\text{FW}(\text{methane hydrate}) = 4(16.043) + 23(18.015) = 478.517 \text{ g/mol}$$

$$\text{FW} (4 \text{ methane units}) = 4(16.043) = 64.172 \text{ g/mol}$$

$$\text{Mass percent of methane in methane hydrate} = 0.134 = 13.4\%$$

- (c) The crystal structure of methane hydrate is cubic and contains two formula units. The density of methane hydrate is approximately  $0.90 \text{ g/cm}^3$ . From this information, estimate the lattice constant for crystalline fully saturated methane hydrate.

$$\text{Mass in one unit cell} = 8(16.043) + 46(18.015) = 957.034 / 6.022 \times 10^{23} = 1.589 \times 10^{-21} \text{ g}$$

$$\text{Volume of unit cell} \sim (1.589 \times 10^{-21} \text{ g}) / (0.90 \text{ g/cm}^3) = 1.766 \times 10^{-21} \text{ cm}^3$$

$$\text{Lattice constant} = 1.209 \times 10^{-7} \text{ cm} = 12.09 \text{ \AA}$$

- (d) Consider 1.00 L of fully saturated methane hydrate solid. How many liters would the amount of methane in this solid occupy at  $0.00^\circ\text{C}$  and 1 atm?

$$1.00 \text{ L saturated methane hydrate} = 900.00 \text{ g}$$

$$\text{Mass of methane} = (0.134)(900.00 \text{ g}) = 120.6 \text{ g methane}$$

$$\# \text{ moles methane} = (120.6) / (16.043) = 7.52 \text{ moles methane in the sample}$$

$$\text{Ideal gas law: Volume} = (7.52)(0.08206)(273.15) / (1.00) = 168.5 \text{ L}$$

Clathrates also occur for binary and ternary compounds consisting of large alkali or alkaline earth metal elements **A** acting formally as cations and smaller metal or metalloid elements **X** from groups 12-15 forming the 3-d tetrahedral, formally polyanionic network. Type I clathrates of this sort adopt the space group  $Pm\bar{3}n$  with 5 atoms in the asymmetric unit: **A**<sub>1</sub> in  $2a$  (0,0,0); **A**<sub>2</sub> in  $6c$  ( $\frac{1}{4}, 0, \frac{1}{2}$ ); **X**<sub>1</sub> in  $6d$  ( $\frac{1}{4}, \frac{1}{2}, 0$ ); **X**<sub>2</sub> in  $16i$  (0.185, 0.185, 0.185); and **X**<sub>3</sub> in  $24k$  (0, 0.118, 0.308).

- (d) Explain the different symbolic components of the space group for Type I clathrates. Why does the **A**<sub>1</sub> site have multiplicity 2?

$Pm\bar{3}n$ : The point group of this space group is  $m\bar{3}m = O_h$ , so the crystal class is *cubic*.

$P$  is for a primitive *cubic* lattice.

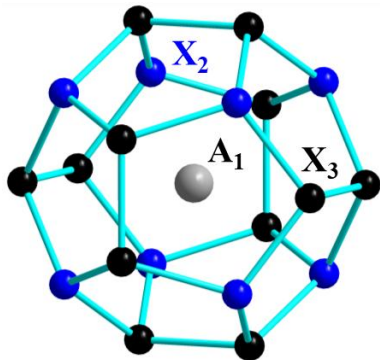
$m$  are reflections perpendicular to the  $a$ -,  $b$ -,  $c$ -axes of the cubic unit cell.

$\bar{3}$  are three-fold improper rotations with respect to the *body-diagonals* of the cubic unit cell.

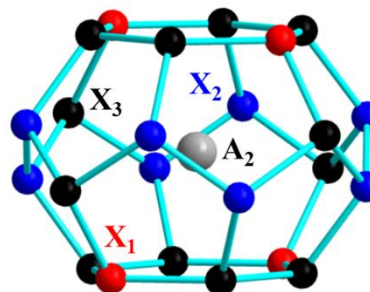
$n$  are diagonal-glide reflections perpendicular to the *face-diagonals* of the cubic unit cell.

The space group is nonsymmorphic because glide reflections are necessary operations to fully describe the space group symmetry. The diagonal glide reflections take the point  $(0, 0, 0)$  to the point  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ . Therefore, both of these points belong to the  $A_1$  site, so it has multiplicity 2.

- (f) Describe the polyhedral cages surrounding the  $A_1$  and  $A_2$  sites by determining their numbers of vertices and the types of faces. Identify the point symmetries of the  $A_1$  and  $A_2$  sites.

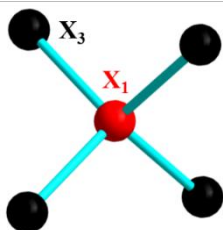


$A_1$ : Pentagonal dodecahedron constructed from 8  $X_2$  and 12  $X_3$  sites. All faces are pentagons. Point symmetry =  $m\bar{3} = T_h$ .

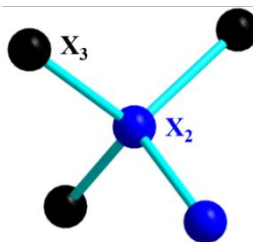


$A_2$ : 24-vertex polyhedron consisting of 2 hexagonal and 12 pentagonal faces. The 18 vertices are 4  $X_1$ , 8  $X_2$  and 12  $X_3$  sites. Point symmetry =  $4m2 = D_{2d}$ .

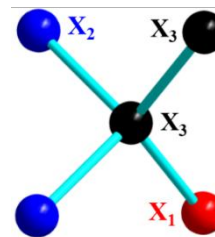
- (g) Identify the connectivities of each of the  $X$  atom Wyckoff sites within the 3-d tetrahedral network.



$X_1$ : 4-bonded to 4  $X_3$  sites



$X_2$ : 4-bonded to 1  $X_2$  + 3  $X_3$  sites



$X_3$ : 4-bonded to 1  $X_1$  + 2  $X_2$  + 1  $X_3$  sites

- (h) What is the ideal number of valence electrons in one unit cell that accounts for saturated two-center, two-electron bonds in the 4-connected tetrahedral network of  $X$  atoms? If the  $A$  atoms are a single type of alkali or alkaline earth metal, can the  $X$  atom sites be fully occupied by a single type of element and satisfy this valence electron count? Explain your answer.

The number of  $X$  atom sites in one unit cell is  $6 + 16 + 24 = 46$  atoms. Each of these atoms is 4-bonded (tetrahedral) as seen above. Therefore, the ideal number of valence electrons per atom is 4 electrons, like Si. The ideal number of valence electrons for one unit cell is  $46(4e^-) = 184e^-$ .

The number of  $A$  atom sites in one unit cell is  $2 + 6 = 8$  atoms. If every  $A$  site were an alkali ( $1e^-$ ) or alkaline earth ( $2e^-$ ) metal, then the  $X$  atom sites *cannot* be fully occupied by a single element and simultaneously satisfy  $184e^-$  per unit cell.

- (i) A binary compound with  $A = Na$  and  $X = Si$  is reported. How many valence electrons per unit cell are expected for this compound? Since Si is a group 14 element, this binary compound is expected to be metallic. How can this compound become semiconducting? Use the Zintl-Klemm

formalism of valence electron counting to explain your answer and provide formal charges for the different atoms in the compound.

The composition is  $\text{Na}_8\text{Si}_{46} = \text{Na}_4\text{Si}_{24}$ .

# valence electrons =  $8(1e^-) + 46(4e^-) = 192e^-$ , which is  $8e^-$  higher than the ideal number of  $184e^-$  valence electrons per unit cell.

To make this compound semiconducting by achieving  $184e^-$ , the number of valence electrons must be lowered from  $192e^-$  by having vacancies on either the A sites or X sites. Although  $184e^-$  can be achieved by removing all Na atoms, the outcome is not a compound but, rather, an allotrope of Si. If all Na atoms are retained, then 2 Si atom sites of 46 total per unit cell must be vacant:  $\text{Na}_8\text{Si}_{44} = \text{Na}_4\text{Si}_{22}$ .

According to the Zintl-Klemm formalism, Na atoms are considered to be  $\text{Na}^+$  cations. Therefore, a total of 8 negative charges must be distributed among 44 Si atoms. When a Si atom is removed from the tetrahedral network of X atom sites, the surrounding X sites are now 3-bonded, each of which can be assigned  $-1$  when the X atom is Si, so that it become isoelectronic with P. Two Si atom vacancies create 8  $\text{Si}^-$  neighbors and leave 36 4-bonded Si atoms with effective 0 charge:

$\text{Na}_8\text{Si}_{44} = (\text{Na}^+)_8\text{Si}_{36}(\text{Si}^-)_8$  is valence electron precise.

- (j) Ternary A-T-X Type I clathrates can exist for alkali metals A, group 12 or 13 elements T, and group 14 or 15 elements X. Using your answer to (h), determine the ideal empirical formulas for these compounds and provide one example. For each example (there are 4), write formulations of formal charges based on (i) the Zintl-Klemm scheme and (ii) relative electronegativities of the T and X elements. What are some implications of these results?

General composition is  $\text{A}_8\text{T}_u\text{X}_w$ . There are two equations that must be simultaneously satisfied:

$u + w = 46$  and  $8 + v_T u + v_X w = 184$ , in which  $v_T$  and  $v_X$  are the numbers of valence electrons for T and X. The number of valence electrons for each element is 10 fewer than the group number.

The Zintl-Klemm formalism requires every 4-bonded atom to offer 4 valence electrons.

Using relative electronegativities allows formally complete electron transfer from the electropositive to the electronegative components, but also needs to consider the connectivity of each element in the 3-d net. A good starting point is to assign the minority component its highest possible formal charge.

In general, these formulations represent two different extremes.

**T = Group 12; X = Group 14:**  $2u + 4w = 176$ . Therefore,  $u = 4$ ;  $w = 42$ , such as “ $\text{Na}_8\text{Zn}_4\text{Si}_{42}$ .”

*Zintl-Klemm:*  $\text{Na} = \text{Na}^+$ ; 4-bonded  $\text{Zn} = \text{Zn}^{2-}$ ; 4-bonded  $\text{Si} = \text{Si}^0$ . Therefore,  $(\text{Na}^+)_8(\text{Zn}^{2-})_4(\text{Si}^0)_{42}$ .

*Electronegativities:*  $\text{Na} = \text{Na}^+$ ;  $\text{Zn} = \text{Zn}^{2+}$ . Then  $(\text{Na}^+)_8(\text{Zn}^{2+})_4[\text{Si}_{42}]^{16-}$ . The average formal charge of Si is  $-0.381$ . Of 42 Si atoms, this formal charge implies a mixture of 26  $\text{Si}^0$  (4-bonded to Si) and 16  $\text{Si}^-$  (3-bonded to Si).

Zn and Si constitute, respectively, 8.7% and 91.3% of the 3-d 4-connected network. We may assume each Zn atom is connected only to Si atoms. By treating each Zn as formally  $\text{Zn}^{2+}$ , the surrounding Si atoms are 3-bonded to other Si atoms and can be assigned  $\text{Si}^-$ . In one unit cell, 4 Zn sites gives 16  $\text{Si}^-$  sites, which leave 26  $\text{Si}^0$  sites:  $(\text{Na}^+)_8(\text{Zn}^{2+})_4(\text{Si}^0)_{26}(\text{Si}^-)_{16}$ .

**T = Group 12; X = Group 15:**  $2u + 5w = 176$ . Therefore,  $u = 18$ ;  $w = 28$ , such as “ $\text{Na}_8\text{Zn}_{18}\text{As}_{28}$ .”

*Zintl-Klemm:*  $\text{Na} = \text{Na}^+$ ; 4-bonded  $\text{Zn} = \text{Zn}^{2-}$ ; 4-bonded  $\text{As} = \text{As}^+$ . Therefore  $(\text{Na}^+)_8(\text{Zn}^{2-})_{18}(\text{As}^+)_{28}$ .

*Electronegativities:*  $\text{Na} = \text{Na}^+$ ;  $\text{Zn} = \text{Zn}^{2+}$ . Then  $(\text{Na}^+)_8(\text{Zn}^{2+})_{18}[\text{As}_{28}]^{44-}$ . The average formal charge of As is  $-1.572$ . Of 28 As atoms, this formal charge implies a mixture of 12  $\text{As}^-$  (2-bonded to As) and 16  $\text{As}^{2-}$  (1-bonded to As).

Zn and As constitute, respectively, 39.1% and 60.9% of the 3-d 4-connected network. Since the 3-d net contains numerous 5-membered rings, at this concentration of Zn atoms, there must be Zn-Zn contacts. If a Zn atom has one Zn neighbor, then the formal charge of Zn is  $+1$ . As a result, the number of 2-bonded  $\text{As}^-$  sites will be larger than 12.

**T = Group 13; X = Group 14:**  $3u + 4w = 176$ . Therefore,  $u = 8$ ;  $w = 38$ , such as “ $\text{Na}_8\text{Ga}_8\text{Sn}_{38}$ .”

*Zintl-Klemm:*  $\text{Na} = \text{Na}^+$ ; 4-bonded  $\text{Ga} = \text{Ga}^-$ ; 4-bonded  $\text{Sn} = \text{Sn}^0$ . Therefore  $(\text{Na}^+)_8(\text{Ga}^-)_8(\text{Sn}^0)_{38}$ .

*Electronegativities:* Na = Na<sup>+</sup>; Ga = Ga<sup>3+</sup>. Then (Na<sup>+</sup>)<sub>8</sub>(Ga<sup>3+</sup>)<sub>8</sub>[Sn<sub>38</sub>]<sup>32-</sup>. The average formal charge of Sn is -0.842. Of 38 Sn atoms, this formal charge implies a mixture of 6 Sn<sup>0</sup> (4-bonded to Sn) and 32 Sn<sup>-</sup> (3-bonded to Sn).

Ga and Sn constitute, respectively, 17.4% and 82.6% of the 3-d 4-connected network. We may assume each Ga atom is connected only to Sn atoms. By treating each Ga as formally Ga<sup>3+</sup>, the surrounding Sn atoms are 3-bonded to other Sn atoms and can be assigned Sn<sup>-</sup>. In one unit cell, 8 Ga sites gives 32 Sn<sup>-</sup> sites, which leave 6 Sn<sup>0</sup> sites: (Na<sup>+</sup>)<sub>8</sub>(Ga<sup>3+</sup>)<sub>8</sub>(Sn<sup>0</sup>)<sub>6</sub>(Sn<sup>-</sup>)<sub>32</sub>.

**T = Group 13; X = Group 15:**  $3u + 5w = 176$ . Therefore,  $u = 27; w = 19$ , such as “Na<sub>8</sub>Ga<sub>27</sub>Sb<sub>19</sub>”.

*Zintl-Klemm:* Na = Na<sup>+</sup>; 4-bonded Ga = Ga<sup>-</sup>; 4-bonded Sb = Sb<sup>+</sup>. Therefore (Na<sup>+</sup>)<sub>8</sub>(Ga<sup>-</sup>)<sub>27</sub>(Sb<sup>+</sup>)<sub>19</sub>.

*Electronegativities:* Na = Na<sup>+</sup>; Sb = Sb<sup>3+</sup>. Then (Na<sup>+</sup>)<sub>8</sub>[Ga<sub>27</sub>]<sup>49+</sup>(Sb<sup>3+</sup>)<sub>19</sub>. The average formal charge of Ga is +1.815. Of 27 Ga atoms, this formal charge implies a mixture of 22 Ga<sup>+2</sup> (1-bonded to Ga forming Ga–Ga single bonds) and 5 Ga<sup>+1</sup> (2-bonded to Ga).

Ga and Sb constitute, respectively, 58.7% and 41.3% of the 3-d 4-connected network atoms. At these concentrations, the 3-d net will have homoatomic Ga–Ga and Sb–Sb contacts as well as heteroatomic Ga–Sb contacts in the 3-d net. Therefore, some Sb atoms will have a formal charge of 2-, which will increase the number of 2-bonded Ga to other Ga atoms in the 3-d net.

- (k) Ternary A-T-X Type I clathrates can exist for alkaline earth metals A, group 12 or 13 elements T, and group 14 or 15 elements X. Using your answer to (h), determine the ideal empirical formulas for these compounds and provide one example. For each example (there are 4), write formulations of formal charges based on (i) the Zintl-Klemm scheme and (ii) relative electronegativities of the T and X elements. What are some implications of these results?

General composition is A<sub>8</sub>T<sub>u</sub>X<sub>w</sub>. There are two equations that must be simultaneously satisfied:

$u + w = 46$  and  $16 + v_T u + v_X w = 184$ , in which  $v_T$  and  $v_X$  are the numbers of valence electrons for T and X. The number of valence electrons for each element is 10 fewer than the group number.

The Zintl-Klemm formalism requires every 4-bonded atom to offer 4 valence electrons; using relative electronegativities allows formally complete electron transfer from the electropositive to the electronegative components. These formulations represent two different extremes.

**T = Group 12; X = Group 14:**  $2u + 4w = 168$ . Therefore,  $u = 8; w = 38$ , such as “Ca<sub>8</sub>Zn<sub>8</sub>Sn<sub>38</sub>”.

*Zintl-Klemm:* Ca = Ca<sup>2+</sup>; 4-bonded Zn = Zn<sup>2-</sup>; 4-bonded Sn = Sn<sup>0</sup>. Therefore, (Ca<sup>2+</sup>)<sub>8</sub>(Zn<sup>2-</sup>)<sub>8</sub>(Sn<sup>0</sup>)<sub>38</sub>.

*Electronegativities:* Ca = Ca<sup>2+</sup>; Zn = Zn<sup>2+</sup>. Then (Ca<sup>2+</sup>)<sub>8</sub>(Zn<sup>2+</sup>)<sub>8</sub>[Sn<sub>38</sub>]<sup>32-</sup>. The average formal charge of Si is -0.842. Of 38 Sn atoms, this formal charge implies a mixture of 6 Sn<sup>0</sup> (4-bonded to Sn) and 32 Sn<sup>-</sup> (3-bonded to Sn).

Zn and Sn constitute, respectively, 17.4% and 82.6% of the 3-d 4-connected network. We may assume each Zn atom is connected only to Sn atoms. By treating each Zn as formally Zn<sup>2+</sup>, the surrounding Sn atoms are 3-bonded to other Sn atoms and can be assigned Sn<sup>-</sup>. In one unit cell, 8 Zn sites gives 32 Sn<sup>-</sup> sites, which leave 6 Sn<sup>0</sup> sites: (Ca<sup>2+</sup>)<sub>8</sub>(Zn<sup>2+</sup>)<sub>8</sub>(Sn<sup>0</sup>)<sub>6</sub>(Sn<sup>-</sup>)<sub>32</sub>.

**T = Group 12; X = Group 15:**  $2u + 5w = 168$ . Therefore,  $u = 20.67; w = 25.33$ ,

such as “Sr<sub>8</sub>Cd<sub>20.67</sub>Sb<sub>25.33</sub>”.

*Zintl-Klemm:* Sr = Sr<sup>2+</sup>; 4-bonded Cd = Cd<sup>2-</sup>; 4-bonded Sb = Sb<sup>+</sup>.

Therefore (Sr<sup>2+</sup>)<sub>8</sub>(Cd<sup>2-</sup>)<sub>20.67</sub>(Sb<sup>+</sup>)<sub>25.33</sub>.

*Electronegativities:* Na = Na<sup>+</sup>; Cd = Cd<sup>2+</sup>. Then (Sr<sup>2+</sup>)<sub>8</sub>(Cd<sup>2+</sup>)<sub>20.67</sub>[Sb<sub>25.33</sub>]<sup>57.33-</sup>. The average formal charge of Sb is -2.263. Of 25.33 Sb atoms, this formal charge implies a mixture of 18.67 Sb<sup>2-</sup> (1-bonded to Sb) and 6.67 Sb<sup>3-</sup> (0-bonded to Sb).

Cd and Sb constitute, respectively, 44.9% and 55.1% of the 3-d 4-connected network. Since the 3-d net contains numerous 5-membered rings, there must be Cd–Cd contacts for which each Cd is assigned a formal charge +1. As a result, there will be fewer than 6.67 Sb<sup>3-</sup> in the unit cell.

**T = Group 13; X = Group 14:**  $3u + 4w = 168$ . Therefore,  $u = 16; w = 30$ , such as “Ca<sub>8</sub>Al<sub>16</sub>Ge<sub>30</sub>”.

*Zintl-Klemm:* Ca = Ca<sup>2+</sup>; 4-bonded Al = Al<sup>-</sup>; 4-bonded Ge = Ge<sup>0</sup>. Therefore (Ca<sup>2+</sup>)<sub>8</sub>(Al<sup>-</sup>)<sub>16</sub>(Ge<sup>0</sup>)<sub>30</sub>.

*Electronegativities:* Ca = Ca<sup>2+</sup>; Al = Al<sup>3+</sup>. Then (Ca<sup>2+</sup>)<sub>8</sub>(Al<sup>3+</sup>)<sub>16</sub>[Ge<sub>30</sub>]<sup>64-</sup>. The average formal charge of Ge is -2.133. Of 30 Ge atoms, this formal charge implies a mixture of 26 Ge<sup>2-</sup> (2-bonded to Ge) and 4 Ge<sup>3-</sup> (1-bonded to Ge).

Al and Ge constitute, respectively, 34.7% and 65.3% of the 3-d 4-connected network. At this concentration of Al atoms, there must be Al–Al contacts, so that some Al atoms will adopt a formal charge +2. As a result, the number of  $\text{Ge}^{3-}$  will be lower than 4.

**T = Group 13; X = Group 15:**  $3u + 5w = 168$ . Therefore,  $u = 31; w = 15$ , such as “ $\text{Sr}_8\text{Ga}_{31}\text{Sb}_{15}$ ”.

*Zintl-Klemm:*  $\text{Ca} = \text{Ca}^{2+}$ ; 4-bonded  $\text{Ga} = \text{Ga}^-$ ; 4-bonded  $\text{Sb} = \text{Sb}^+$ . Therefore  $(\text{Ca}^{2+})_8(\text{Ga}^-)_{31}(\text{Sb}^+)_{15}$ .

*Electronegativities:*  $\text{Ca} = \text{Ca}^{2+}$ ;  $\text{Sb} = \text{Sb}^{3-}$ . Then  $(\text{Ca}^{2+})_8[\text{Ga}_{31}]^{29+}(\text{Sb}^{3-})_{15}$ . The average formal charge of Ga is +0.935. Of 31 Ga atoms, this formal charge implies a mixture of 2  $\text{Ga}^0$  (3-bonded to Ga) and 29  $\text{Ga}^+$  (2-bonded to Ga).

Ga and Sb constitute, respectively, 67.4% and 32.6% of the 3-d 4-connected network atoms. There are most likely homoatomic Sb–Sb contacts which creates  $\text{Sb}^{2-}$  sites and lowers the number of 2-bonded  $\text{Ga}^+$  sites.

The various predicted compositions of A-T-X Type I clathrates are typically not well aligned with the different sites of the asymmetric unit, which means that some or all of the T/X sites must be mixed occupied, on average, over several unit cells. As a result, superstructures or other clathrate structures may be preferred if the predicted composition exists.