

SourcesU. Müller, *Inorganic Structural Chemistry*, John Wiley & Sons, Chichester, England, 1993A.R. West, *Basic Solid State Chemistry*, 2nd 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/cm³) of the following allotropes of carbon. Briefly discuss the variation in these values.

Graphite-2H	<i>hP4</i>	$a = 2.464 \text{ \AA}$, $c = 6.711 \text{ \AA}$, $\gamma = 120^\circ$
Graphite-3R	<i>hR2</i>	$a = 3.635 \text{ \AA}$, $\alpha = 39.82^\circ$ (Primitive cell)
Diamond	<i>cF8</i>	$a = 3.567 \text{ \AA}$
Buckminsterfullerene	<i>cF240</i>	$a = 14.16 \text{ \AA}$

- (2) Calculate the densities (in g/cm³) and average molar volumes (L/mol) for the following sequence of 5th period elements at 298 K. Discuss any trends you see in the results.

Ag (<i>cF4</i>)	$a = 4.0863 \text{ \AA}$		
Cd (<i>hP2</i>)	$a = 2.9794 \text{ \AA}$,	$c = 5.6186 \text{ \AA}$,	$\gamma = 120^\circ$
In (<i>tI2</i>)	$a = 3.2509 \text{ \AA}$,	$c = 4.9474 \text{ \AA}$	
Sn (<i>tI4</i>)	$a = 5.8318 \text{ \AA}$,	$c = 3.1819 \text{ \AA}$	
Sb (<i>hR6</i>)	$a = 4.3084 \text{ \AA}$,	$c = 11.2740 \text{ \AA}$	$\gamma = 120^\circ$
Te (<i>hP3</i>)	$a = 4.457 \text{ \AA}$,	$c = 5.929 \text{ \AA}$	$\gamma = 120^\circ$
I (<i>oS8</i>)	$a = 7.255 \text{ \AA}$, $b = 4.795 \text{ \AA}$,	$c = 9.780 \text{ \AA}$	

- (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/cm³) and the coordination environment of the atom. Discuss how each structure compares to one of HCP, CCP, or BCC.

Cd (<i>hP2</i>)	$a = 2.979 \text{ \AA}$, $c = 5.619 \text{ \AA}$, $\gamma = 120^\circ$;	Cd atoms at $(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$ and $(\frac{2}{3}, \frac{1}{3}, \frac{3}{4})$.
Hg (<i>hR3</i>)	$a = 3.458 \text{ \AA}$, $c = 6.684 \text{ \AA}$, $\gamma = 120^\circ$;	Hg atoms at $(0,0,0)$, $(\frac{2}{3}, \frac{1}{3}, \frac{1}{3})$ and $(\frac{1}{3}, \frac{2}{3}, \frac{2}{3})$.
In (<i>tI2</i>)	$a = 3.251 \text{ \AA}$, $c = 4.947 \text{ \AA}$;	In atoms at $(0,0,0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.
Pa (<i>tI2</i>)	$a = 3.925 \text{ \AA}$, $c = 3.238 \text{ \AA}$;	Pa atoms at $(0,0,0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.
Zn (<i>hP2</i>)	$a = 2.659 \text{ \AA}$, $c = 4.937 \text{ \AA}$, $\gamma = 120^\circ$;	Zn atoms at $(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$ and $(\frac{2}{3}, \frac{1}{3}, \frac{3}{4})$.

- (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, α -Mn (*cI58*) \rightarrow β -Mn (*cP20*); (2) at 1373 K, β -Mn (*cP20*) \rightarrow γ -Mn (*cF4*, FCC); and (3) at 1411 K, γ -Mn (*cF4*, FCC) \rightarrow δ -Mn (*cI2*, BCC).

- (a) At 1000 K, the lattice constants for α -Mn and β -Mn are, respectively, 9.092 \AA and 6.477 \AA . Evaluate their densities (in g/cm³) and molar volumes (in L/mol). Determine the change in molar volume at the transition temperature of 1000 K.
- (b) At 1519 K, the lattice constant for δ -Mn is 3.092 \AA and density of Mn(*l*) is 5.95 g/cm^3 . Evaluate the density (in g/cm³) of δ -Mn and molar volumes (in L/mol) of δ -Mn and Mn(*l*) at 1519 K. Determine the change in molar volume at the melting point.

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) $a_1 = 3.00 \text{ \AA}$, $a_2 = 2.68 \text{ \AA}$, $\alpha_3 = 63.44^\circ$ (d) $a_1 = 3.50 \text{ \AA}$, $a_2 = 5.32 \text{ \AA}$, $\alpha_3 = 48.81^\circ$
 (b) $a_1 = 4.00 \text{ \AA}$, $a_2 = 8.94 \text{ \AA}$, $\alpha_3 = 153.43^\circ$ (e) $a_1 = 3.50 \text{ \AA}$, $a_2 = 7.94 \text{ \AA}$, $\alpha_3 = 160.89^\circ$
 (c) $a_1 = 3.46 \text{ \AA}$, $a_2 = 9.16 \text{ \AA}$, $\alpha_3 = 160.89^\circ$
- (6) Considering the geometry and symmetry of various crystallographic lattices:
- (a) Explain why there is no body-centered hexagonal lattice.
 (b) Show that face-centered (*F*) and body-centered (*I*) tetragonal lattices are the same lattice.
 (c) Show that base-centered (*C*) and body-centered (*I*) monoclinic lattices are the same lattice.
 (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 α .
- (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.
- (a) $P 1 2_1/a 1$ (d) $I 2_1/b 2_1/c 2_1/a$ (g) $P 3 m 1$ (j) $P 6_3/m 2/m 2/c$
 (b) $C 1 2/m 1$ (e) $I 4_1$ (h) $P \bar{3} 2/m 1$ (k) $F 2/m \bar{3}$
 (c) $P n a 2_1$ (f) $I 4_1/a 2/m 2/d$ (i) $P \bar{6} 2 m$ (l) $F 4_1/d \bar{3} 2/m$
- (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 \AA) in crystalline iodine?
 (c) How many I_2 molecules are there in one unit cell?
 (d) What is the density (in g/cm^3) of crystalline iodine?
 (e) What is the point symmetry of each I_2 molecule in the crystal?
- (9) WOBr_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).
 (b) What is the point symmetry of the WOBr_4 molecule in the crystal and what would the point symmetry be in the gas phase? Explain any differences.

- (10) CaC_2 and 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:



- (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 $(\frac{1}{2}, 0, \frac{1}{2})$.

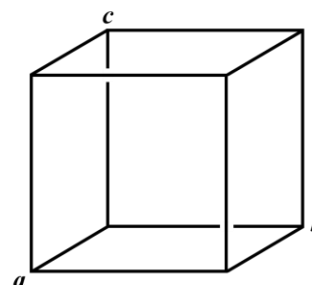
- Determine the empirical formula of this compound;
- Calculate the density (in g/cm^3) of this compound;
- For each atom in the asymmetric unit, determine all first-, second-, and third-nearest neighbors, i.e., determine the coordination polyhedron for each site.
- Draw the planes of atoms at $z = 0$ and $z = \frac{1}{2}$ for four contiguous unit cells. Label the atoms.
- Draw the (110) plane of atoms for four contiguous unit cells. Label the atoms.

- (12) A compound of lanthanum (gadolinium) and carbon adopts a cubic unit cell, $a = 8.817(3) \text{ \AA}$ ($8.322(1) \text{ \AA}$), 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 $(0.300, 0, \frac{1}{4})$.

- Determine the empirical formula of this compound.
- What is the density (in g/cm^3) of this compound?
- 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.)
- Each C atom is 6-coordinate with La. What is the coordination number for La by C?
- 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.
- Write an ionic formulation for this compound, using the appropriate cation and anion. Explain your assignments of oxidation numbers to lanthanum and carbon.

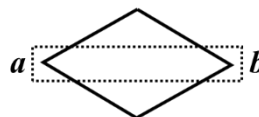
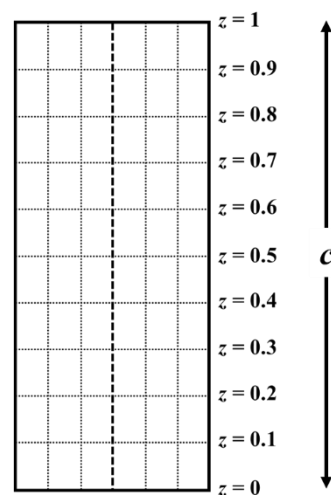
- (13) An important intermetallic compound involves a combination of titanium and antimony. Its space group is $Pm\bar{3}n$ (#223) with a lattice constant $a = 5.218 \text{ \AA}$ at ambient conditions. The asymmetric unit has antimony atoms at $2a$ sites and titanium atoms at $6c$ sites.

- Use the accompanying grid of a unit cell to sketch a projection of the structure. Use filled circles \bullet for Sb and open circles \circ for Ti.
- Determine the empirical formula of this compound.
- Calculate the density (in g/cm^3) of this compound at ambient conditions.
- Describe the coordination environments at the Sb and Ti atoms.
- 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?



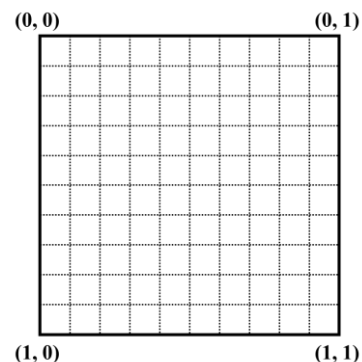
- (14) A compound of cobalt and arsenic adopts a cubic structure with space group $Im\bar{3}$ (#204) and lattice constant $a = 8.195(3) \text{ \AA}$ at ambient temperature. The asymmetric unit has cobalt at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ and arsenic at $(0, 0.1503, 0.3401)$.
- Determine the empirical formula of this compound.
 - How many formula units are there in one unit cell?
 - What is the density (in g/cm^3) of this compound?
 - 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?

- (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.



This projection, which is the above grid rotated by 90° , is to help you locate atoms in the grid.

- (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.



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?
- (a) ... *ABACBC* ... (d) ... *ABABAC* ...
 (b) ... *ABCAB* ... (e) ... *ABCBABCAB* ...
 (c) ... *ABCBCAB* ... (f) ... *ABABACABC* ...
- (18) Write the ...*ABC*... notation for each of the following progressions of close-packed planes of atoms. How many planes constitute one unit cell?
- (a) ... *hcc* ... (d) ... *hhchc* ...
 (b) ... *hhcc* ... (e) ... *hcchc* ...
 (c) ... *hhhc* ... (f) ... *hcchhc* ...
- (19) Consider the following percent environments of close-packed planes of atoms. Write the Jagodzinski symbol and the corresponding ... *ABC* ... notation for three possible solutions:
- (a) 25% HCP, 75% CCP (d) 67% HCP, 33% CCP
 (b) 40% HCP, 60% CCP (e) 75% HCP, 25% CCP
 (c) 43% HCP, 57% CCP (f) 55% HCP, 45% CCP

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

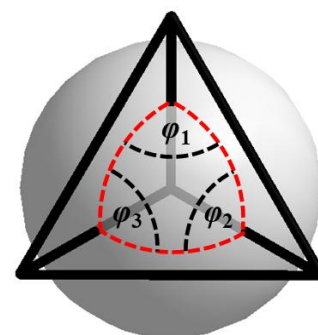
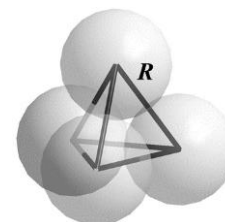
Helpful geometrical relations:

Volume of a Pyramid = $\frac{1}{3} A h$ (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)

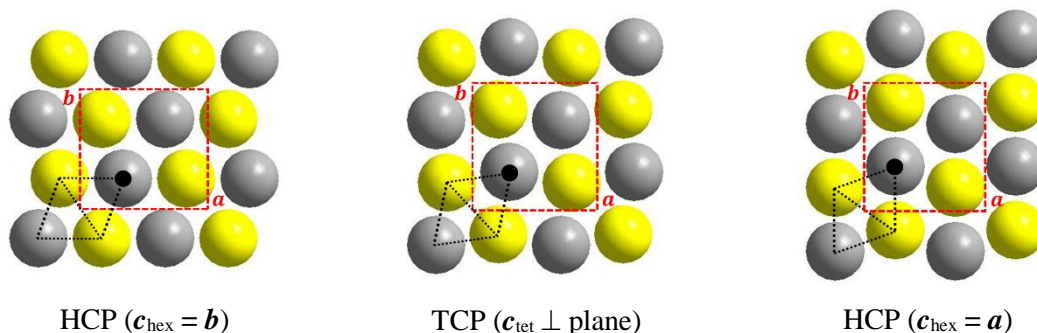
$A' = \varphi_1 + \varphi_2 + \varphi_3 - \pi$; $\varphi_1, \varphi_2, \varphi_3$ are the interior angles of the spherical triangle;
 R = radius of the sphere.

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.



- (21) Evaluate the packing efficiencies using equally sized spheres for:
- (a) Face-centered cubic packing (d) Body-centered tetragonal packing
 (b) Hexagonal close packing (e) Simple hexagonal packing
 (c) Body-centered cubic (f) Simple cubic packing
- (22) Consider the 3-d sphere packing sequence ...*AABB*... . What is the coordination number for each sphere in this packing? Evaluate the packing efficiency using equally sized spheres.

- (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 φ 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 $Pnmm$.
- (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.
- (c) Let R = radius of each sphere that just touch in these sphere packings. In terms of the angle φ , 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:
- $$a = \left[\left(1 + \frac{1}{\sqrt{2}} \right) \cos \varphi - \left(1 - \frac{1}{\sqrt{2}} \right) \sin \varphi \right] (2R);$$
- $$b = \left[\left(1 + \frac{1}{\sqrt{2}} \right) \cos \varphi + \left(1 - \frac{1}{\sqrt{2}} \right) \sin \varphi \right] (2R);$$
- $$c = 2R.$$
- (d) Evaluate the packing efficiency η as a function of φ . For which angle(s) φ is the packing efficiency the highest; the lowest?
- (e) Determine the fractional coordinates of the sphere marked by the black dot in the figures above.
- (f) What is the polyhedron that surrounds the body-centered point $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ of the unit cell?
- (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.

- | | |
|------------------------|--------------------|
| (a) Tetrahedron | (d) Trigonal prism |
| (b) Trigonal bipyramid | (e) Cube |
| (c) Octahedron | (f) Icosahedron |

- (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.

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.

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?
 (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.

- (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 ...

- (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
... [ABC] <i>c</i> ...	7.604
... [ABCACB] ...		
	... <i>hchcc</i> ...	
	... <i>hchccc</i> ...	
... [ABACABC] ...		
	... <i>hccc</i> ...	

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

Atomic and Ionic Sizes

- (28) β -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.
- 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.
 - 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.
 - Use the following sequence of CCP Cu-Zn alloys, α -Cu_{0.95}Zn_{0.05} ($a = 3.6187 \text{ \AA}$), α -Cu_{0.75}Zn_{0.25} ($a = 3.6669 \text{ \AA}$), and α -Cu_{0.64}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).
 - Use your answers to (a) and (b) as well as to (a) and (c) to estimate the lattice constant (in Å) of β -brass (CuZn).
- (29) α -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, $\frac{1}{4}$).
- Draw projections of the structure along the a -, b -, and c -directions. From these diagrams, identify the type of sphere packing the structure of α -U most closely resembles.
 - Determine the coordination environment for the U atom and evaluate the interatomic distances.
 - Estimate the metallic radius of 12-coordinate U from this information.
 - Using your answer in (c), what is the packing efficiency?

(30) An ammonium halide, NH_4X , adopts the CsCl-type structure at room temperature, $a = 4.059 \text{ \AA}$, and transforms to the NaCl-type structure at 138°C , $a = 6.867 \text{ \AA}$. (From West)

- The density of the room temperature polymorph is 2.431 g/cm^3 . Identify the substance.
- Calculate the percent difference in molar volume between the high-temperature NaCl-type and room-temperature CsCl-type polymorphs. Ignore any thermal expansion effects.
- Assuming an effective radius of 1.50 \AA 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?

(31) In crednerite CuMnO_2 , the Cu–O distance is 1.835 \AA (2 \times) and the Mn–O distances are 1.928 \AA (4 \times) and 2.260 \AA (2 \times). Use the bond-valence method to determine the formulation of this compound.

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

(32) Two different forms of CuVO_3 have been prepared at high pressure. In rhombohedral CuVO_3 , the Cu–O distances are 2.039 \AA (3 \times) and 2.241 \AA (3 \times) and the V–O distances are 1.788 \AA (3 \times) and 2.073 \AA (3 \times). In triclinic CuVO_3 , the different bond distances are:

Cu–O: 1.984 \AA , 2.009 \AA , 2.103 \AA , 2.148 \AA , 2.161 \AA , 2.372 \AA ;
V–O: 1.776 \AA , 1.789 \AA , 1.814 \AA , 2.071 \AA , 2.079 \AA , 2.079 \AA .

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

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

(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 \AA , 1.982 \AA , and 2.337 \AA ; the O2–Mn distances are 1.881 \AA , 1.893 \AA , and 2.213 \AA . Use the bond-valence method to identify which O atom site is hydroxide.

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

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 $tR30$: $a = 4.764 \text{ \AA}$, $c = 13.009 \text{ \AA}$, $\gamma = 120^\circ$.

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

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 $a = 7.9382(1) \text{ \AA}$.

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

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 $hP30$: $a = 6.438 \text{ \AA}$, $c = 17.898 \text{ \AA}$, $\gamma = 120^\circ$.

- What is the fraction of tetrahedral holes occupied by Al ions in the HCP array of sulfide ions?
- 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?
- What is the density (in g/cm^3) of $\alpha\text{-Al}_2\text{S}_3$ at room temperature?

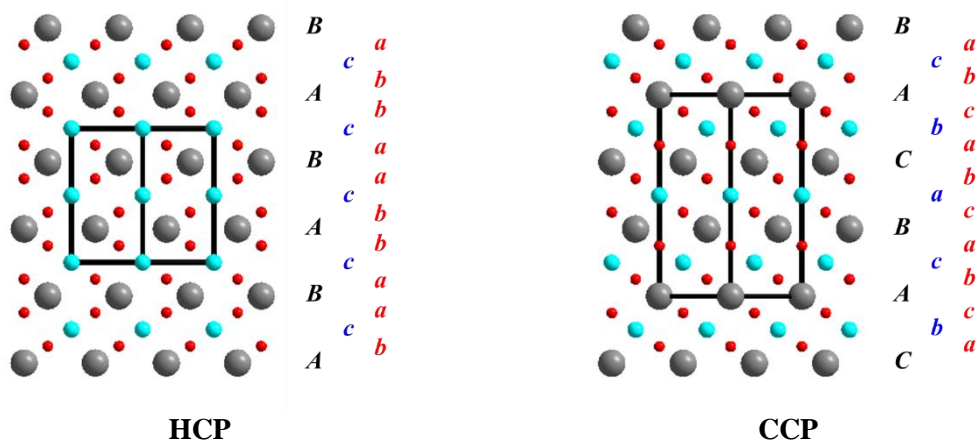
MgSiO_3 can be prepared under high pressure in the ilmenite-type structure, which is a ternary variant of $\alpha\text{-Al}_2\text{O}_3$. This crystal structure is metastable at ambient conditions and adopts a trigonal unit cell, Pearson symbol $tR30$: $a = 4.728 \text{ \AA}$, $c = 13.559 \text{ \AA}$, $\gamma = 120^\circ$.

- What is the density (in g/cm^3) of ilmenite-type MgSiO_3 at room temperature and pressure?

The preferred structure of 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.

- How many octahedral and tetrahedral holes are occupied in one unit cell?
- What is the average coordination number at the O atoms by Mg and Si atoms?
- One diffraction study reports the unit cell volume to be 834.76 \AA^3 . What is the density (in 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.

- (35) Important classes of metal(III) oxides M_2O_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 $\cdots ABC \cdots$ notation:



Consider the following three scenarios leading to M_2O_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.

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.

- (36) An important class of complex oxides is based on a quaternary compound in the Mg-Al-Si-O system that contains 24 separated $[\text{SiO}_4]^{4-}$ molecular ions in a cubic unit cell with $a = 11.459 \text{ \AA}$. 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,

- (a) Determine the empirical formula of the compound.
- (b) Determine the coordination numbers of Mg and Al atoms by oxide ions.
- (c) Estimate the density (in g/cm^3) of the compound.

- (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
- (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.

(38) 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 \AA ($2\times$); $M(\text{oct})\text{--O} = 1.9842 \text{ \AA}$ ($2\times$) and 2.0487 \AA ($4\times$).

- What fractions of octahedral and tetrahedral holes are occupied in the CCP oxide array?
- What are likely coordination geometries at the oxide ions?
- 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 CrVO_4 . By considering the brief structural description, identify the likelihood of each formulation. Explain your assignments.
- Use the Bond-Valence Method to assess which formulation is the best choice for CrVO_4 .

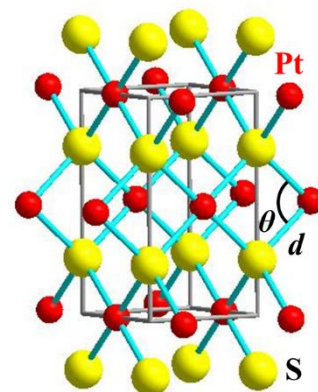
Information: $B = 0.37 \text{ \AA}$

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

- 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_4 . How do these results compare with your conclusions in parts (c) and (d)?

(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 θ .

- Express the lattice constants a and c and unit cell volume in terms of the parameters d and θ .
- Determine the maximum and minimum unit cell volume for fixed d . What is the significance of these two extreme volumes?
- 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 θ for PtS.
- Using $d(\text{Pt--S})$ from (c), evaluate the lattice constants for the case of square planar coordinated Pt; for ideally tetrahedrally coordinated S.



- (40) Uranium carbides and nitrides are classes of metallic compounds useful as nuclear fuels and show 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)
UN:	$Fm\bar{3}m$,	$a = 4.89 \text{ \AA}$,	U at (0, 0, 0), N at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$)
U_2N_3 :	$P\bar{3}m1$,	$a = 3.70 \text{ \AA}$, $c = 5.83 \text{ \AA}$,	U at ($\frac{1}{3}$, $\frac{2}{3}$, 0.255), N1 at (0, 0, 0), N2 at ($\frac{1}{3}$, $\frac{2}{3}$, 0.655)
UN_2 :	$Fm\bar{3}m$,	$a = 5.30 \text{ \AA}$,	U at (0, 0, 0), N at ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$)

- (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.
- (b) Calculate the densities (in g/cm^3) 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.
- (c) UC_2 is C deficient, i.e., $\sim UC_{1.8}$. 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?
- (d) N-rich uranium sesquinitride U_2N_{3+x} adopts a cubic structure, space group $Ia\bar{3}$, $a = 10.628 \text{ \AA}$. The asymmetric unit is U1 at (0, 0, 0), U2 at (0.271, 0, $\frac{1}{4}$), 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_2N_3 ? Why do you think the structure type changes upon nitrogen doping? Discuss possible changes in oxidation state at U atoms from U_2N_3 to U_2N_{3+x} .
- (41) The BCC packing of atoms involves a cubic unit cell of side a with atoms at (0,0,0) and ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$). 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?
- (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?
- (c) For ideal BCC packing, what is the optimal radius ratio for spheres filling an “octahedral” hole?
- (d) For ideal BCC packing, what is the optimal radius ratio for spheres filling an “tetrahedral” hole?
- (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?
- (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?

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 has been studied as a hydrogen storage material.

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

- (42) An early report of “NbF₃” was, in fact, a range of oxyfluorides with variable proportions of anions, NbO_xF_y. The structural framework closely resembles the cubic ReO₃-type structure, but with disordered arrangements of O and F atoms. The ReO₃-type structure has space group $Pm\bar{3}m$ with Re atoms at $1a$ sites (0,0,0) and O atoms at $3d$ sites ($\frac{1}{2},0,0$).

Assume NbO_xF_y adopts a *defect-free* ReO₃-type structure, i.e., no anion or cation vacancies.

- Write the chemical formula of NbO_xF_y using the single stoichiometric variable x . What is the allowed range of x ?
- Which of these formulations in part (a) give integral oxidation states for Nb?
- 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.

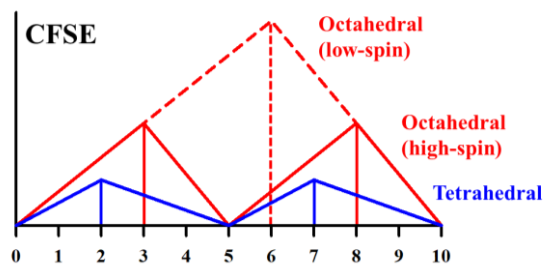
Now, assume NbO_xF_y allows defects at just at the anion sites, but all cation sites are fully occupied and the oxidation state of Nb remains fixed at Nb(III).

- Write the chemical formula of NbO_xF_y using just the single stoichiometric variable x . What is the allowed range of x ?
- Which of these formulations in (d) give integral average coordination numbers at Nb atoms?
- 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.
- To maintain its structural stability, the ReO₃-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 NbO_xF_y? For this composition, what are the most probable coordination environments at the Nb atoms? (Be specific concerning arrangement of ligands.)

“BiF₃” (in the anti-Li₃Bi structure) also involves oxyfluorides BiO_xF_y.

- Which of the two models described above for NbO_xF_y, i.e., defect-free or anion defects, is *better suited* for BiO_xF_y? Explain your selection. What types of environments surround Bi in this anti-Li₃Bi-type structure for your choice of model?

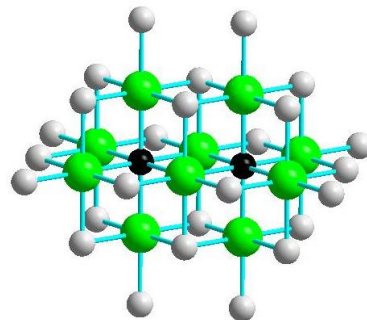
- (43) The spinel-type structure occurs for numerous oxides formulated as A^{II}B^{III}₂O₄ in which the cations A and B occupy tetrahedral and octahedral voids of a CCP array of oxide ions. “Normal” spinels have the divalent metal in tetrahedral holes and the trivalent metals in octahedral holes. “Inverse” 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 Mn₃O₄, Fe₃O₄, and Co₃O₄.



- (44) The structure of wüstite, iron(II) oxide, is halite-type (*cF8*) but iron deficient Fe_{1-x}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.
- Determine an expression for the density (in g/cm^3) of Fe_{1-x}O in terms of x and a (in \AA), the length of an edge of the halite-type unit cell, assuming there are vacancies on Fe sites only.
 - Determine an expression for the density (in g/cm^3) of FeO_{1+y} in terms of y and a (in \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.
 - For a wüstite sample analyzed to be $\text{Fe}_{0.93}\text{O}$ with $a = 4.312 \text{ \AA}$, calculate the densities (in g/cm^3) for each model in (a) and (b).
 - Assuming that $a = 4.312 \text{ \AA}$ and a density difference of 0.1 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 FeO ?
 - Mössbauer spectroscopy indicates the presence of Fe(II) and Fe(III) in Fe_{1-x}O . What are the molar fractions of Fe(II) and Fe(III) relative to O in this system?
 - Fe(III) can occupy tetrahedral holes rather than octahedral holes in oxide close packings. In Fe_{1-x}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 Fe_{1-x}O occupy tetrahedral holes?

- (45) ScS is one composition of a broad homogeneity range with S/Sc ratio ranging from ~ 0.9 to ~ 1.24 . Although the exact vacancy distribution is not known for these halite-type structures, calculations suggest two types of behavior: (i) 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; (ii) for the Sc-rich region, single site vacancies at S atom sites create Sc_6 octahedra clusters embedded in the halite-type crystal, so that there is a mixture of 6-coordinate and 5-coordinate Sc atoms.

- 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 Sc_{1-x}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?
- Using your answer to (a), determine the fractions of 6-coordinate, 5-coordinate, and 4-coordinate S atoms in S-rich Sc_{1-x}S phases in terms of x . What is the maximum value of x allowed by this vacancy model?
- Using the vacancy model described above for Sc-rich ScS_{1-y} phases, determine the fraction of 6-coordinate and 5-coordinate Sc atoms in ScS_{1-y} . What is the maximum value of y allowed by this vacancy model?
- 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?



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

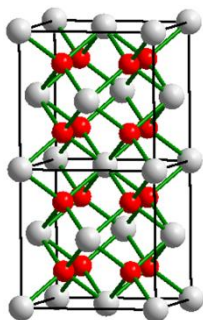
Gamma brass structures can form in each of the following binary systems:

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

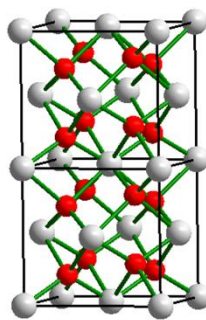
- (d) For each pair of elements, determine a possible gamma brass composition.
(e) Assuming their crystal structures adopt the space group $I\bar{4}3m$, what is the composition of the gamma brass cluster in each binary system? According to your answer, can the elements be ordered or not in the cluster for each binary system?
(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?
- (47) Re_3As_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 Re_3As_7 while considering relative electronegativities and possible oxidation states of the components, Re_3As_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?
(b) The crystal structure of Re_3As_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?
(c) Consider the generic composition M_3X_7 with transition metal M occupying the $12e$ sites and main group element X occupying the $12d$ and $16f$ sites. If each dimer in M_3X_7 is held together by one electron pair, how many valence electrons per M_3X_7 formula unit may give semiconducting behavior?
(d) Re_3As_7 is metallic. Explain this observation based upon your answer to (c). Discuss the nature of bonding in this compound.
(e) The Re_3As_7 -type structure ($cI40$) 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.

- (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.
- Determine the empirical formulas for each compound. Explain your reasoning.
 - Determine the densities (in g/cm^3) of each compound. Discuss their differences.
 - 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?
 - 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 1st and 2nd nearest $16c$ neighbors surrounding each $12a$ site; also for the $12a$ sites surrounding each $16c$ site.
 - 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 La-Te compound is metallic and corresponds to one end of a homogeneity range. The other end is a semiconducting compound with $a = 9.619 \text{ \AA}$. 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^3)?

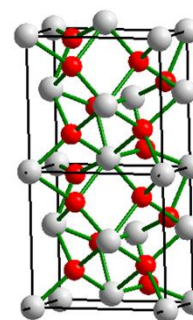
- (49) Zirconium dioxide adopts three different crystal structures with increasing temperature: (i) monoclinic baddeleyite; (ii) tetragonal zirconia; and (iii) cubic zirconia. High-temperature cubic zirconia can be stabilized by replacing some Zr atoms with Y (yttria-stabilized cubic zirconia). These 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 \AA^3) of one formula unit?
- (b) How is tetragonal zirconia related to cubic zirconia? Identify the coordination number and geometry at Zr and O. What is the volume (in \AA^3) of one formula unit?
- (c) How is monoclinic baddeleyite related to cubic zirconia? Identify the coordination number and geometry at Zr and O. What is the volume (in \AA^3) of one formula unit?
- (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?
- (e) Yttria (Y_2O_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 CaF_2 -type”. Explain your selection.
- (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 \AA^3) of one formula unit? How does it compare with that of cubic zirconia?

The eight Y-anion (X) distances are $\text{Y-X1} = 2.414 \text{ \AA}$ (3 \times), 2.471 \AA (1 \times); $\text{Y-X2} = 2.242 \text{ \AA}$ (3 \times), 2.346 \AA (1 \times). Using the bond-valence method, propose how O and F atoms are distributed on the X1 and X2 sites.

Information: $B = 0.37 \text{ \AA}$ $d_0(\text{Y}^{\text{III}}\text{-O}) = 2.014 \text{ \AA}$ $d_0(\text{Y}^{\text{III}}\text{-F}) = 1.875 \text{ \AA}$

- (g) Niobium oxynitride (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 \AA^3) of one formula unit? How does it compare with that of monoclinic baddeleyite?

The Nb-anion (X) distances are $\text{Nb-X1} = 2.055 \text{ \AA}$, 2.087 \AA , 2.135 \AA , 2.167 \AA ; $\text{Nb-X2} = 1.994 \text{ \AA}$, 2.066 \AA , 2.138 \AA . Using the bond-valence method, propose how N and O atoms are distributed on the X1 and X2 sites.

Information: $B = 0.37 \text{ \AA}$ $d_0(\text{Nb}^{\text{V}}\text{-O}) = 1.911 \text{ \AA}$ $d_0(\text{Nb}^{\text{V}}\text{-N}) = 2.06 \text{ \AA}$

- (h) Provide a rationale for the structural differences between YOF and 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.
- Write a chemical formula for fully saturated methane hydrate in the form $(\text{CH}_4)_m(\text{H}_2\text{O})_n$.
 - What is the mass percent of methane in fully saturated methane hydrate?
 - The crystal structure of methane hydrate is cubic and contains two formula units. The density of methane hydrate is approximately 0.90 g/cm^3 . From this information, estimate the lattice constant for crystalline fully saturated methane hydrate.
 - 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°C and 1 atm?

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**₁ in $2a$ (0,0,0); **A**₂ in $6c$ ($\frac{1}{4}, 0, \frac{1}{2}$); **X**₁ in $6d$ ($\frac{1}{4}, \frac{1}{2}, 0$); **X**₂ in $16i$ (0.185, 0.185, 0.185); and **X**₃ in $24k$ (0, 0.118, 0.308).

- Explain the different symbolic components of the space group for Type I clathrates. Why does the **A**₁ site have multiplicity 2?
- 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.
- Identify the connectivities of each of the **X** atom Wyckoff sites within the 3-d tetrahedral network.
- 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.
- 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.
- 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?
- 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?