Supplemental Problems for Chapter 4

1. Use the data in the table below to answer the questions that follow.

The structure of Al₃Zr

Formula unit	Al₃Zr
Space group:	I4/m mm
Cell dimensions:	a =3.998 Å; c = 17.28 Å
Cell contents:	4 formula units
Atomic positions:	Al(1) in (4c) 0, 1/2, 0; 1/2, 0, 0
	Al(2) in (4d) 0, 1/2, 1/4; 1/2, 0, 1/4
	Al(2) in (4e) 0, 0, z; 0, 0, $\bar{z}$; z = 0.366
	Zr in (4e) 0, 0, z; 0, 0, $\bar{z}$; z = 0.119

(i) What is the Bravais lattice of this crystal structure?
(ii) What is the point group from which this space group derives?
(iii) Draw a sketch of the general equivalent positions in this point group.
(iv) How many general equivalent positions are there in this space group?
(v) Sketch the atomic structure, projected along the *a*-axis.
(vi) How many nearest neighbors do the Zr atoms have? What is the distance to these neighbors?
(vii) Describe this structure as a close packed arrangement. In other words, if close packed sites are occupied, specify which atoms occupy them and what the packing arrangement is (bcc, ccp, or hcp). If interstitial sites are occupied, specify the type of sites (O or T), the fraction that are occupied, and which atoms occupy them.
(viii) Compare the structure to a common prototype structure.

2. Use the data in Table 3B.42 (AuCd) to answer the questions that follow.
(i) Identify the point group from which Pmma is derived, make a sketch illustrating the general equivalent positions in this point group, and list the coordinates.
(ii) Specify at least one set of special positions in this point group.
(iii) Does this point group have a center of symmetry?
(iv) Make a sketch of this structure (with appropriate labels), projected along the [010] axis.
(v) Describe the coordination of the Cd atoms. Specify the relevant interatomic distances.
(vi) Describe the packing in this structure. In other words, if close-packed sites are occupied, specify the packing arrangement (bcc, ccp, or hcp), which atoms occupy them, and if there is ordering. If interstitial sites are occupied, specify the type of sites (O or T), the fraction that are occupied, and which atoms occupy them.
(vii) compare this structure to one of the common binary prototype structures that we have discussed in class.

3. Use the data in Table 3B.41 (zircon) to answer the questions that follow.
 (i) Sketch a c-axis projection of this structure
(ii) Describe the coordination environments of the atoms in the structure
(iii) Does this structure have any similarities to prototypes described in class?
(iv) Using a graph of the type illustrated in Fig. 4.26, compare the types of ABO₄ compounds that assume the zircon structure with those that form the rutile and scheelite structures.

4. In supplemental problem 3.4, you sketched a picture of $LaMnO_3$.

(i) can you describe this structure as a close packed arrangement? In other words, if close packed sites are occupied, specify which atoms occupy them and what the packing arrangement is (bcc, ccp, or hcp). If interstitial sites are occupied, specify the type of sites (O or T), the fraction that are occupied, and which atoms occupy them.
(ii) Compare the structure to a common prototype structure.

5) All of the questions below refer to the Ga_2S_3 structure, which is described completely by the table below.
(i) Sketch a projection of this structure. The grid on the next page might be helpful.
(ii) Specify the x,y coordinates where the 6_5 operator intersects the (0001) plane.
(iii) Describe the coordination of the Ga atoms and compute the near-neighbor bond lengths.
(iv) Describe the packing in this structure. In other words, specify the packing arrangement and which atoms are in the eutactic (close-packed) sites. If interstitial sites are occupied, specify the type of sites, the fraction that are occupied, and which atoms occupy them.
(v) What type of bonding do you think is dominant in this compound? Explain the reason for your choice.
(vi) What common prototype structure is this most like?
(vii) When Ga_2S_3 is initially synthesized, it crystallizes in a cubic structure with a cell edge length of 5.441 Å. In the cubic polymorph, the atoms are coordinated in the same way as in the hexagonal form. As it ages, it eventually transforms to the hexagonal polymorph. Propose a structure for the cubic polymorph.

 The Structure of Ga₂S₃

Formula unit	Ga₂S₃
Space group:	$P6_5$ (no. 170)
Cell dimensions:	a = 6.389 Å, c = 18.086 Å
Cell contents:	6 formula units per cell
Atomic positions:	All atoms are in (6a) sites

$$x, y, z; \qquad \bar{y}, x - y, z + 2/3;$$
$$y - x, \bar{x}, z + 1/3; \quad \bar{x}, \bar{y}, z + 1/2;$$
$$y, y - x, z + 1/6; \quad x - y, x, z + 5/6;$$

Approximate coordinates (rounded to fractions)

Atom	x	y	z
S(1)	1/3	0	0
S(3)	0	1/3	0
S(3)	2/3	2/3	0
Ga(1)	0	1/3	1/8
Ga(2)	2/3	2/3	1/8

6. The Structure of KAlF$_4$ is described in the table below.

Formula unit	KAlF$_4$
Space group:	P4/m mm (no. 123)
Cell dimensions:	a = 3.350 Å c = 6.139 Å
Cell contents:	1 formula units per cell
Atomic positions:	K in 1a 0,0,0
	Al in 1d 1/2,1/2,1/2
	F(1) in 2e 0,1/2,1/2; 1/2,0,1/2
	F(2) in 2h 1/2,1/2,z; 1/2,1/2,$\square$
	z = 0.21

(i) (1 pt.) What is the Bravais lattice of this crystal structure?

(ii) (2 pt.) Make a sketch illustrating the relative positions of the symmetry elements in the point group from which this space group is derived.

(iii) (2 pt.) Sketch the pattern produced by this point group.

(iv) (4 pt.) List the coordinates of the general equivalent positions in this group.

(v) (4 pt.) Make a sketch, projected along [010], illustrating the atomic structure of KAlF$_4$.

(vi) (4 pt.) The atoms in this structure occupy special positions. Name the symmetry elements that the 1d, 2e, and 2h sites are situated on.

(vi) (8 pt.) If a powder diffraction pattern of this compound were recorded, at what values of θ would the first three peaks be observed (the first three are the peaks with the three smallest values of θ).