

Sources

H.F. Franzen, *Physical Chemistry of Inorganic Crystalline Solids*, Springer-Verlag, New York, 1986

H.J. Goldsmid, *Problems in Solid State Physics*, Academic Press, New York, 1968

A.R. West, *Solid State Chemistry and Its Applications*, John Wiley & Sons, New York, 1984

Diffraction

(1) Spectroscopic vs. X-ray (Siegbahn) Notation:

- (a) Give the X-ray symbols for the electronic levels: $4s$, $5p_{3/2}$, $3d_{5/2}$, $4f_{7/2}$, $6p_{1/2}$.

Shells are given in order K, L, M, N, O, P, \dots

Subshells are given as numerical subscripts ordered sequentially by quantum numbers l and j .

$$4s = N_1 \quad 5p_{3/2} = O_3 \quad 3d_{5/2} = M_5 \quad 4f_{7/2} = N_7 \quad 6p_{1/2} = P_2$$

- (b) Give the spectroscopic symbols for the electronic levels: N_2 , L_3 , O_4 , M_5 , N_6 .

$$N_2 = 4p_{1/2} \quad L_3 = 2p_{3/2} \quad O_4 = 5d_{3/2} \quad M_5 = 3d_{5/2} \quad N_6 = 4f_{5/2}$$

- (c) Give the spectroscopic and X-ray symbols for all levels in the $n = 4$ shell.

$$4s = N_1 \quad 4p_{1/2} = N_2 \quad 4d_{3/2} = N_4 \quad 4f_{5/2} = N_6$$

$$4p_{3/2} = N_3 \quad 4d_{5/2} = N_5 \quad 4f_{7/2} = N_7$$

- (d) Give the spectroscopic and X-ray symbols for all possible transitions from the $n = 3$ shell to the $n = 1$ shell.

Since $\Delta n = 2$, these are β transitions: $3p_{1/2} \rightarrow 1s = M_2 \rightarrow K$

$$3p_{3/2} \rightarrow 1s = M_3 \rightarrow K$$

- (e) Give the spectroscopic and X-ray symbols for all possible transitions from the $n = 3$ shell to the $n = 2$ shell.

Since $\Delta n = 1$, these are α transitions: $3p_{1/2} \rightarrow 2s = M_2 \rightarrow L_1$

$$3p_{3/2} \rightarrow 2s = M_3 \rightarrow L_1$$

$$3d_{3/2} \rightarrow 3p_{1/2} = M_4 \rightarrow L_2$$

$$3d_{5/2} \rightarrow 3p_{1/2} = M_5 \rightarrow L_2$$

$$3d_{3/2} \rightarrow 3p_{3/2} = M_4 \rightarrow L_3$$

$$3d_{5/2} \rightarrow 3p_{3/2} = M_5 \rightarrow L_3$$

- (2) The energies of X-ray emission lines for Cu that are important for X-ray diffraction are: $K\alpha_1 = 8047.78$ eV, $K\alpha_2 = 8027.83$ eV, and $K\beta = 8905.29$ eV. Also, the relative intensities for $K\alpha_1:K\alpha_2 = 2:1$.

- (a) What are the wavelengths (in \AA) for each transition?

$$\lambda(K\alpha_1) = \frac{hc}{E} = \frac{1.23984 \times 10^4 \text{ eV}\cdot\text{\AA}}{8047.78 \text{ eV}} = 1.54060 \text{ \AA}$$

$$\lambda(K\alpha_2) = \frac{hc}{E} = \frac{1.23984 \times 10^4 \text{ eV}\cdot\text{\AA}}{8027.83 \text{ eV}} = 1.54443 \text{ \AA}$$

$$\lambda(K\beta) = \frac{hc}{E} = \frac{1.23984 \times 10^4 \text{ eV}\cdot\text{\AA}}{8905.29 \text{ eV}} = 1.39225 \text{ \AA}$$

- (b) What is the wavelength (in \AA) of Cu $K\alpha$ radiation?

$K\alpha$ X-radiation is the average of $K\alpha_1$ and $K\alpha_2$ radiation.

The average energy of $K\alpha$ X-radiation is $(2 \cdot 8047.78 \text{ eV} + 1 \cdot 8027.83 \text{ eV})/3 = 8041.13 \text{ eV}$.

$$\lambda(K\alpha) = \frac{hc}{E} = \frac{1.23984 \times 10^4 \text{ eV}\cdot\text{\AA}}{8041.13 \text{ eV}} = 1.54188 \text{ \AA}$$

- (c) Identify the spectroscopic symbols for the initial and final levels of each transition for each X-ray emission and explain the intensity ratio for $K\alpha_1:K\alpha_2$.

Transition $K\alpha_1: 2p_{3/2} \rightarrow 1s$ There are 4 levels for the initial state ($m_j = +\frac{3}{2}, +\frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$) and 2 levels for the final state ($m_j = +\frac{1}{2}, -\frac{1}{2}$).

Transition $K\alpha_2: 2p_{1/2} \rightarrow 1s$ There are 2 levels for the initial state ($m_j = +\frac{1}{2}, -\frac{1}{2}$) and 2 levels for the final state ($m_j = +\frac{1}{2}, -\frac{1}{2}$).

Transition $K\beta: 3p \rightarrow 1s$ There are 6 microstates for the initial state ($(m_l m_s) = (+1, +\frac{1}{2}), (+1, -\frac{1}{2}), (0, +\frac{1}{2}), (0, -\frac{1}{2}), (-1, +\frac{1}{2}), (-1, -\frac{1}{2})$) and 2 levels for the final state ($(m_l m_s) = (0, +\frac{1}{2}), (0, -\frac{1}{2})$).

There are twice the number of possible transitions for $K\alpha_1$ as for $K\alpha_2$, which nicely accounts for the difference in intensities.

The $K\beta$ transition corresponds to an average of transitions between the $n = 3$ shell and the $n = 1$ shell. I have designated the possible $K\beta$ transitions according to their orbital and spin quantum numbers, rather than the total angular momentum quantum numbers.

- (d) If the first four diffraction peaks for a solid are observed at scattering angles 42.88° , 49.32° , 73.30° , and 88.85° using Cu $K\alpha_1$ radiation, at what scattering angles would these reflections be observed for Cu $K\alpha_2$ and for Cu $K\beta$ radiation?

The Bragg equation is $\lambda = 2d_{hkl} \sin \theta_{hkl}$. For a given crystal, the d_{hkl} values remain fixed. Therefore, for two different X-ray wavelengths λ_1 and λ_2 , then

$$\sin \theta_{hkl}^{(2)} = \frac{\lambda_2}{\lambda_1} \sin \theta_{hkl}^{(1)}$$

$$\lambda_2 = 1.54443 \text{ \AA}; \lambda_1 = 1.54060 \text{ \AA}$$

$2\theta_{hkl}^{(1)}$	$\sin \theta_{hkl}^{(1)}$	$\sin \theta_{hkl}^{(2)}$	$2\theta_{hkl}^{(2)}$
42.88°	0.36553	0.36643	42.99°
49.32°	0.41723	0.41826	49.45°
73.30°	0.59693	0.59840	73.51°
88.85°	0.69998	0.70170	89.13°

$$\lambda_2 = 1.39225 \text{ \AA}; \lambda_1 = 1.54060 \text{ \AA}$$

$2\theta_{hkl}^{(1)}$	$\sin \theta_{hkl}^{(1)}$	$\sin \theta_{hkl}^{(2)}$	$2\theta_{hkl}^{(2)}$
42.88°	0.36553	0.33034	38.58°
49.32°	0.41723	0.37707	44.30°
73.30°	0.59693	0.53946	65.29°
88.85°	0.69998	0.63259	78.48°

- (e) If an X-ray filter only allows Cu $K\alpha$ radiation and the detector can resolve peaks that differ by 0.1° , for what scattering angles can Cu $K\alpha_1$ and Cu $K\alpha_2$ peaks be resolved?

Since $\lambda = 2d_{hkl} \sin \theta_{hkl}$, then $\Delta\lambda = 2d_{hkl} \cos \theta_{hkl} \Delta\theta_{hkl}$. Taking the ratio between both sides of these 2 equations gives

$$\frac{\Delta\lambda}{\lambda} = \frac{\cos \theta_{hkl}}{\sin \theta_{hkl}} \Delta\theta_{hkl} = \cot \theta_{hkl} \Delta\theta_{hkl}$$

$$\Delta\lambda = \lambda_{K\alpha_2} - \lambda_{K\alpha_1} = 1.54443 \text{ \AA} - 1.54069 \text{ \AA} = 0.00374 \text{ \AA}; \quad \Delta\theta_{hkl} = \frac{1}{2} \Delta(2\theta_{hkl}) = 0.05^\circ$$

Therefore, since $\Delta\lambda > 0.00374 \text{ \AA}$ and $\Delta\lambda = \lambda \cot \theta_{hkl} \Delta\theta_{hkl} = (1.54188 \text{ \AA}) \cot \theta_{hkl} (0.05)$, then

$$\cot \theta_{hkl} > 0.048512 \text{ or } \theta_{hkl} > 87.22^\circ$$

- (3) In neutron diffraction experiments, thermal free neutrons are scattered by the sample. These neutrons follow a Maxwell-Boltzmann distribution, but they are also unstable by beta-decay with a half-life of 611 seconds. Neutrons bound in nuclei are stable with respect to this beta decay.

- (a) Write the decay process for a free neutron.

A free neutron has mass number 1 and charge number 0. It releases a beta particle, which has mass number 0 and charge number -1 . By conservation of mass and charge, the other decay particle must have mass number 1 and charge number $+1$, which is a proton: ${}_0^1n \rightarrow {}_1^1p + {}_{-1}^0e$.

- (b) What is the average lifetime for a free neutron? (HINT: for a particle undergoing first-order decay with rate constant k , the average lifetime is $1/k$.)

$$\text{After 611 seconds, the number of free neutrons} = N(611 \text{ s}) = \frac{1}{2}N(0) = N(0)e^{-k(611 \text{ s})}.$$

$$\text{Then, } k = \ln 2 / 611 \text{ s} = 1.134 \times 10^{-3} \text{ s}^{-1}.$$

Average lifetime of a free neutron is 881 seconds = 14.7 minutes.

- (c) Consider a thermal neutron with a kinetic energy of 25.0 meV. If this value of kinetic energy is the most probable in the Maxwell-Boltzmann distribution, what is the temperature (in K), the de Broglie wavelength (in Å), and the speed (in cm/sec) of this thermal neutron? How far (in m) can this free neutron travel before it decays, on average? The Maxwell-Boltzmann distribution for particles of mass m and speed v at temperature T is

$$f_{MB}(v)dv = \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi v^2 e^{-mv^2/2kT} dv.$$

The most probable kinetic energy of a thermal neutron corresponds to the most probable speed v_p in the Maxwell-Boltzmann distribution, the value that is the maximum of the distribution. Then,

$$\frac{df_{MB}(v)}{dv} = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv_p^2/2kT} \left[2v_p - \frac{mv_p^3}{kT}\right] = 0, \text{ or } v_p = \sqrt{\frac{2kT}{m}}.$$

$$25.0 \text{ meV} = 4.005 \times 10^{-21} \text{ J} = \frac{1}{2}(1.6749 \times 10^{-27} \text{ kg})v_p^2$$

$$v_p = 2190 \text{ m/sec} = 219,000 \text{ cm/sec}$$

$$\lambda = \frac{6.6261 \times 10^{-34} \text{ J}\cdot\text{sec}}{(1.6749 \times 10^{-27} \text{ kg})(2,190 \text{ m/sec})} = 1.809 \times 10^{-10} \text{ m} = 1.809 \text{ \AA}$$

$$T = 290 \text{ K}$$

- (4) In an X-ray diffraction pattern of a cubic structure taken with Cu $K\alpha$ radiation ($\lambda = 1.542 \text{ \AA}$), the first 8 peaks are observed at the scattering angles 2θ : 24.6° , 28.5° , 40.7° , 48.1° , 50.4° , 58.9° , 64.9° , and 66.7° .

- (a) Decide the lattice type for the cubic cell and assign Miller indices to each peak.

$$\text{For cubic structures, } \frac{1}{d_{hkl}^2} = \frac{h^2+k^2+l^2}{a^2} = \frac{4 \sin^2 \theta_{hkl}}{\lambda^2}. \text{ Therefore, } \frac{\sin^2 \theta_{hkl}}{h^2+k^2+l^2} = \frac{\lambda^2}{4a^2} = \text{constant.}$$

For a cubic structure, there are three distinct lattice types:

Primitive: no restrictions on h, k, l . The first 8 peaks are

$$\{hkl\} = \{100\}, \{110\}, \{111\}, \{200\}, \{210\}, \{211\}, \{220\}, \{221\}, \{300\}$$

($\{221\}$ and $\{300\}$ have the same scattering angles)

Body-centered: $h + k + l = \text{even integer}$. The first 8 peaks are

$$\{hkl\} = \{110\}, \{200\}, \{211\}, \{220\}, \{310\}, \{222\}, \{321\}, \{400\}$$

Face-centered: h, k, l either all even or all odd integers. The first 8 peaks are

$$\{hkl\} = \{111\}, \{200\}, \{220\}, \{311\}, \{222\}, \{400\}, \{331\}, \{420\}$$

The values $\sin^2 \theta_n / (h^2 + k^2 + l^2)$ for each lattice type are:

n	$2\theta_n$	$\sin \theta_n$	$\frac{\sin^2 \theta_n}{h^2+k^2+l^2}$	Primitive Cell	BCC Cell	FCC Cell	$\{hkl\}$
1	24.6°	0.2130	0.04538	0.02269	0.01513	0.01513	$\{111\}$
2	28.5°	0.2436	0.03030	0.01515	0.01515	0.01515	$\{200\}$
3	40.7°	0.3453	0.04031	0.02016	0.01512	0.01512	$\{220\}$
4	48.1°	0.4067	0.04152	0.02076	0.01510	0.01510	$\{311\}$
5	50.4°	0.4242	0.03626	0.01813	0.01511	0.01511	$\{222\}$
6	58.9°	0.4894	0.04029	0.02014	0.01511	0.01511	$\{400\}$
7	64.9°	0.5329	0.03599	0.02056	0.01515	0.01515	$\{331\}$
8	66.7°	0.5750	0.03358	0.01889	0.01511	0.01511	$\{420\}$

Therefore, the assigned lattice type is FCC.

- (b) Evaluate the cubic lattice constant a (in Å).

For each diffraction peak, we can calculate the lattice constant a using its Miller index, the X-ray wavelength, and the scattering angle:

$2\theta_n$	$\sin \theta_n$	$\{hkl\}$	Mult.	a (Å)
24.6°	0.2130	{111}	8	6.269
28.5°	0.2436	{200}	6	6.264
40.7°	0.3453	{220}	12	6.271
48.1°	0.4067	{311}	24	6.275
50.4°	0.4242	{222}	8	6.273
58.9°	0.4894	{400}	6	6.273
64.9°	0.5329	{331}	24	6.263
66.7°	0.5750	{420}	48	6.272

The cubic lattice constant can be determined by the weighted average of the value determined for each Bragg peak. The weight is determined by the multiplicity associated with each peak, as required by cubic symmetry. This weighted average is 6.270 Å.

- (c) If the density of the substance is 8.31 g/cm³, propose its formula weight. What are some possible compounds that fit this solution?

$$\text{Volume of the unit cell} = (6.270 \text{ \AA})^3 = 246.49 \text{ \AA}^3 = 2.465 \times 10^{-22} \text{ cm}^3$$

$$\text{Mass of one formula unit} = (8.31 \text{ g/cm}^3)(2.465 \times 10^{-22} \text{ cm}^3) / 4 = 5.121 \times 10^{-22} \text{ g}$$

$$\text{FW} = (5.121 \times 10^{-22} \text{ g})(6.022 \times 10^{23} \text{ units/mole}) = 308.4 \text{ g/mol}$$

Face-centered cubic structures include sphalerite (ZnS), rocksalt (NaCl), and fluorite (CaF₂) type structures. For the binary 1:1 examples, the average atomic weight is 154 g/mol; for the 1:2 example, the average atomic weight is 103 g/mol. By examining the atomic weights of the various elements, some possible compounds include LuSb (FW = 296.7 g/mol), YbTe (FW = 300.6 g/mol), YBi (FW = 297.9 g/mol), UAs (FW = 312.9 g/mol), or CeSe₂ (FW = 298.1 g/mol).

- (5) A metallic element is examined using Mo $K\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$) on a Debye-Scherrer camera. The first six reflections have scattering angles $2\theta = 14.70^\circ, 15.68^\circ, 16.66^\circ, 21.55^\circ, 25.58^\circ,$ and 27.92° .

- (a) Most metals adopt FCC, BCC, or HCP structures. With this fact in mind, what is the crystal class of this structure?

For cubic structures, $\frac{1}{d_{hkl}^2} = \frac{h^2+k^2+l^2}{a^2} = \frac{4 \sin^2 \theta_{hkl}}{\lambda^2}$. Therefore, $\frac{\sin^2 \theta_{hkl}}{h^2+k^2+l^2} = \frac{\lambda^2}{4a^2} = \text{constant}$.

For an FCC structure, h, k, l are either all even or all odd integers. The first 6 peaks are:

$$\{hkl\} = \{111\}, \{200\}, \{220\}, \{311\}, \{222\}, \{400\}.$$

For a BCC structure, $h + k + l = \text{even integer}$. The first 6 peaks are

$$\{hkl\} = \{110\}, \{200\}, \{211\}, \{220\}, \{310\}, \{222\}.$$

The values $\sin^2 \theta_n / (h^2 + k^2 + l^2)$ for each lattice type are:

n	$2\theta_n$	$\sin \theta_n$	$\frac{\sin^2 \theta_{hkl}}{h^2 + k^2 + l^2}$	FCC Cell	BCC Cell
1	14.70°	0.1279		0.005455	0.008183
2	15.68°	0.1364		0.004652	0.004652
3	16.66°	0.1449		0.002624	0.003498
4	21.55°	0.1870		0.003177	0.004369
5	25.58°	0.2214		0.004084	0.004901
6	27.92°	0.2412		0.003637	0.004850

The values are not constant for either FCC or BCC structures, so the structure must be HCP.

- (b) Determine the Miller indices for each reflection.
(c) Evaluate the lattice constant(s) (in Å) of the unit cell.

$$\text{For a hexagonal structure, } \frac{1}{d_{hkl}^2} = \frac{4(h^2+hk+k^2)}{3a^2} + \frac{l^2}{c^2} = \frac{4 \sin^2 \theta_{hkl}}{\lambda^2}$$

The HCP structure has atoms at $(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$ and $(\frac{2}{3}, \frac{1}{3}, \frac{3}{4})$ in one unit cell. The structure factor S_{hkl} for the unit cell is:

$$\begin{aligned} S_{hkl} &= f_M \exp\left(\frac{2\pi ih}{3} + \frac{4\pi ik}{3} + \frac{\pi il}{2}\right) + f_M \exp\left(\frac{4\pi ih}{3} + \frac{2\pi ik}{3} + \frac{3\pi il}{2}\right) \\ &= f_M \exp\left(\frac{2\pi ih}{3} - \frac{2\pi ik}{3} + \frac{\pi il}{2}\right) + f_M \exp\left(-\frac{2\pi ih}{3} + \frac{2\pi ik}{3} - \frac{\pi il}{2}\right) \\ &= f_M \left[\exp\left(i\pi\left(\frac{2(h-k)}{3} + \frac{l}{2}\right)\right) + \exp\left(-i\pi\left(\frac{2(h-k)}{3} + \frac{l}{2}\right)\right) \right] = 2f_M \cos\left(\pi\left(\frac{2(h-k)}{3} + \frac{l}{2}\right)\right). \end{aligned}$$

Extinctions occur when $S_{hkl} = 0$. Therefore, all observed reflections in the diffraction pattern will occur for the following indices:

- {00l}: $l = 2n$ (even integer) = {002}, {004}, ...
{hhl}: $l = 2n$ (even integer) = {110}, {220}, {112}, {222}, ...
{hkl}: either $l = 2n$ (even integer) or, if $l = 2n + 1$ (odd integer), then $h-k = 3n + 1$ or $3n + 2$ = {100}, {200}, {300}, {101}, {102}, {103}, {201}, ...

In HCP, since $c/a \sim 1.63$, the first two reflections are assumed to be {100} and {002} in either order. By taking the ratios $\sin^2 \theta_n / \sin^2 \theta_1$ for each case, we can identify which of the remaining 4 reflections n is {110} or {004}:

- If $2\theta_{100} = 14.70^\circ$, then $\sin^2 \theta_{110} / \sin^2 \theta_{100} = 3$ and $2\theta_{110} = 25.60^\circ$;
 $2\theta_{002} = 15.68^\circ$, then $\sin^2 \theta_{004} / \sin^2 \theta_{002} = 4$ and $2\theta_{004} = 31.66^\circ$.
 If $2\theta_{100} = 15.68^\circ$, then $\sin^2 \theta_{110} / \sin^2 \theta_{100} = 3$ and $2\theta_{110} = 27.33^\circ$;
 $2\theta_{002} = 14.70^\circ$, then $\sin^2 \theta_{004} / \sin^2 \theta_{002} = 4$ and $2\theta_{004} = 29.65^\circ$.

Therefore, #1 is {100}, #2 is {002}, and #5 is {110}:

n	{hkl}	$2\theta_n$	$\sin \theta_n$	$\frac{4 \sin^2 \theta_n}{\lambda^2}$	a (Å)	c (Å)
1	{100}	14.70°	0.1279	0.12961	3.2074	---
2	{002}	15.68°	0.1364	0.14735	---	5.2101
3		16.66°	0.1449			
4		21.55°	0.1870			
5	{110}	25.58°	0.2214	0.38811	3.2103	
6		27.92°	0.2412			

Using these first assignments of the unit cell a and c parameters, the indices for reflections #3, #4, and #6 can be derived from the relationship above for $1/d_{hkl}^2$: since $h^2 + hk + k^2$ and l^2 must both be integers, the only possible solutions for the 3 scattering angles are $h^2 + hk + k^2 = 1$ and $l^2 = 1, 4$, and 9. Therefore, the indices for the first 6 reflections are:

n	{hkl}	$2\theta_n$	$\sin \theta_n$	$\frac{4 \sin^2 \theta_n}{\lambda^2}$	a (Å)	c (Å)
1	{100}	14.70°	0.1279	0.12961	3.2074	---
2	{002}	15.68°	0.1364	0.14735	---	5.2101
3	{101}	16.66°	0.1449	0.16621		
4	{102}	21.55°	0.1870	0.27679		
5	{110}	25.58°	0.2214	0.38811	3.2103	
6	{103}	27.92°	0.2412	0.46089		

From these data, we conclude that $a = 3.210$ Å and $c = 5.210$ Å.

(d) The density of the element is 1.74 g/cm^3 . Identify the element.

$$\text{Volume of the unit cell} = (3.210 \text{ \AA})^2(5.210 \text{ \AA}) \sin 120^\circ = 46.492 \text{ \AA}^3 = 4.6492 \times 10^{-23} \text{ cm}^3$$

$$\text{Mass of one unit cell} = (1.74 \text{ g/cm}^3)(4.6492 \times 10^{-23} \text{ cm}^3) = 8.0896 \times 10^{-23} \text{ g}$$

Since the unit cell contains 2 atoms, then the atomic weight of the element is

$$\text{AW} = (8.0896 \times 10^{-23} \text{ g})(6.022 \times 10^{23} \text{ units/mole})/2 = 24.36 \text{ g/mol}$$

The metallic element is Mg.

(6) Calculate the expected scattering angle 2θ for the $\{300\}$ reflection of iron pyrite, which has space group $Pa\bar{3}$ and lattice constant $a = 5.42 \text{ \AA}$, with Fe $K\alpha$ radiation ($\lambda = 1.937 \text{ \AA}$). This peak is *not* expected to be observed. Explain why.

The space group $Pa\bar{3}$ consists of axial glide reflections perpendicular to the edges of the cubic unit cell. Therefore, $\{h00\}$ reflections are expected to be observed only for even integer h .

On experimental diffraction patterns, the line occurs at this scattering angle *only if* the incident Fe-radiation is unfiltered, i.e., both $K\alpha$ and $K\beta$ characteristic X-rays are part of the incident radiation. Since Fe $K\beta$ radiation has wavelength $\lambda = 1.757 \text{ \AA}$, account for this observation.

Iron pyrite is FeS_2 with Fe atoms in $4a$ Wyckoff sites and S atoms in $8c$ Wyckoff sites. The general reflection conditions for this structure are $\{hkl\}$: $\{0kl\}, k = 2n$; $\{h00\}, h = 2n$. If both Fe $K\alpha$ and $K\beta$ radiation are diffracted, then the position of the extinct $\{300\}$ reflection with $K\alpha$ radiation must arise from an allowed reflection with $K\beta$ radiation. Using the Bragg equation:

$$\lambda_{K\alpha} = 2d_{300} \sin \theta_{300} = 2 \cdot \frac{a}{3} \cdot \sin \theta$$

$$\lambda_{K\beta} = 2d_{hkl} \sin \theta_{hkl} = 2 \cdot \frac{a}{\sqrt{h^2+k^2+l^2}} \cdot \sin \theta$$

Taking the ratio of these two equations gives

$$\frac{\lambda_{K\alpha}}{\lambda_{K\beta}} = \frac{\sqrt{h^2+k^2+l^2}}{3} = \frac{1.937}{1.757} = 1.1024; \quad h^2 + k^2 + l^2 \sim 11.$$

Therefore, the $\{311\}$ reflection with $K\beta$ radiation occurs at very nearly the same scattering angle as the extinct $\{300\}$ reflection with $K\alpha$ radiation.

(7) What is the smallest value of the Bragg angle at which the Cu $K\alpha$ doublet will be resolved when an X-ray diffraction pattern is taken using a 6.00-cm diameter camera. Assume a 0.03 cm linewidth and that peaks separated by twice the observed linewidth can be resolved. The X-ray wavelengths are:

$$\text{Cu } K\alpha_1 = 1.5408 \text{ \AA}; \quad K\alpha_2 = 1.5443 \text{ \AA}.$$

Since $\lambda_{K\alpha} = 2d_{hkl} \sin \theta_{hkl}$, then $d\lambda_{K\alpha} = 2d_{hkl} \cos \theta_{hkl} d\theta_{hkl}$. Therefore, taking the ratio: $\frac{d\lambda}{\lambda} = \cot \theta d\theta$.

Now, if L = measured distance between reflections (peaks) on the film and R = radius of the camera, then $2\theta = L/R$ and $d\theta = dL/2R$. Therefore,

$$\frac{d\lambda}{\lambda} = \cot \theta \frac{dL}{2R}, \text{ which means } \Delta L = 2R \cdot \frac{\Delta\lambda}{\lambda} \cdot \tan \theta = (6.00 \text{ cm}) \left(\frac{0.0035 \text{ \AA}}{1.5420 \text{ \AA}} \right) \tan \theta > 0.06 \text{ cm}.$$

Or, $\tan \theta > 4.406$, i.e., $\theta > 77.2^\circ$.

- (8) Powder specimens of three different monatomic cubic crystals are analyzed with a Debye-Scherrer camera using Cu $K\alpha$ radiation ($\lambda = 1.542 \text{ \AA}$). One is body-centered cubic, one has the diamond structure, and one is body-centered cubic. The approximate 2θ values of the first four diffraction maxima in each case are:

A:	42.2°	49.2°	72.0°	87.3°
B:	28.8°	41.0°	50.8°	59.6°
C:	42.8°	73.2°	89.0°	115.0°

- (a) Identify the crystal structures of A, B, and C.

Each structure type has extinctions. Observed reflections are:

For a BCC structure (space group $Im\bar{3}m$), $h + k + l = \text{even integer}$.

The first 4 peaks are $\{hkl\} = \{110\}, \{200\}, \{211\}, \{220\}$.

For an FCC structure (space group $Fm\bar{3}m$), h, k, l are either all even or all odd integers.

The first 4 peaks are: $\{hkl\} = \{111\}, \{200\}, \{220\}, \{311\}$.

For a diamond structure (space group $Fd\bar{3}m$), h, k, l are either all even or all odd integers due to F -type lattice. Also, for h, k, l all even, then $\frac{1}{2}(h + k + l) = \text{even integer}$.

The first 4 peaks are $\{hkl\} = \{111\}, \{220\}, \{311\}, \{400\}$.

Now, for cubic structures, $\frac{1}{d_{hkl}^2} = \frac{h^2+k^2+l^2}{a^2} = \frac{4 \sin^2 \theta_{hkl}}{\lambda^2}$. Therefore, $\frac{\sin^2 \theta_{hkl}}{h^2+k^2+l^2} = \frac{\lambda^2}{4a^2} = \text{constant}$.

The values $\sin^2 \theta_n / (h^2 + k^2 + l^2)$ for each lattice type are:

Sample	2θ	$\sin \theta$	$\sin^2 \theta / (h^2 + k^2 + l^2)$		
			BCC Cell	FCC Cell	Diamond Cell
A	42.2°	0.3600	0.06480	0.04320	0.04320
	49.2°	0.4163	0.04332	0.04332	0.02166
	72.0°	0.5878	0.05758	0.04319	0.03141
	87.3°	0.6903	0.05956	0.04331	0.02978
B	28.8°	0.2487	0.03092	0.02062	0.02062
	41.0°	0.3502	0.03066	0.03066	0.01533
	50.8°	0.4289	0.03066	0.02300	0.01673
	59.6°	0.4970	0.03087	0.02245	0.01544
C	42.8°	0.3649	0.06657	0.04438	0.04438
	73.2°	0.5962	0.08887	0.08887	0.04444
	89.0°	0.7009	0.08188	0.06141	0.04466
	115.0°	0.8434	0.08891	0.06466	0.04446

Therefore, A = FCC, B = BCC, C = Diamond.

- (b) What is the length of the side of the conventional cubic cell in each case?
(c) What would be the expected scattering angles if Mo $K\alpha$ radiation ($\lambda = 0.711 \text{ \AA}$) was used?

Sample A: FCC

2θ	$\sin \theta$	$\{hkl\}$	$a \text{ (\AA)}$	$2\theta \text{ (Mo } K\alpha)$	The lattice constant is 3.707 \AA , using a weighted average of the four observed reflections.
42.2°	0.3600	{111}	3.710	19.1°	
49.2°	0.4163	{200}	3.704	22.1°	
72.0°	0.5878	{220}	3.710	31.5°	
87.3°	0.6903	{311}	3.705	37.1°	

Sample B: BCC

2θ	$\sin \theta$	$\{hkl\}$	a (Å)	2θ (Mo $K\alpha$)	The lattice constant is 4.395 Å, using a weighted average of the four observed reflections.
28.8°	0.2487	{110}	4.384	13.1°	
41.0°	0.3502	{200}	4.403	18.6°	
50.8°	0.4289	{211}	4.403	22.9°	
59.6°	0.4970	{220}	4.388	26.5°	

Sample C: Diamond

2θ	$\sin \theta$	$\{hkl\}$	a (Å)	2θ (Mo $K\alpha$)	The lattice constant is 3.653 Å, using a weighted average of the four observed reflections.
42.8°	0.3649	{111}	3.660	19.4°	
73.2°	0.5962	{220}	3.658	32.0°	
89.0°	0.7009	{311}	3.648	37.7°	
115.0°	0.8434	{400}	3.657	45.8°	

- (d) If the diamond structure were replaced by a zinc blende structure with a cubic unit cell of the same side, at what angles would the first four maxima now occur?

Zinc Blende structure using lattice constant of Sample C = 3.653 Å.

The space group of the diamond-type structure is $Fd\bar{3}m$; the space group of the zinc blende structure is $F43m$, which have observed reflections $\{hkl\}$: $h + k, h + l, k + l = 2n$ (even integers).

$\{hkl\}$	$\sin \theta$	2θ
{111}	0.3656	42.8°
{200}	0.4221	49.9°
{220}	0.5970	73.3°
{311}	0.7000	88.9°

- (9) Describe the difference between the diffraction patterns of NbO (*cP6*) and that of a hypothetical NbO with the NaCl structure type (*cF8*) by identifying the scattering angles, indices, and geometrical structure factors for the first observed reflections using Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$).

$$\begin{array}{ll}
 cP6: a = 4.211 \text{ \AA}; & cF8: a = 4.211 \text{ \AA}; \\
 \text{Nb at } (1/2, 0, 0), (0, 1/2, 0), (0, 0, 1/2) & \text{Nb at } (1/2, 0, 0), (0, 1/2, 0), (0, 0, 1/2), (1/2, 1/2, 1/2) \\
 \text{O at } (1/2, 1/2, 0), (1/2, 0, 1/2), (0, 1/2, 1/2) & \text{O at } (0, 0, 0), (1/2, 1/2, 0), (1/2, 0, 1/2), (0, 1/2, 1/2)
 \end{array}$$

NbO (*cP6*) is cubic, primitive so there are no restrictions on reflection indices $\{hkl\}$. The geometrical structure factor is

$$\begin{aligned}
 S_{hkl} &= f_{\text{Nb}}[e^{2\pi i(h/2)} + e^{2\pi i(k/2)} + e^{2\pi i(l/2)}] + f_{\text{O}}[e^{2\pi i((h+k)/2)} + e^{2\pi i((h+l)/2)} + e^{2\pi i((k+l)/2)}] \\
 &= f_{\text{Nb}}[(-1)^h + (-1)^k + (-1)^l] + f_{\text{O}}[(-1)^{h+k} + (-1)^{h+l} + (-1)^{k+l}]
 \end{aligned}$$

Using the Bragg equation, then

$$h^2 + k^2 + l^2 \leq 4 \left(\frac{a}{\lambda}\right)^2 \sin^2 \frac{\pi}{4} = 14.9.$$

With this restriction on the reflection indices, NbO (*cP6*) will have the following 14 diffraction peaks for scattering angles less than 90° :

$\{hkl\}$	$2\theta_{hkl}$	$ S_{hkl} $	Multiplicity
{100}	21.10°	$f_{\text{Nb}} - f_{\text{O}}$	6
{110}	30.01°	$f_{\text{Nb}} + f_{\text{O}}$	12
{111}	36.97°	$3(f_{\text{Nb}} - f_{\text{O}})$	8
{200}	42.96°	$3(f_{\text{Nb}} + f_{\text{O}})$	6
{210}	48.33°	$f_{\text{Nb}} - f_{\text{O}}$	24
{211}	53.29°	$f_{\text{Nb}} + f_{\text{O}}$	24
{220}	62.37°	$3(f_{\text{Nb}} + f_{\text{O}})$	12
{221}	66.62°	$f_{\text{Nb}} - f_{\text{O}}$	24
{300}	66.62°	$f_{\text{Nb}} - f_{\text{O}}$	6
{310}	70.75°	$f_{\text{Nb}} + f_{\text{O}}$	24
{311}	74.77°	$3(f_{\text{Nb}} - f_{\text{O}})$	24
{222}	78.72°	$3(f_{\text{Nb}} + f_{\text{O}})$	8
{320}	82.61°	$f_{\text{Nb}} - f_{\text{O}}$	24
{321}	86.47°	$f_{\text{Nb}} + f_{\text{O}}$	48

NbO (*cF8*) is cubic, face-centered so there are restrictions on reflection indices $\{hkl\}$. The geometrical structure factor is

$$S_{hkl} = f_{\text{Nb}}[(-1)^h + (-1)^k + (-1)^l + (-1)^{h+k+l}] + f_{\text{O}}[1 + (-1)^{h+k} + (-1)^{h+l} + (-1)^{k+l}]$$

Using the Bragg equation, NbO (*cF8*) will have the following 5 diffraction peaks for scattering angles less than 90° :

$\{hkl\}$	$2\theta_{hkl}$	$ S_{hkl} $	Multiplicity
{111}	36.97°	$4(f_{\text{Nb}} - f_{\text{O}})$	8
{200}	42.96°	$4(f_{\text{Nb}} + f_{\text{O}})$	6
{220}	62.37°	$4(f_{\text{Nb}} + f_{\text{O}})$	12
{311}	74.77°	$4(f_{\text{Nb}} - f_{\text{O}})$	24
{222}	78.72°	$4(f_{\text{Nb}} + f_{\text{O}})$	8

(10) The structure of α -Hg(s) is rhombohedral, space group $R\bar{3}m$ with $a = 2.992 \text{ \AA}$ and $\alpha = 70.612^\circ$. The asymmetric unit is Hg atoms at Wyckoff sites (0,0,0).

(a) Determine the 2θ values and multiplicities for all reflections of α -Hg(s) with $|h|, |k|, |l| \leq 1$ and using Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The d -spacings for a rhombohedral unit cell are:

$$\frac{1}{d_{hkl}^2} = \frac{(h^2 + k^2 + l^2) \sin^2 \alpha + 2(hk + hl + kl)(\cos^2 \alpha - \cos \alpha)}{a^2(1 - 3 \cos^2 \alpha + 2 \cos^3 \alpha)}$$

For the rhombohedral setting, there are no restrictions on the values of the Miller indices. Therefore, all 26 combinations of $h, k, l = -1, 0, 1$ are allowed, excluding (000). The d -spacings are given by:

$$\begin{aligned} \frac{1}{d_{hkl}^2} &= \frac{(h^2 + k^2 + l^2) \sin^2 70.612^\circ + 2(hk + hl + kl)(\cos^2 70.612^\circ - \cos 70.612^\circ)}{(2.992 \text{ \AA})^2(1 - 3 \cos^2 70.612^\circ + 2 \cos^3 70.612^\circ)} \\ &= 0.1339(h^2 + k^2 + l^2) - 0.0667(hk + hl + kl). \end{aligned}$$

By considering the rotational symmetry of the point group $\bar{3}m = \mathcal{D}_{3d}$, the 26 reflections occur in the following 5 sets:

$\{hkl\}$	$\frac{1}{d_{hkl}} (\text{\AA}^{-1})$	2θ	Multiplicity
(100), (010), (001), ($\bar{1}00$), ($0\bar{1}0$), ($00\bar{1}$)	0.3659	32.77°	6
(110), (101), (011), ($\bar{1}\bar{1}0$), ($\bar{1}0\bar{1}$), ($0\bar{1}\bar{1}$)	0.4484	40.45°	6
(111), ($\bar{1}\bar{1}\bar{1}$)	0.4490	40.50°	2
($\bar{1}\bar{1}0$), ($\bar{1}0\bar{1}$), ($0\bar{1}\bar{1}$), ($\bar{1}\bar{1}0$), ($10\bar{1}$), ($0\bar{1}1$)	0.5784	52.96°	6
($\bar{1}\bar{1}\bar{1}$), ($1\bar{1}\bar{1}$), ($\bar{1}1\bar{1}$), ($\bar{1}\bar{1}1$), ($\bar{1}\bar{1}\bar{1}$), ($1\bar{1}\bar{1}$)	0.6844	63.69°	6

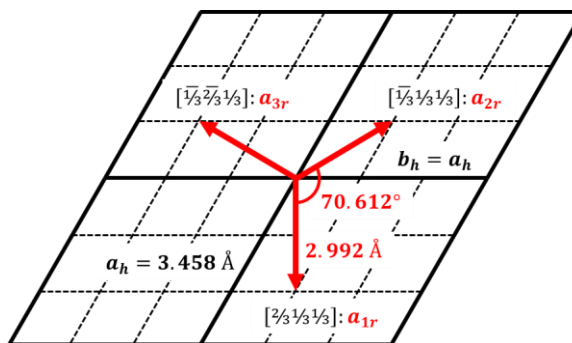
(b) Evaluate the parameters a^* and α^* of the rhombohedral unit cell in reciprocal space.

$$a^* = \frac{2\pi}{d_{100}} = 2\pi(0.3659 \text{ \AA}^{-1}) = 2.299 \text{ \AA}^{-1}$$

$$\cos \frac{\alpha^*}{2} = \frac{1/2d_{110}}{1/d_{100}} = \frac{0.2242}{0.3659} = 0.6127; \text{ therefore, } \alpha^* = 104.42^\circ.$$

(c) Transform the unit cell to the hexagonal setting. Determine the hexagonal unit cell parameters and re-index the reflections identified in (a).

The following figure illustrates the projection of the rhombohedral unit cell vectors (in red) down the c -axis of its hexagonal setting. The coordinates of each primitive vector in the hexagonal setting is given in square brackets.



Using vector notation, the three lattice vectors of the primitive rhombohedral cell are a_1, a_2, a_3 , such that $|a_1|^2 = |a_2|^2 = |a_3|^2 = a^2$ and $a_1 \cdot a_2 = a_1 \cdot a_3 = a_2 \cdot a_3 = a^2 \cos \alpha$.

In the hexagonal setting, the length of $a_{\text{hex}} = |a_1 - a_2|$. Therefore,

$$\begin{aligned} a_{\text{hex}}^2 &= (a_1 - a_2) \cdot (a_1 - a_2) = |a_1|^2 + |a_2|^2 - 2|a_1||a_2|\cos \alpha = 2a^2(1 - \cos \alpha) = 11.9606 \text{ \AA}^2 \\ a_{\text{hex}} &= 3.458 \text{ \AA} = b_{\text{hex}} \end{aligned}$$

The length of $c_{\text{hex}} = |a_1 + a_2 + a_3|$. Therefore,

$$c_{\text{hex}}^2 = (a_1 + a_2 + a_3) \cdot (a_1 + a_2 + a_3) = 3a^2(1 + 2\cos \alpha) = 44.6867 \text{ \AA}^2$$

$$c_{\text{hex}} = 6.685 \text{ \AA}$$

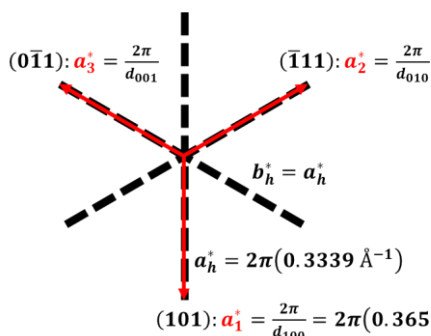
The reciprocal lattice based upon this hexagonal cell is:

$$a_{\text{hex}}^* = \frac{2\pi b_{\text{hex}} c_{\text{hex}}}{V_{\text{hex}}} = 2\pi \frac{23.1167 \text{ \AA}^2}{69.228 \text{ \AA}^3} = 2\pi(0.3339 \text{ \AA}^{-1}) \text{ perpendicular to } b_{\text{hex}} \text{ and } c_{\text{hex}}.$$

$$b_{\text{hex}}^* = \frac{2\pi a_{\text{hex}} c_{\text{hex}}}{V_{\text{hex}}} = 2\pi \frac{23.1167 \text{ \AA}^2}{69.228 \text{ \AA}^3} = 2\pi(0.3339 \text{ \AA}^{-1}) \text{ perpendicular to } a_{\text{hex}} \text{ and } c_{\text{hex}}.$$

$$c_{\text{hex}}^* = \frac{2\pi a_{\text{hex}}^2 \sin 120^\circ}{V_{\text{hex}}} = 2\pi \frac{10.3557 \text{ \AA}^2}{69.228 \text{ \AA}^3} = 2\pi(0.1496 \text{ \AA}^{-1}) \text{ perpendicular to } a_{\text{hex}} \text{ and } b_{\text{hex}}.$$

To transform the Miller indices from the rhombohedral setting $\{hkl\}_{\text{rho}}$ to the hexagonal setting $\{hkl\}_{\text{hex}}$, we make use of the following figure which projects down the c_{hex}^* axis:



The primitive reciprocal unit cell vectors (in red) include their lengths and hexagonal cell (dashed lines) indices. Then,

$$(100)_{\text{rho}} \rightarrow (101)_{\text{hex}}$$

$$(010)_{\text{rho}} \rightarrow (\bar{1}11)_{\text{hex}}$$

$$(001)_{\text{rho}} \rightarrow (0\bar{1}1)_{\text{hex}} \text{ and}$$

$$(hkl)_{\text{hex}} = (hkl)_{\text{rho}} \begin{pmatrix} 1 & 0 & 1 \\ -1 & 1 & 1 \\ 0 & -1 & 1 \end{pmatrix}$$

Using this transformation matrix, the observed reflections can be indexed by the hexagonal setting:

2θ	Mult.	$\{hkl\}_{\text{rho}}$	$\{hkl\}_{\text{hex}}$
32.77°	6	$(100), (010), (001), (\bar{1}00), (0\bar{1}0), (00\bar{1})$	$(101), (\bar{1}11), (0\bar{1}1), (\bar{1}0\bar{1}), (1\bar{1}\bar{1}), (01\bar{1})$
40.45°	6	$(110), (101), (011), (\bar{1}\bar{1}0), (\bar{1}0\bar{1}), (0\bar{1}\bar{1})$	$(012), (1\bar{1}2), (\bar{1}02), (0\bar{1}2), (\bar{1}\bar{1}2), (102)$
40.50°	2	$(111), (\bar{1}\bar{1}\bar{1})$	$(003), (00\bar{3})$
52.96°	6	$(1\bar{1}0), (\bar{1}01), (01\bar{1}), (\bar{1}10), (10\bar{1}), (0\bar{1}1)$	$(2\bar{1}0), (\bar{1}\bar{1}0), (\bar{1}20), (\bar{2}10), (110), (120)$
63.69°	6	$(1\bar{1}\bar{1}), (\bar{1}\bar{1}1), (\bar{1}11), (\bar{1}\bar{1}1), (\bar{1}\bar{1}\bar{1}), (1\bar{1}\bar{1})$	$(021), (2\bar{2}1), (\bar{2}01), (0\bar{2}\bar{1}), (\bar{2}2\bar{1}), (20\bar{1})$

- (d) Consider a distortion of the structure of $\alpha\text{-Hg}(s)$ by decreasing the rhombohedral angle to $\alpha = 60^\circ$. Determine the new 2θ values for the reflections in (a). What is another description of this distorted structure of $\alpha\text{-Hg}(s)$?

The d -spacings are given by:

$$\frac{1}{a_{hkl}^2} = \frac{(h^2 + k^2 + l^2) \sin^2 60^\circ + 2(hk + hl + kl)(\cos^2 60^\circ - \cos 60^\circ)}{(2.992 \text{ \AA})^2 (1 - 3 \cos^2 60^\circ + 2 \cos^3 60^\circ)}$$

$$= 0.1676(h^2 + k^2 + l^2) - 0.1117(hk + hl + kl).$$

Using this expression, the reflections are:

$\{hkl\}$	$\frac{1}{d_{hkl}} (\text{\AA}^{-1})$	2θ	$\{hkl\}_{\text{FCC}} (a = 4.231 \text{ \AA})$
$(100), (010), (001), (\bar{1}00), (0\bar{1}0), (00\bar{1})$	0.4094	36.79°	$\{111\}$
$(110), (101), (011), (\bar{1}\bar{1}0), (\bar{1}0\bar{1}), (0\bar{1}\bar{1})$	0.4728	42.75°	$\{200\}$
$(111), (\bar{1}\bar{1}\bar{1})$	0.4094	36.79°	$\{111\}$
$(1\bar{1}0), (\bar{1}01), (01\bar{1}), (\bar{1}10), (10\bar{1}), (0\bar{1}1)$	0.6685	62.04°	$\{220\}$
$(1\bar{1}\bar{1}), (\bar{1}\bar{1}1), (\bar{1}11), (\bar{1}\bar{1}1), (\bar{1}\bar{1}\bar{1}), (1\bar{1}\bar{1})$	0.7839	74.36°	$\{311\}$

A rhombohedral unit cell with an angle of 60° between unit cell vectors is the primitive cell for FCC with $a_{\text{FCC}} = \sqrt{2}a_{\text{rho}}$. For this model, $a_{\text{FCC}} = 4.231 \text{ \AA}$ and the corresponding Miller indices are listed above right. Notice that the 6-fold $\{100\}$ and 2-fold $\{111\}$ rhombohedral reflections coalesce into the

8-fold {111} FCC reflections. Likewise, the 12-fold set of FCC reflections {220} consists of two 6-fold sets of rhombohedral reflections: $\{1\bar{1}0\}$ and $\{211\}$; the 24-fold set of FCC reflections $\{311\}$ consists of four 6-fold sets of rhombohedral reflections: $\{11\bar{1}\}$, $\{210\}$, $\{120\}$, and $\{221\}$.

- (e) Consider another distortion of the structure of α -Hg(s) by increasing the rhombohedral angle to $\alpha = 90^\circ$. Determine the new 2θ values for the reflections in (a). What is another description of this distorted structure of α -Hg(s)?

The d -spacings are given by:

$$\frac{1}{d_{hkl}^2} = \frac{(h^2+k^2+l^2)\sin^2 90^\circ + 2(hk+hl+kl)(\cos^2 90^\circ - \cos 90^\circ)}{(2.992 \text{ \AA})^2(1-3\cos^2 90^\circ + 2\cos^3 90^\circ)} = 0.1676(h^2 + k^2 + l^2).$$

Using this expression, the reflections are:

$\{hkl\}$	$\frac{1}{d_{hkl}} (\text{\AA}^{-1})$	2θ
$(100), (010), (001), (\bar{1}00), (0\bar{1}0), (00\bar{1})$	0.4094	36.79°
$(110), (101), (011), (\bar{1}\bar{1}0), (\bar{1}0\bar{1}), (0\bar{1}\bar{1})$	0.5790	53.02°
$(111), (\bar{1}\bar{1}\bar{1})$	0.7091	66.27°
$(\bar{1}\bar{1}0), (\bar{1}0\bar{1}), (0\bar{1}\bar{1}), (\bar{1}\bar{1}0), (10\bar{1}), (0\bar{1}1)$	0.5790	53.02°
$(11\bar{1}), (1\bar{1}1), (\bar{1}11), (\bar{1}\bar{1}1), (\bar{1}\bar{1}\bar{1}), (1\bar{1}\bar{1})$	0.7091	66.27°

A rhombohedral unit cell with an angle of 90° between unit cell vectors is the primitive cell of a simple cubic structure. Notice that the 6-fold $\{110\}$ and 6-fold $\{\bar{1}\bar{1}0\}$ rhombohedral reflections coalesce into the 12-fold $\{110\}$ simple cubic reflections. Likewise, the 8-fold set of simple cubic reflections $\{111\}$ consists of the 6-fold $\{11\bar{1}\}$ set and the 2-fold $\{111\}$ set of rhombohedral reflections.

(11) A metallic element adopts a tetragonal distortion of a BCC packing of atoms. With Cu $K\alpha_1$ radiation, $\lambda = 1.5406 \text{ \AA}$, the first eight reflections are observed at 2θ values of 32.23° , 35.90° , 46.22° , 56.75° , 59.87° , 66.78° , 67.43° , and 76.10° .

(a) Determine the lattice type and index these eight reflections. The d -spacings for a tetragonal unit cell are:

$$\frac{1}{d_{hkl}^2} = \frac{(h^2+k^2)}{a^2} + \frac{(l^2)}{c^2} = \frac{4 \sin^2 \theta_{hkl}}{\lambda^2}.$$

(b) Determine the lattice constants for this element.

The lattice type is body-centered tetragonal (BCT) with a unit cell with $a \neq c$ and atoms at $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Observed reflections $\{hkl\}$ must obey $h + k + l = \text{even integer}$. Therefore, the first eight reflections for this BCT structure are most likely:

$$h + k + l = 2: \{110\} \text{ and } \{101\}; \quad h + k + l = 4: \{200\} \text{ and } \{002\};$$

$$h + k + l = 6: \{211\} \text{ and } \{112\}; \quad h + k + l = 8: \{220\} \text{ and } \{202\}.$$

According to this analysis, the reflections $\{110\}$, $\{200\}$ and $\{220\}$ involve the single lattice parameter a . The ratios $\sin^2 \theta_{220} / \sin^2 \theta_{110} = 4/2 = 2$ and $\sin^2 \theta_{220} / \sin^2 \theta_{110} = 8/2 = 4$. So, let's evaluate these ratios:

n	$2\theta_n$	$\sin \theta_n$	$\sin^2 \theta_n / \sin^2 \theta_1$	$\{hkl\}$	a (\AA)	$\{hkl\}$	c (\AA)
1	32.23°	0.2776	1	$\{110\}$	3.9247		
2	35.90°	0.3082	1.2328			$\{101\}$	3.2417
3	46.22°	0.3925	1.9996 ~ 2	$\{200\}$	3.9251		
4	56.75°	0.4752	2.9315			$\{002\}$	3.2417
5	59.87°	0.4990	3.2322			$\{211\}$	3.2424
6	66.78°	0.5503	3.9312			$\{112\}$	3.2418
7	67.43°	0.5551	3.9990 ~ 4	$\{220\}$	3.9252		
8	76.10°	0.6163	4.9308			$\{202\}$	3.2420

Average values: $a = 3.9250$ $c = 3.2420$

(c) What is the coordination environment of each metal atom in this structure?

Each metal atom is 10 + 4 coordinate. The 10 nearest neighbors consist of 8 atoms forming a tetragonally compressed cube at 3.2141 \AA and 2 atoms capping opposite square faces along the c -axis at 3.2420 \AA . The additional 4 atoms cap the rectangular faces at 3.9250 \AA .

(d) The density of this element is 15.37 g/cm^3 . Identify the element.

$$\text{Volume of 1 unit cell} = (3.9250 \text{ \AA})^2 (3.2420 \text{ \AA}) = 49.9450 \text{ \AA}^3 = 49.9450 \times 10^{-24} \text{ cm}^3$$

$$\text{Mass of 1 atom} = (15.37 \text{ g/cm}^3)(49.9450 \times 10^{-24} \text{ cm}^3) / 2 = 3.8383 \times 10^{-22} \text{ g}$$

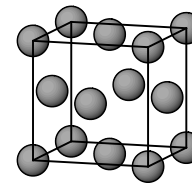
$$\text{AW} = (3.8383 \times 10^{-22} \text{ g})(6.022 \times 10^{23} \text{ mol}^{-1}) = 231.14 \text{ g/mol}$$

The metallic element is Protactinium (element #91)

- (12) Evaluate the geometrical structure factors S_{hkl} and 2θ values of the diffraction peaks predicted to be observed in an X-ray powder diffraction pattern for $2\theta < 90^\circ$ using Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) of five possible modifications of CuAu listed below. For the atomic scattering factors of Cu and Au, use the total number of electrons for each element and treat the atoms as point sources.

$$Z(\text{Cu}) = 29, Z(\text{Au}) = 79; f_{\text{Cu}} = 29; f_{\text{Au}} = 79; f_{\text{Cu/Au}} = 54.$$

- (a) A cubic unit cell with a statistically random arrangement of Cu and Au atoms. The lattice constant is 3.866 \AA . Cu/Au atoms at $(0,0,0)$, $(\frac{1}{2}, \frac{1}{2}, 0)$, $(\frac{1}{2}, 0, \frac{1}{2})$ and $(0, \frac{1}{2}, \frac{1}{2})$.



$$\begin{aligned} S_{hkl} &= 54(1 + (-1)^{h+k} + (-1)^{h+l} + (-1)^{k+l}) \\ &= 216, \text{ if } h, k, l \text{ are all even or all odd;} \\ &= 0, \text{ otherwise.} \end{aligned}$$

$$\sin^2 \theta_{hkl} = \frac{\lambda^2}{4} \cdot \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right) = 0.5943 \left(\frac{h^2+k^2+l^2}{3.866^2} \right); \quad h^2 + k^2 + l^2 \leq 12$$

The predicted reflections are $\{111\}$, $\{200\}$, $\{220\}$, $\{311\}$, $\{222\}$.

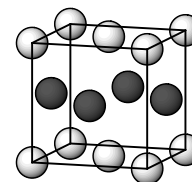
- (b) A cubic-shaped unit cell with an ordered arrangement of Cu and Au atoms. The crystal symmetry is, therefore, tetragonal, with lattice constants $a = 3.866 \text{ \AA}$ and $c = 3.866 \text{ \AA}$. Au atoms at $(0,0,0)$ and $(\frac{1}{2}, \frac{1}{2}, 0)$; Cu atoms at $(\frac{1}{2}, 0, \frac{1}{2})$ and $(0, \frac{1}{2}, \frac{1}{2})$.

$$\begin{aligned} S_{hkl} &= 79(1 + (-1)^{h+k}) + 29((-1)^{h+l} + (-1)^{k+l}) \\ &= 216, \text{ if } h, k, l \text{ are all even or all odd;} \\ &= 100, \text{ if } h \text{ and } k \text{ are both even or both odd;} \\ &= 0, \text{ otherwise.} \end{aligned}$$

$$\sin^2 \theta_{hkl} = \frac{\lambda^2}{4} \cdot \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right) = 0.5943 \left(\frac{h^2+k^2+l^2}{3.866^2} \right); \quad h^2 + k^2 + l^2 \leq 12$$

The predicted reflections are $\{001\}$, $\{110\}$, $\{111\}$, $\{002\}$, $\{200\}$, $\{201\}$, $\{112\}$, $\{202\}$, ...
... $\{220\}$, $\{221\}$, $\{003\}$, $\{310\}$, $\{113\}$, $\{311\}$, $\{222\}$.

- (c) A tetragonal unit cell with an ordered arrangement of Cu and Au atoms and lattice constants $a = 3.966 \text{ \AA}$ and $c = 3.673 \text{ \AA}$. Au atoms at $(0,0,0)$ and $(\frac{1}{2}, \frac{1}{2}, 0)$; Cu atoms at $(\frac{1}{2}, 0, \frac{1}{2})$ and $(0, \frac{1}{2}, \frac{1}{2})$.



$$\begin{aligned} S_{hkl} &= 79(1 + (-1)^{h+k}) + 29((-1)^{h+l} + (-1)^{k+l}) \\ &= 216, \text{ if } h, k, l \text{ are all even or all odd;} \\ &= 100, \text{ if } h \text{ and } k \text{ are both even or both odd;} \\ &= 0, \text{ otherwise.} \end{aligned}$$

$$\sin^2 \theta_{hkl} = \frac{\lambda^2}{4} \cdot \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right) = 0.5943 \left(\frac{h^2+k^2}{3.966^2} + \frac{l^2}{3.673^2} \right) = 0.5943 \left(\frac{h^2+k^2+1.1669 l^2}{3.966^2} \right);$$

$$h^2 + k^2 + 1.1669 l^2 \leq 13$$

The predicted reflections are $\{001\}$, $\{110\}$, $\{111\}$, $\{002\}$, $\{200\}$, $\{201\}$, $\{112\}$, $\{202\}$, ...
... $\{220\}$, $\{221\}$, $\{003\}$, $\{310\}$, $\{113\}$, $\{311\}$, $\{222\}$.

- (d) A tetragonal unit cell with an ordered arrangement of Cu and Au atoms and lattice constants $a = 4.339 \text{ \AA}$ and $c = 3.068 \text{ \AA}$. Au atoms at $(0,0,0)$ and $(\frac{1}{2}, \frac{1}{2}, 0)$; Cu atoms at $(\frac{1}{2}, 0, \frac{1}{2})$ and $(0, \frac{1}{2}, \frac{1}{2})$.

$$\begin{aligned} S_{hkl} &= 79(1 + (-1)^{h+k}) + 29((-1)^{h+l} + (-1)^{k+l}) \\ &= 216, \text{ if } h, k, l \text{ are all even or all odd;} \\ &= 100, \text{ if } h \text{ and } k \text{ are both even or both odd;} \\ &= 0, \text{ otherwise.} \end{aligned}$$

$$\sin^2 \theta_{hkl} = \frac{\lambda^2}{4} \cdot \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right) = 0.5943 \left(\frac{h^2+k^2}{4.339^2} + \frac{l^2}{3.068^2} \right) = 0.5943 \left(\frac{h^2+k^2+2l^2}{4.339^2} \right);$$

$$h^2 + k^2 + 2l^2 \leq 15$$

The predicted reflections are {001}, {110}, {111}, {002}, {200}, {201}, {112}, {202}, ...
... {220}, {221}, {310}, {311}.

- (e) A tetragonal unit cell with a statistically random arrangement of Cu and Au atoms and lattice constants $a = 4.339 \text{ \AA}$ and $c = 3.068 \text{ \AA}$. Cu/Au atoms at $(0,0,0)$, $(\frac{1}{2},\frac{1}{2},0)$, $(\frac{1}{2},0,\frac{1}{2})$ and $(0,\frac{1}{2},\frac{1}{2})$.

$$S_{hkl} = 54(1 + (-1)^{h+k} + (-1)^{h+l} + (-1)^{k+l})$$

= 216, if h, k, l are all even or all odd;
= 0, otherwise.

$$\sin^2 \theta_{hkl} = \frac{\lambda^2}{4} \cdot \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right) = 0.5943 \left(\frac{h^2+k^2}{4.339^2} + \frac{l^2}{3.068^2} \right) = 0.5943 \left(\frac{h^2+k^2+2l^2}{4.339^2} \right):$$

$$h^2 + k^2 + 2l^2 \leq 15$$

The predicted reflections are {001}, {110}, {111}, {002}, {200}, {201}, {112}, {202}, ...
... {220}, {221}, {310}, {311}.

- (f) Discuss significant differences among these diffraction patterns.

{hkl}	m	(a)		(b)	(c)	(d)	(e)		
		2θ	S _{hkl}	2θ	2θ	2θ	S _{hkl}	2θ	S _{hkl}
{001}	2		0	23.00	24.23	29.10	100		0
{110}	4		0	32.76	31.91	29.10	100		0
{111}	8	40.41	216	40.41	40.47	41.63	216	41.63	216
{200}	4	47.01	216	47.01	45.75	41.63	216	41.63	216
{002}	2	47.01	216	47.01	49.64	60.33	216	60.33	216
{201}	8		0	52.96	52.44	51.97	100		0
{112}	8		0	58.48	60.23	68.37	100		0
{220}	4	68.67	216	68.67	66.70	60.33	216	60.33	216
{202}	8	68.67	216	68.67	69.80	75.97	216	75.97	216
{221}	8		0	73.48	72.10	68.37	100		0
{003}	2		0	73.48	78.05	97.84	100		0
{310}	8		0	78.19	75.86	68.37	100		0
{311}	16	82.81	216	82.81	81.01	75.97	216	75.97	216
{113}	8	82.81	216	82.81	86.79	105.23	216	105.23	216
{222}	8	87.38	216	87.53	87.53	90.58	216	90.58	216

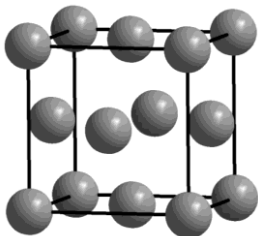
Structures (a) and (b) have the same unit cell constants so their diffraction peaks occur at the same scattering angles 2θ . Disordering among Au and Cu atoms in structure (a) creates extinctions when the Miller indices h, k, l are not all even or all odd. In fact, structure (a) is an FCC alloy and follows the extinction pattern for the FCC structure.

Structures (b), (c), and (d) are ordered arrangements of Au and Cu atoms with steadily decreasing c/a ratios of the tetragonal unit cell. As the c-axis shortens, the scattering angle increases; as the a-axis lengthens, the scattering angle decreases. Thus, the reflections {003}, {113}, and {222} for structure (d) occur at 2θ values above 90° . The ordered atomic arrangement introduces additional peaks in the diffraction patterns.

Structures (d) and (e) have the same unit cell constants so their diffraction peaks occur at the same scattering angles 2θ . Disordering among Au and Cu atoms in structure (e) creates extinctions when the Miller indices h, k, l are not all even or all odd. In fact, structure (e) is a BCC alloy which creates these extinctions. Structure (e) will only have 3 observed peaks for 2θ values below 90° .

(13) Evaluate the d -spacings, 2θ values, geometrical structure factors $|S_{hkl}|$, Lorentz-polarization factors LP_{hkl} and multiplicities m_{hkl} for the first six diffraction peaks predicted to be observed in an X-ray powder diffraction pattern using Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) of the following samples. For the atomic scattering factors of Ni and Pt, use the total number of electrons for each element and treat the atoms as point sources.

(a) A 1:1 Ni:Pt alloy that is face-centered cubic with statistically disordered Ni and Pt atoms. The lattice constant is 3.75 \AA .



Space Group = $Fm\bar{3}m$

Ni/Pt mixture at $4a$: $(0, 0, 0)$, $(\frac{1}{2}, \frac{1}{2}, 0)$, $(\frac{1}{2}, 0, \frac{1}{2})$, $(0, \frac{1}{2}, \frac{1}{2})$

$$S_{hkl} = f_{\text{Ni/Pt}} [e^{i0} + e^{i\pi(h+k)} + e^{i\pi(h+l)} + e^{i\pi(k+l)}]$$

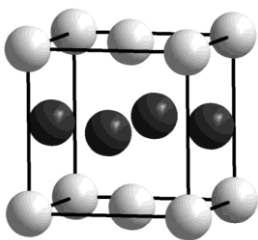
$$f_{\text{Ni/Pt}} = \frac{1}{2}(Z_{\text{Ni}} + Z_{\text{Pt}}) = \frac{1}{2}(28 + 78) = 53$$

$$S_{hkl} = 53 [1 + (-1)^{h+k} + (-1)^{h+l} + (-1)^{k+l}]$$

h , k , and l must be either all EVEN or all ODD.

$\{hkl\}$	$d_{hkl} (\text{\AA}^{-1})$	$2\theta_{hkl}$	$ S_{hkl} $	LP_{hkl}	m_{hkl}
{111}	2.165	41.72°	$4f_{\text{Ni/Zn}} = 212$	6.572	8
{200}	1.875	48.55°	$4f_{\text{Ni/Zn}} = 212$	4.666	6
{220}	1.326	71.11°	$4f_{\text{Ni/Zn}} = 212$	2.008	12
{311}	1.131	85.97°	$4f_{\text{Ni/Zn}} = 212$	1.478	24
{222}	1.083	90.82°	$4f_{\text{Ni/Zn}} = 212$	1.405	8
{400}	0.938	110.63°	$4f_{\text{Ni/Zn}} = 212$	1.461	6

(b) A 1:1 Ni:Pt alloy that is tetragonal with Pt at $(0,0,0)$ and $(\frac{1}{2}, \frac{1}{2}, 0)$ and Ni at $(\frac{1}{2}, 0, \frac{1}{2})$ and $(0, \frac{1}{2}, \frac{1}{2})$. The lattice constants are $a = 3.75 \text{ \AA}$, $c = 3.75 \text{ \AA}$.



Space Group = $P4/nmm$

Pt at $(0, 0, 0)$, $(\frac{1}{2}, \frac{1}{2}, 0)$; Ni at $(\frac{1}{2}, 0, \frac{1}{2})$, $(0, \frac{1}{2}, \frac{1}{2})$

$$S_{hkl} = f_{\text{Pt}} [e^{i0} + e^{i\pi(h+k)}] + f_{\text{Ni}} [e^{i\pi(h+l)} + e^{i\pi(k+l)}]$$

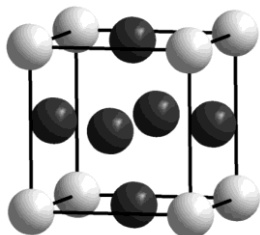
$$= 78 [1 + (-1)^{h+k}] + 28 [(-1)^{h+l} + (-1)^{k+l}]$$

h and k must be either both EVEN or both ODD.

$\{hkl\}$	$d_{hkl} (\text{\AA}^{-1})$	$2\theta_{hkl}$	$ S_{hkl} $	LP_{hkl}	m_{hkl}
{001}	3.750	23.73°	$2 f_{\text{Pt}} - f_{\text{Ni}} = 100$	22.222	2
{110}	2.652	33.80°	$2 f_{\text{Pt}} - f_{\text{Ni}} = 100$	10.452	4
{111}	2.165	41.72°	$2 f_{\text{Pt}} + f_{\text{Ni}} = 212$	6.572	8
{200}	1.875	48.55°	$2 f_{\text{Pt}} + f_{\text{Ni}} = 212$	4.666	4
{201}	1.677	54.73°	$2 f_{\text{Pt}} + f_{\text{Ni}} = 212$	3.553	8
{112}	1.531	60.47°	$2 f_{\text{Pt}} - f_{\text{Ni}} = 100$	2.837	8

Ordering Pt and Ni atoms introduces Bragg reflections that are not observed in the powder pattern for the disordered FCC alloy. The observed intensities will be affected by the geometrical structure factors, Lorentz-polarization factors, and multiplicities.

- (c) A 3:1 Ni:Pt alloy that is cubic with Pt at (0,0,0) and Ni at $(\frac{1}{2}, \frac{1}{2}, 0)$, $(\frac{1}{2}, 0, \frac{1}{2})$, and $(0, \frac{1}{2}, \frac{1}{2})$. The lattice constant is $a = 3.75 \text{ \AA}$.



Space Group = $Pm\bar{3}m$

Pt at $(0, 0, 0)$; Ni at $(\frac{1}{2}, \frac{1}{2}, 0)$, $(\frac{1}{2}, 0, \frac{1}{2})$, $(0, \frac{1}{2}, \frac{1}{2})$

$$S_{hkl} = f_{\text{Pt}}e^{i0} + f_{\text{Ni}}[e^{i\pi(h+k)} + e^{i\pi(h+l)} + e^{i\pi(k+l)}]$$

$$= 78 + 28[(-1)^{h+k} + (-1)^{h+l} + (-1)^{k+l}]$$

NO restrictions on h , k , and l .

$\{hkl\}$	$d_{hkl} (\text{\AA}^{-1})$	$2\theta_{hkl}$	$ S_{hkl} $	LP_{hkl}	m_{hkl}
{100}	3.750	23.73°	$ f_{\text{Pt}} - f_{\text{Ni}} = 50$	22.222	6
{110}	2.652	33.80°	$ f_{\text{Pt}} - f_{\text{Ni}} = 50$	10.452	12
{111}	2.165	41.72°	$ f_{\text{Pt}} + 3f_{\text{Ni}} = 162$	6.572	8
{200}	1.875	48.55°	$ f_{\text{Pt}} + 3f_{\text{Ni}} = 162$	4.666	6
{210}	1.677	54.73°	$ f_{\text{Pt}} - f_{\text{Ni}} = 50$	3.553	12
{211}	1.531	60.47°	$ f_{\text{Pt}} - f_{\text{Ni}} = 50$	2.837	24

- (14) Transition metal nitrides exhibit various physical properties that make them potentially useful materials. However, their synthesis typically requires both high pressures and temperatures and their subsequent characterization is challenging.

In 2004, a platinum nitride was reported after treating Pt metal and N_2 at $\sim 50 \text{ GPa}$ and $\sim 2000 \text{ K}$. The product, as characterized by X-ray powder diffraction, Raman spectroscopy, and energy-dispersive X-ray spectroscopy (EDX), was assigned to be cubic zinc-blende type “PtN” with $a = 4.8041(2) \text{ \AA}$. Subsequent theoretical studies suggested that a pyrite-type “PtN₂” with dinitrogen units was a better choice; this suggestion was later affirmed.

See: E. Gregoryanz, et al., *Nat. Mater.* **2004**, 3, 294.
 J. von Appen, et al., *Angew. Chem. Int. Ed.* **2006**, 45, 4365-4368.
 J. C. Crawford, et al., *Science* **2006**, 311, 1275-1278.

- (a) To examine the challenge of distinguishing different structure types for a Pt-N cubic phase with $a = 4.8041 \text{ \AA}$, calculate the $2\theta_{hkl}$ values, $|S_{hkl}|$ values (use atomic numbers of the elements for their atomic structure factors), and multiplicities for diffraction peaks observed for 2θ values below 85° using Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) for the following three structural models:

- (i) ZnS-type “PtN”: $F\bar{4}3m$; Pt at $4a$ (0, 0, 0), N at $4c$ ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$)
 (ii) NaCl-type “PtN”: $Fm\bar{3}m$; Pt at $4a$ (0, 0, 0) N at $4b$ ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$)
 (iii) CaF₂-type “PtN₂”: $Fm\bar{3}m$; Pt at $4a$ (0, 0, 0); N at $8c$ ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$) and $(-\frac{1}{4}, -\frac{1}{4}, -\frac{1}{4})$.

Use the Bragg equation for cubic systems: $\lambda = 2d_{hkl} \sin \theta_{hkl} = 2 \left(\frac{a}{\sqrt{h^2 + k^2 + l^2}} \right) \sin \theta_{hkl}$.

The limits on $\{hkl\}$ are: $h^2 + k^2 + l^2 \leq \frac{4a^2}{\lambda^2} \sin^2 \theta_{\text{max}} = 4 \left(\frac{4.8041 \text{ \AA}}{1.5418 \text{ \AA}} \right)^2 \sin^2 42.5^\circ = 17.7$

For cubic structures, the “possible” indices $\{hkl\}$ that meet this condition are:

{100}, {110}, {111}, {200}, {210}, {211}, {220}, {221}, {222}, {300}, {310}, {311}, {320}, {321}, {322}, {400}, and {410}.

Since all three structures are face-centered cubic, the indices $\{hkl\}$ must be either all EVEN or all ODD integers. The only $\{hkl\}$ indices that satisfy this criterion are: $\{111\}$, $\{200\}$, $\{220\}$, $\{222\}$, $\{311\}$, and $\{400\}$. So, there will be 6 reflections observed for 2θ values less than 85° .

$$\text{So, } \sin \theta_{hkl} = \left(\frac{\lambda}{2a}\right) \sqrt{h^2 + k^2 + l^2} = (0.160467) \sqrt{h^2 + k^2 + l^2}.$$

The multiplicity for each reflection $\{hkl\}$ is determined by considering all permutations of the indices and their possible inverses.

The geometrical structure factors for one primitive unit cell are ($f_{\text{Pt}} = 78$; $f_{\text{N}} = 7$):

$$\text{ZnS-type: } S_{hkl} = f_{\text{Pt}}e^{i0} + f_{\text{N}}e^{i\pi(h+k+l)/2} = 78 + 7(i)^{h+k+l}$$

$$\text{NaCl-type: } S_{hkl} = f_{\text{Pt}}e^{i0} + f_{\text{N}}e^{i\pi(h+k+l)} = 78 + 7(-1)^{h+k+l}$$

$$\text{CaF}_2\text{-type: } S_{hkl} = f_{\text{Pt}}e^{i0} + f_{\text{N}}e^{i\pi(h+k+l)/2} + f_{\text{N}}e^{-i\pi(h+k+l)/2} = 78 + 7[(i)^{h+k+l} + (-i)^{h+k+l}]$$

The results are:

$\{hkl\}$	$2\theta_{hkl}$	Mult.	ZnS-Type		NaCl-Type		CaF ₂ -Type	
			S_{hkl}	$ S_{hkl} $	S_{hkl}	$ S_{hkl} $	S_{hkl}	$ S_{hkl} $
$\{111\}$	32.27°	8	$78 - 7i$	78.31	$78 - 7$	71	$78 + 0$	78
$\{200\}$	37.44°	6	$78 - 7$	71	$78 + 7$	85	$78 - 14$	64
$\{220\}$	53.98°	12	$78 + 7$	85	$78 + 7$	85	$78 + 14$	92
$\{311\}$	64.31°	24	$78 + 7i$	78.31	$78 - 7$	71	$78 + 0$	78
$\{222\}$	67.54°	8	$78 - 7$	71	$78 + 7$	85	$78 - 14$	64
$\{400\}$	79.86°	6	$78 + 7$	85	$78 + 7$	71	$78 + 14$	92

- (b) For ZnS-type, NaCl-type, CaF₂-type, and pyrite-type structures of platinum nitride (either “PtN” or “PtN₂”), briefly describe the coordination environments and oxidation states for Pt and N.

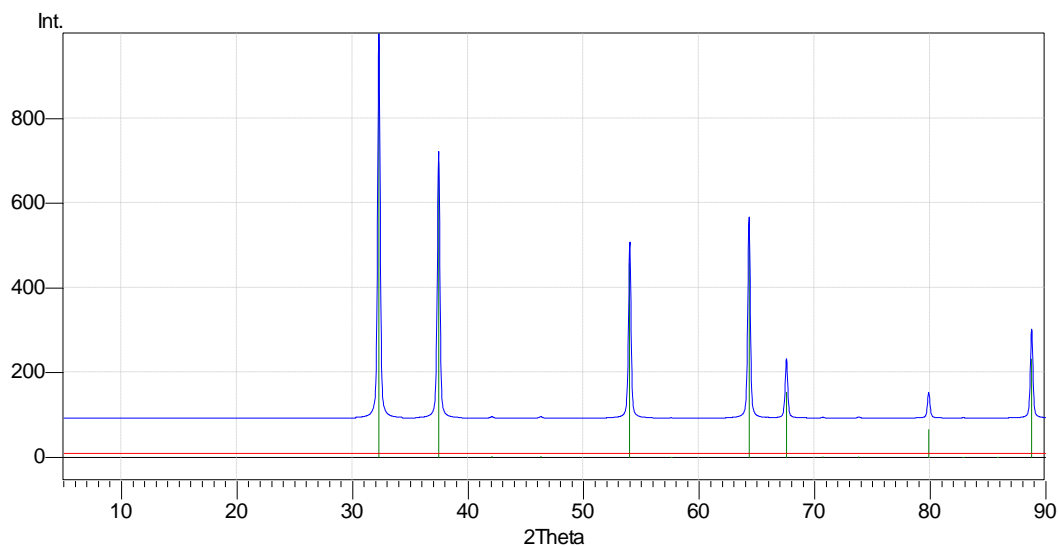
ZnS-Type: Pt – tetrahedral coordination by N; N – tetrahedral coordination by Pt
 Pt³⁺ (d^7); N³⁻ (no N–N bonds in the structure). This d -configuration for Pt is reasonable for local tetrahedral coordination with 3 unpaired electrons: $(e)^4(t_2)^3$.

NaCl-Type: Pt – octahedral coordination by N; N – octahedral coordination by Pt
 Pt³⁺ (d^7); N³⁻ (no N–N bonds in the structure). This d -configuration for Pt is not optimal for local octahedral coordination, which could be either high-spin $(t_{2g})^5(e_g)^2$ or low-spin $(t_{2g})^6(e_g)^1$.

CaF₂-Type: Pt – cubic coordination by N; N – tetrahedral coordination by Pt
 Pt⁶⁺ (d^4); N³⁻ (no N–N bonds in the structure). This d -configuration for Pt is reasonable for local cubic coordination $(e_g)^4(t_{2g})^0$.

Pyrite-Type: Pt – octahedral coordination by N; N – trigonal pyramidal coordination by 3 Pt, but they occur as [N₂]-dimers
 Pt⁴⁺ (d^6) is the optimal choice for octahedral coordination $(t_{2g})^6(e_g)^0$; N²⁻ so that there are [N₂]⁴⁻-dimers. These dimers would have formal N–N single bonds because they are isoelectronic with halogen dimers like F₂.

- (c) Here is a theoretical diffraction pattern for pyrite-type PtN_2 (the intensities are given in arbitrary units, scaled against the most intense peak). Given your results to part (a), briefly discuss the specific challenges to ascertain this platinum nitride from X-ray powder diffraction alone.



This X-ray diffraction pattern for pyrite-type PtN_2 shows 6 peaks for $2\theta_{hkl}$ values below 85° . Therefore, accurate relative intensities are needed to determine the structure from a powder diffraction pattern, an outcome that could be challenging because Pt is a much greater scatterer of X-rays than N.

(15) Manganese adopts different cubic crystal structures with various complexities. Three different vials labeled “Mn” were found in a cabinet. In addition to measuring their densities, X-ray powder diffraction patterns determined using Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) with a low-resolution detector gave the following 4 most intense peaks for each sample:

A: $42.89^\circ, 45.34^\circ, 47.69^\circ, 76.85^\circ$; $\rho = 7.21 \text{ g/cm}^3$

B: $42.97^\circ, 47.77^\circ, 52.23^\circ, 78.75^\circ$; $\rho = 7.43 \text{ g/cm}^3$

C: $41.63^\circ, 60.34^\circ, 75.97^\circ, 90.58^\circ$; $\rho = 6.32 \text{ g/cm}^3$

For each sample, determine the lattice type in the cubic system, the lattice constant, and the number of Mn atoms in one unit cell.

Use the Bragg equation for cubic systems: $\lambda = 2d_{hkl} \sin \theta_{hkl} = 2 \left(\frac{a}{\sqrt{h^2+k^2+l^2}} \right) \sin \theta_{hkl}$.

Rearranging and squaring gives: $h^2 + k^2 + l^2 = 4 \left(\frac{a}{\lambda} \right)^2 \sin^2 \theta_{hkl} = \text{integer}$, so we can take ratios with the lowest angle reflection and look for possible rational fractions.

For a cubic system, the possible lattice types are: *P* (no restrictions on h, k, l ; *F* (h, k, l must be all even or all odd integers); and *I* ($h + k + l$ must be even).

A:	n	$2\theta_n$	$\sin \theta_n$	$\frac{\sin^2 \theta_n}{\sin^2 \theta_1}$	Rational Fraction	Possible Indices	Rational Fraction	Possible Indices
	1	42.89°	0.3656	1		{300}, {221}		{411}, {330}
	2	45.34°	0.3854	1.111	10 / 9	{310}	20 / 18	{420}
	3	47.69°	0.4042	1.223	11 / 9	{311}	22 / 18	{332}
	4	76.85°	0.6215	2.890	26 / 9	{510}, {431}	52 / 18	{640}

Lattice Type: *P* *I*
 Lattice Constant (\AA): 6.325 8.945
 # Mn atoms in 1 unit cell: 20.00 56.56

Sample A is primitive cubic, with 20 Mn atoms in a cell with constant 6.325 \AA .

B:	n	$2\theta_n$	$\sin \theta_n$	$\frac{\sin^2 \theta_n}{\sin^2 \theta_1}$	Rational Fraction	Possible Indices	Rational Fraction	Possible Indices
	1	42.97°	0.3663	1		{300}, {221}		{411}, {330}
	2	47.77°	0.4049	1.222	11 / 9	{311}	22 / 18	{332}
	3	52.23°	0.4402	1.444	13 / 9	{320}	26 / 18	{510}, {431}
	4	78.75°	0.6344	3.000	27 / 9	{511}, {333}	54 / 18	{721}, {633}, {552}

Lattice Type: *P* *I*
 Lattice Constant (\AA): 6.314 8.930
 # Mn atoms in 1 unit cell: 20.51 58.00

Sample B is body-centered cubic, with 58 Mn atoms in a cell with constant 8.930 \AA .

C:	n	$2\theta_n$	$\sin \theta_n$	$\frac{\sin^2 \theta_n}{\sin^2 \theta_1}$	Rational Fraction	Possible Indices	Rational Fraction	Possible Indices
1	41.63°	0.3554	1			{100}		{110}
2	60.34°	0.5025	2.000		2 / 1	{110}	4 / 2	{200}
3	75.97°	0.6155	3.000		3 / 1	{111}	6 / 2	{211}
4	90.58°	0.7107	4.000		4 / 1	{200}	8 / 2	{220}

Lattice Type: P I

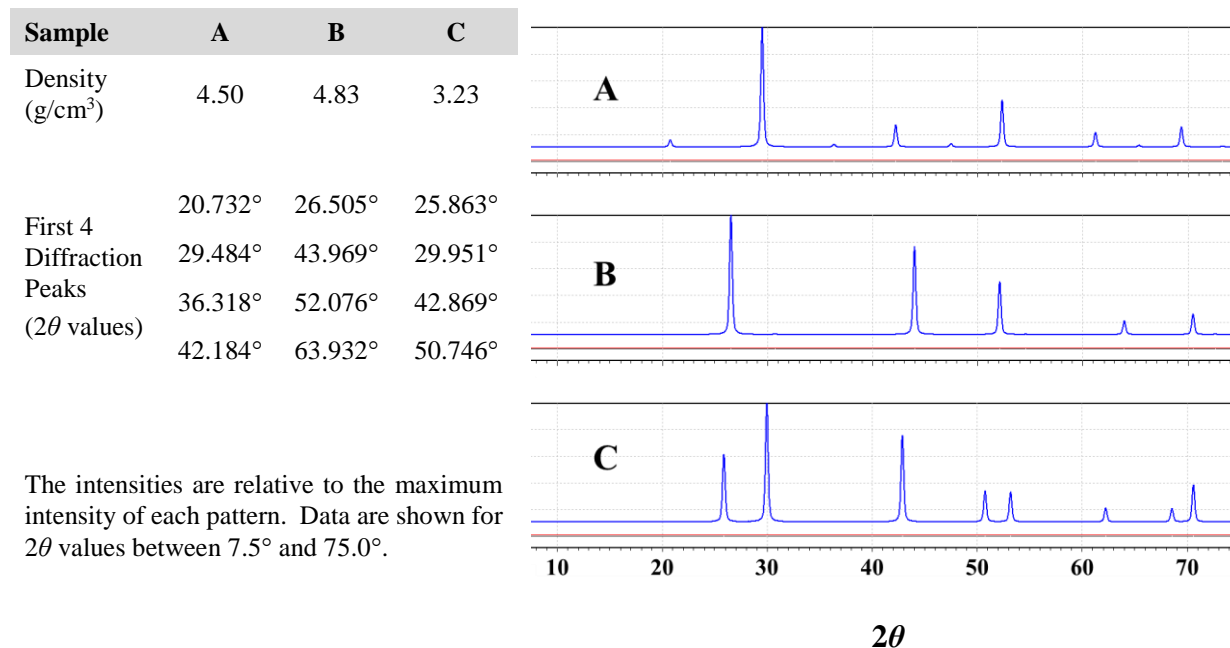
Lattice Constant (Å): 2.169 3.068

Mn atoms in 1 unit cell: 0.71 2.00

Sample C is body-centered cubic, with 2 Mn atoms in a cell with constant 3.068 Å.

- (16) The containers of three different binary metal halide salts **MX** are unlabeled and you have been tasked with determining their chemical identities, but there are limited resources available to you. You are told that one salt is cubic NaCl-type ($Fm\bar{3}m$; **M** in $4b$, **X** in $4a$ sites), one is cubic CsCl-type ($Pm\bar{3}m$; **M** in $1b$, **X** in $1a$ sites), and the other one is cubic ZnS-type ($F\bar{4}3m$; **M** in $4c$, **X** in $4a$ sites).

To determine their chemical identities, you measure densities and X-ray powder diffraction patterns using Cu $K\alpha_1$ radiation, $\lambda = 1.5406 \text{ \AA}$. The results are:



- (a) Identify the chemical formulas and crystal structures of **A**, **B**, and **C**. Briefly discuss how you reached your choices.
 (b) For each of the first 4 diffraction peaks listed, assign the (hkl) indices for each sample.
 (c) Determine the lattice constants (in \AA) for each salt **A**, **B**, and **C**.

For cubic structures, $\frac{1}{d_{hkl}^2} = \frac{h^2+k^2+l^2}{a^2} = \frac{4 \sin^2 \theta_{hkl}}{\lambda^2}$. Therefore, $\frac{\sin^2 \theta_{hkl}}{h^2+k^2+l^2} = \frac{\lambda^2}{4a^2} = \text{constant}$.

The lattice types of these structures are either primitive or face-centered, which have the following possible restrictions on observed reflection indices:

Primitive: no restrictions on h, k, l . The first few peaks are

$$\{hkl\} = \{100\}, \{110\}, \{111\}, \{200\}, \{210\}, \{211\}, \{220\}, \dots$$

Face-centered: h, k, l either all even or all odd integers. The first few peaks are

$$\{hkl\} = \{111\}, \{200\}, \{220\}, \{311\}, \{222\}, \{400\}, \{331\}, \dots$$

The intensities of the reflections will be influenced by the geometrical structure factors:

NaCl-Type: $S_{hkl} = f_X e^{i0} + f_M e^{i\pi(h+k+l)} = f_X + f_M (-1)^{h+k+l}$ with F -lattice restrictions

CsCl-Type: $S_{hkl} = f_X e^{i0} + f_M e^{i\pi(h+k+l)} = f_X + f_M (-1)^{h+k+l}$ with P -lattice restrictions

ZnS-Type: $S_{hkl} = f_X e^{i0} + f_M e^{i\pi(h+k+l)/2} = f_X + f_M (i)^{h+k+l}$ with F -lattice restrictions

The following table summarizes the data analysis:

Sample	n	$2\theta_n$	$\sin \theta_n$	P-Cell	F-Cell	$\{hkl\}$	Analysis
A	1	20.732°	0.17994	0.03238		$\{100\}$	$a = 4.281 \text{ \AA}$ FW = 212.6
	2	29.484°	0.25447	0.03238		$\{110\}$	
	3	36.318°	0.31166	0.03238		$\{111\}$	

	4	42.184°	0.35987	0.03238	{200}	
B	1	26.505°	0.22924		0.01752	{111}
	2	43.969°	0.37436		0.03504	{200}
	3	52.076°	0.43897		0.01752	{220}
	4	63.932°	0.52942		0.01752	{311}
					0.02336	{222}
	4	63.932°	0.52942		0.01752	{400}
C	1	25.863°	0.22379		0.01669	{111}
	2	29.951°	0.25841		0.01669	{200}
	3	42.869°	0.36544		0.01669	{220}
	4	50.746°	0.42851		0.01669	{311}

$a = 5.820 \text{ \AA}$
 FW = 143.3

$a = 5.962 \text{ \AA}$
 FW = 102.9

Sample A is CsCl-type. Based on the FW, it could be either RbI or CsBr. Since this structure type is preferred for relatively large cations, the better choice is CsBr. Among the first 4 reflections, the 2nd and 4th peaks, {110} and {200}, should have higher intensities than the 1st and 3rd peaks, {100} and {111}.

Sample B is either NaCl- or ZnS-type. Based on the FW, it could be either AgCl or CuBr. Since the {200} and {222} reflections are not observed, the atomic numbers of M and X must be close to each other, based on S_{hkl} . Therefore, we may conclude the better choice is CuBr, which adopts the ZnS-type structure.

Sample C must then be NaCl-type. Based on the FW, it is NaBr.

- (17) Half-Heusler compounds **ABC** are cubic, space group $F\bar{4}3m$, with one element at Wyckoff site $4a$ (0, 0, 0), a second element at $4b$ ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$), and the third element at $4c$ ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$). For every ternary example **ABC** such as TiNiSn, there are three different possible motifs. Discuss how these three motifs differ from each other. For the first six reflections that can be observed in an X-ray powder diffraction pattern, evaluate their multiplicities and expressions for the geometrical structure factors S_{hkl} in terms of atomic form factors f_A , f_B , and f_C .

The structure of half-Heusler compounds involve 3 interpenetrating FCC arrangements of different atoms. Wyckoff sites $4a$ and $4b$ form the NaCl-type arrangement with sites $4c$ filling one-half of the cubes in an alternating pattern along each of the three cubic unit cell directions. As a result, each $4c$ site is 8-coordinate (4 by $4a$ and 4 by $4b$). Likewise, each $4a$ site is 4-coordinate by $4c$ and 6-coordinate by $4b$; each $4b$ site is 4-coordinate by $4a$ and 6-coordinate by $4c$.

For ternary ABC compounds, we can use this description to differentiate the 3 distinct motifs:

- (1) Elements A and B form the NaCl-network with A at $4a$ sites and B at $4b$ sites = "ABC". C occupies the $4c$ sites, so that "AC" and "BC" each form a 3d tetrahedral network.
- (2) Elements A and C form the NaCl-network with A at $4a$ sites and C at $4b$ sites = "CAB". B occupies the $4c$ sites, so that "AB" and "BC" each form a 3d tetrahedral network.
- (3) Elements B and C form the NaCl-network with B at $4a$ sites and C at $4b$ sites = "BCA". A occupies the $4c$ sites, so that "AB" and "AC" each form a 3d tetrahedral network.

Since the structure has an F -centered lattice, then reflections $\{hkl\}$ occur for the indices h, k , and l either all even or all odd integers. The geometrical structure factor for observed reflection is:

$$S_{hkl} = f_{4a}e^{i0} + f_{4b}e^{i\pi(h+k+l)} + f_{4c}e^{i\pi(h+k+l)/2} = f_{4a} + f_{4b}(-1)^{h+k+l} + f_{4c}(i)^{h+k+l}$$

Therefore,

$\{hkl\}$	Mult.	$ S_{hkl}(\text{"ABC"}) $	$ S_{hkl}(\text{"CAB"}) $	$ S_{hkl}(\text{"BCA"}) $
{111}	8	$\sqrt{f_{4a}^2 + f_{4b}^2 + f_{4c}^2 - 2f_{4a}f_{4b}}$	$\sqrt{f_{4c}^2 + f_{4a}^2 + f_{4b}^2 - 2f_{4c}f_{4a}}$	$\sqrt{f_{4b}^2 + f_{4c}^2 + f_{4a}^2 - 2f_{4b}f_{4c}}$
{200}	6	$ f_{4a} + f_{4b} - f_{4c} $	$ f_{4c} + f_{4a} - f_{4b} $	$ f_{4b} + f_{4c} - f_{4a} $
{220}	12	$f_{4a} + f_{4b} + f_{4c}$	$f_{4c} + f_{4a} + f_{4b}$	$f_{4b} + f_{4c} + f_{4a}$
{311}	24	$\sqrt{f_{4a}^2 + f_{4b}^2 + f_{4c}^2 - 2f_{4a}f_{4b}}$	$\sqrt{f_{4c}^2 + f_{4a}^2 + f_{4b}^2 - 2f_{4c}f_{4a}}$	$\sqrt{f_{4b}^2 + f_{4c}^2 + f_{4a}^2 - 2f_{4b}f_{4c}}$
{222}	8	$ f_{4a} + f_{4b} - f_{4c} $	$ f_{4c} + f_{4a} - f_{4b} $	$ f_{4b} + f_{4c} - f_{4a} $
{400}	6	$f_{4a} + f_{4b} + f_{4c}$	$f_{4c} + f_{4a} + f_{4b}$	$f_{4b} + f_{4c} + f_{4a}$

The lattice constant of TiNiSn is 5.93 Å. Determine the 2θ values and the 3 possible geometrical structure factors $|S_{hkl}|$ for the first six reflections using Cu $K\alpha_1$ radiation ($\lambda = 1.5406$ Å). Use atomic numbers for the atomic form factors. How might an experimental powder pattern determine the arrangement of atoms in TiNiSn?

For cubic structures, $\sin \theta_{hkl} = \frac{\lambda\sqrt{h^2+k^2+l^2}}{2a}$. For TiNiSn, $f_{\text{Ti}} = 22$, $f_{\text{Ni}} = 28$, $f_{\text{Sn}} = 50$.

$\{hkl\}$	Mult.	$2\theta_{hkl}$	$ S_{hkl}(\text{"TiNiSn"}) $	$ S_{hkl}(\text{"SnTiNi"}) $	$ S_{hkl}(\text{"NiSnTi"}) $
{111}	8	26.01°	50.4	39.6	31.1
{200}	6	30.12°	0	44	56
{220}	12	43.11°	100	100	100
{311}	24	51.04°	50.4	39.6	31.1
{222}	8	53.49°	0	44	56
{400}	6	62.61°	100	100	100

The relative intensities of the Bragg reflections provide the means to determine the arrangement of elements in the half-Heusler structure. For X-ray scattering, the atomic form factors all decrease as scattering angle increases. Nevertheless, for TiNiSn, the arrangement with Ti and Ni forming the NaCl-network gives effective extinction for two of the first 6 possible reflections: {200} and {222}. Differentiating the other two arrangements requires careful analysis of the intensities by measuring diffraction on good samples.

NOTE: In the experimental structure of TiNiSn, Sn and Ti form the NaCl-network.

- (18) Alloys of copper and zinc, called brasses, occur from 100 mole percent Cu to 100 mole percent Zn and their structures vary systematically with Zn content. Among the known Cu-Zn brasses, α -brass is FCC, β -brass is BCC, and ϵ -brass is HCP. Using Cu $K\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$), these three brasses give the following first four reflections in their corresponding diffraction patterns:

A: 37.185°, 38.812°, 43.250°, 54.838°

B: 42.881°, 49.932°, 73.298°, 88.845°

C: 43.342°, 62.965°, 79.525°, 95.217°

- (a) Assign each of these patterns to α -, β -, or ϵ -brass. For each case, provide the Miller indices for each observed reflection.
(b) Determine the lattice constants (in \AA) for each Cu-Zn brass structure.

For cubic structures, $\frac{1}{d_{hkl}^2} = \frac{h^2+k^2+l^2}{a^2} = \frac{4 \sin^2 \theta_{hkl}}{\lambda^2}$. Therefore, $\frac{\sin^2 \theta_{hkl}}{h^2+k^2+l^2} = \frac{\lambda^2}{4a^2} = \text{constant}$.

For an FCC structure, h, k, l are either all even or all odd integers. The first 4 peaks are:

{ hkl } = {111}, {200}, {220}, {311}.

For a BCC structure, $h + k + l = \text{even integer}$. The first 4 peaks are

{ hkl } = {110}, {200}, {211}, {220}.

The values $\sin^2 \theta_n / (h^2 + k^2 + l^2)$ for each lattice type are:

Sample	$\sin^2 \theta_{hkl} / (h^2 + k^2 + l^2)$					
	n	$2\theta_n$	$\sin \theta_n$	FCC Test	BCC Test	
A	1	37.185°	0.31884	0.033885	0.050828	HCP-Type (see below)
	2	38.812°	0.33226	0.027599	0.027599	
	3	43.250°	0.36934	0.017052	0.022736	
	4	54.838°	0.46049	0.019278	0.026507	
B	1	42.881°	0.36553	0.044539	0.066808	FCC-Type $a = 3.650 \text{ \AA}$
	2	49.932°	0.42208	0.044538	0.044538	
	3	73.298°	0.59691	0.044538	0.059384	
	4	88.845°	0.69994	0.044538	0.061240	
C	1	43.342°	0.36928	0.045455	0.068183	BCC-Type $a = 2.950 \text{ \AA}$
	2	62.965°	0.52224	0.068183	0.068183	
	3	79.525°	0.63961	0.051137	0.068183	
	4	95.217°	0.73856	0.049588	0.068183	

For a hexagonal structure, $\frac{1}{d_{hkl}^2} = \frac{4(h^2+hk+k^2)}{3a^2} + \frac{l^2}{c^2} = \frac{4 \sin^2 \theta_{hkl}}{\lambda^2}$

The HCP structure has atoms at $(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$ and $(\frac{2}{3}, \frac{1}{3}, \frac{3}{4})$ in one unit cell. The structure factor S_{hkl} for the unit cell creates extinctions so that all observed reflections occur for the following indices:

{00l}: $l = 2n$ (even integer) = {002}, {004}, ...

{hhl}: $l = 2n$ (even integer) = {110}, {220}, {112}, {222}, ...

{hkl}: either $l = 2n$ (even integer) or, if $l = 2n + 1$ (odd integer), then $h-k = 3n + 1$ or $3n + 2$ = {100}, {200}, {300}, {101}, {102}, {103}, {201}, ...

In HCP, since $c/a \sim 1.63$, the first two reflections are assumed to be {100} and {002} in either order. For this case, trial-and-error is the best approach:

If $2\theta_{100} = 37.185^\circ$ and $2\theta_{002} = 38.812^\circ$, then $a = 2.790 \text{ \AA}$ and $c = 4.637 \text{ \AA}$; ($c/a = 1.662$).

Using this information, $2\theta_{101} = 42.138^\circ$ and $2\theta_{102} = 54.833^\circ$.

If $2\theta_{002} = 37.185^\circ$ and $2\theta_{100} = 38.812^\circ$, then $a = 2.677 \text{ \AA}$ and $c = 4.832 \text{ \AA}$; ($c/a = 1.805$).

Using this information, $2\theta_{101} = 43.250^\circ$ and $2\theta_{102} = 54.838^\circ$.

The **second assignment** gives excellent agreement with the observed data

- (c) For each structure, evaluate the average atomic volume (in \AA^3). Since Zn has a slightly larger 12-coordinate metallic radius than Cu, assign the trend in Zn composition for the different Cu-Zn brasses.

Sample A: HCP, # atoms / unit cell = 2, $V_{\text{cell}} = 29.988 \text{ \AA}^3$. $\langle V_{\text{atom}} \rangle = 14.994 \text{ \AA}^3$.

Sample B: FCC, # atoms / unit cell = 4, $V_{\text{cell}} = 48.627 \text{ \AA}^3$. $\langle V_{\text{atom}} \rangle = 12.157 \text{ \AA}^3$.

Sample C: BCC, # atoms / unit cell = 2, $V_{\text{cell}} = 25.672 \text{ \AA}^3$. $\langle V_{\text{atom}} \rangle = 12.836 \text{ \AA}^3$.

Since the average atomic volume increases from FCC to BCC to HCP structures in the Cu-Zn brasses, then the Zn composition also increases along this structural trend.

- (d) At ~61 mole percent Zn, a cubic structure forms in the Cu-Zn system γ -brass with a lattice constant less than 1.00 nm. A low-resolution X-ray diffraction pattern using Cu $K\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) reveals two reflections at scattering angles 43.7° and 80.3° . Deduce possible lattice constants, lattice types, and approximate numbers of atoms in one unit cell from this limited data.

For a cubic structure, $(h^2 + k^2 + l^2)\lambda^2 = 4a^2 \sin^2 \theta_{hkl}$. Since $a < 10 \text{ \AA}$, then $h^2 + k^2 + l^2 < 23$.

Comparison of the two observed reflections reveals $\sin^2 \theta_{h'k'l'} / \sin^2 \theta_{hkl} = 3$.

Since the intensity of a reflection depends on the multiplicity, let's consider the indices that have the 3 highest multiplicities under the above restriction. The possible multiplicities are $\{h00\}$: 6, $\{hh0\}$: 12, $\{hhh\}$: 8, $\{hk0\}$: 24, $\{hkk\}$: 24, $\{hkl\}$: 48. For $h^2 + k^2 + l^2$ below 23, these values are 14, 18, and 21:

$h^2 + k^2 + l^2 = 14$: $\{321\}$, $m = 48$, then $h'^2 + k'^2 + l'^2 = 42$: $\{541\}$, $m = 48$

$a = 7.74 \text{ \AA}$; lattice type can be either *P* or *I* ($h + k + l = \text{even}$); ~36 atoms / unit cell

$h^2 + k^2 + l^2 = 18$: $\{411\}$, $m = 24$ and $\{330\}$, $m = 12$, then

$h'^2 + k'^2 + l'^2 = 54$: $\{721\}$, $m = 48$, $\{633\}$, $m = 24$, and $\{552\}$, $m = 24$

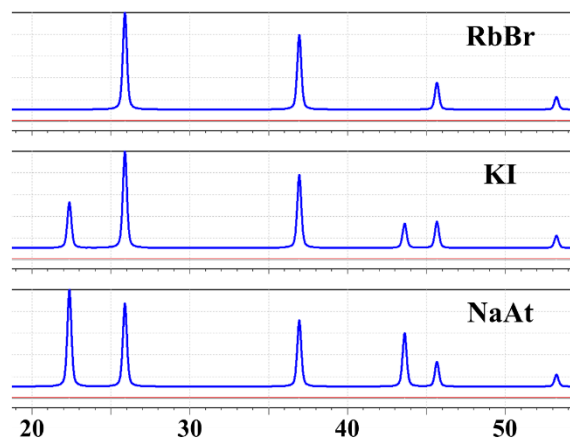
$a = 8.78 \text{ \AA}$; lattice type can be either *P* or *I* ($h + k + l = \text{even}$); ~52 atoms / unit cell

$h^2 + k^2 + l^2 = 21$: $\{421\}$, $m = 48$, then $h'^2 + k'^2 + l'^2 = 63$: NO indices

This solution is not an option.

From the limited information, there are two reasonable solutions. In fact, γ -brass is body-centered cubic with 52 atoms per unit cell.

- (19) Here are three model X-ray powder diffraction patterns for rocksalt-type halides RbBr, KI, and “NaAt” calculated for lattice constant 6.877 Å and Cu $K\alpha_1$ radiation ($\lambda = 1.5406$ Å). There are six possible reflections in this region at scattering angles 22.374°, 25.891°, 36.941°, 43.616°, 45.662°, and 53.237°. For each of these reflections of each chemical substance, determine the Miller indices, multiplicity, Lorentz-polarization factor, and the magnitude of the geometrical structure factor. To calculate the atomic form factors, the following approximation may be used:



$$f_Z(d_{hkl}) = a_1 \exp\left(-\frac{b_1}{d_{hkl}^2}\right) + a_2 \exp\left(-\frac{b_2}{d_{hkl}^2}\right) + a_3 \exp\left(-\frac{b_3}{d_{hkl}^2}\right) + a_4 \exp\left(-\frac{b_4}{d_{hkl}^2}\right) + c$$

Element	a_1	b_1	a_2	b_2	a_3	b_3	a_4	b_4	c
Rb	17.1784	1.7888	9.6435	17.3151	5.1399	0.2748	1.5292	164.934	3.4873
Br	17.1789	2.1723	5.2358	16.5796	5.6377	0.2609	3.9851	41.4328	2.9557
K	8.2186	12.7949	7.4398	0.7748	1.0519	213.187	0.8659	41.6841	1.4228
I	20.1472	4.347	18.9949	0.3814	7.5138	27.766	2.2735	66.8776	4.0712
Na	4.7626	3.285	3.1736	8.8422	1.2674	0.3136	1.1128	129.424	0.676
At	35.3163	0.68587	19.0211	3.97458	9.49887	11.3824	7.42518	45.4715	13.7108

Source: <https://lampz.tugraz.at/~hadley/ss1/crystaldiffraction/atomicformfactors/formfactors.php>

From this analysis, explain each calculated diffraction pattern.

The NaCl-type structure has a face-centered cubic lattice, so that the first six observable peaks are:

$$\{hkl\} = \{111\}, \{200\}, \{220\}, \{311\}, \{222\}, \{400\}.$$

The Lorentz-polarization factor for a powder diffraction pattern varies as $\frac{1+\cos^2 2\theta}{\sin \theta \sin 2\theta}$.

The geometrical structure factor is $S_{hkl} = f_X e^{i0} + f_M e^{i\pi(h+k+l)} = f_X + f_M (-1)^{h+k+l}$.

The intensity for any diffraction peak is proportional to the product of the multiplicity, Lorentz-polarization factor, and the square of the geometrical structure factor.

The following table summarizes these data (you can use a spreadsheet program like Excel to evaluate this information). The intensities are scaled with respect to the highest intensity:

$2\theta_{hkl}$	$\{hkl\}$	Mult.	LP	S_{hkl} ("MX")	RbBr		KI		"NaAt"	
					S_{hkl}	I_{rel}	S_{hkl}	I_{rel}	S_{hkl}	I_{rel}
22.374°	{111}	8	25.12	$f_X - f_M$	1.50	0.17	27.01	56.54	59.74	100.00
25.891°	{200}	6	18.50	$f_X + f_M$	49.68	100.00	48.34	100.00	71.43	78.96
36.941°	{220}	12	8.61	$f_X + f_M$	42.17	67.06	40.50	65.33	61.58	54.61
43.616°	{311}	24	5.95	$f_X - f_M$	1.08	0.06	20.74	23.68	47.56	45.02
45.662°	{222}	8	5.36	$f_X + f_M$	37.52	22.06	35.86	21.28	55.11	18.17
53.237°	{400}	6	3.78	$f_X + f_M$	33.95	9.56	32.65	9.33	50.42	8.05

RbBr has two near extinctions because the atomic form factors of Rb and Br are nearly equal. Therefore, reflections {111} and {311} are not observed in the pattern. The intensities of the remaining peak decrease as scattering angle increases.

KI displays all six peaks, with the most intense peak being {200}. Destructive interference between the cation and anion lowers the intensity of {111}.

“NaAt” also displays all six peaks with decreasing intensity with increasing scattering angle. In this case, each peak is dominated by the form factor for At and the Lorentz-polarization along with the multiplicity affects the trend in intensities.

- (20) SrSnO₃ and Sr₃SnO are both cubic, space group $Pm\bar{3}m$, and belong to the (anti)-perovskite family of structures. Evaluate the 2θ values, multiplicities, Lorentz-polarization factors, and geometrical structure factors S_{hkl} for the peaks predicted to be observed in an X-ray powder diffraction pattern using Cu $K\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$) for scattering angles less than 90° .

SrSnO₃: $a = 4.0254 \text{ \AA}$; Sr at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, Sn at $(0,0,0)$, O at $(\frac{1}{2}, 0, 0)$, $(0, \frac{1}{2}, 0)$, $(0, 0, \frac{1}{2})$

Sr₃SnO: $a = 5.1394 \text{ \AA}$; Sn at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, O at $(0,0,0)$, Sr at $(\frac{1}{2}, 0, 0)$, $(0, \frac{1}{2}, 0)$, $(0, 0, \frac{1}{2})$

The atomic form factors may be evaluated using the following approximation:

$$f_Z(d_{hkl}) = a_1 \exp\left(-\frac{b_1}{d_{hkl}^2}\right) + a_2 \exp\left(-\frac{b_2}{d_{hkl}^2}\right) + a_3 \exp\left(-\frac{b_3}{d_{hkl}^2}\right) + a_4 \exp\left(-\frac{b_4}{d_{hkl}^2}\right) + c$$

Element	a_1	b_1	a_2	b_2	a_3	b_3	a_4	b_4	c
O	3.0485	13.2771	2.2868	5.7011	1.5463	0.3239	0.867	32.9089	0.2508
Sr	17.5663	1.5564	9.8184	14.0988	5.422	0.1664	2.6694	132.376	2.5064
Sn	19.1889	5.8303	19.1005	0.5031	4.4585	26.8909	2.4663	83.9571	4.7821

Source: <https://lampz.tugraz.at/~hadley/ss1/crystaldiffraction/atomicformfactors/formfactors.php>

Discuss important *qualitative* differences in these two patterns.

For cubic structures, $(h^2 + k^2 + l^2)\lambda^2 = 4a^2 \sin^2 \theta_{hkl}$. For $\theta_{\max} = 45^\circ$, $h^2 + k^2 + l^2 < 0.8427a^2$.

SrSnO₃: $a = 4.0254 \text{ \AA}$; $h^2 + k^2 + l^2 < 13.7$

Sr₃SnO: $a = 5.1394 \text{ \AA}$; $h^2 + k^2 + l^2 < 22.3$

For primitive cubic lattices, there are no restrictions on the Miller indices.

The Lorentz-polarization factor for a powder diffraction pattern varies as $\frac{1+\cos^2 2\theta}{\sin \theta \sin 2\theta}$.

The geometrical structure factor is $S_{hkl} = f_A e^{i0} + f_B e^{i\pi(h+k+l)} + f_X (e^{i\pi h} + e^{i\pi k} + e^{i\pi l})$
 $= f_A + f_B (-1)^{(h+k+l)} + f_X [(-1)^h + (-1)^k + (-1)^l]$

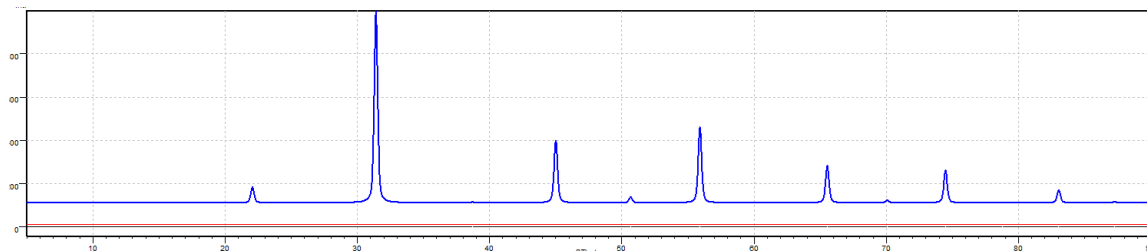
The intensity for any diffraction peak is proportional to the product of the multiplicity, Lorentz-polarization factor, and the square of the geometrical structure factor.

The following table summarizes these data. The intensities are scaled with respect to the highest intensity:

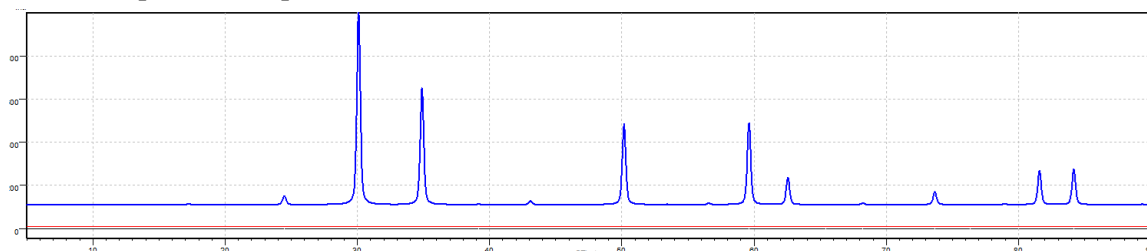
{hkl}	Mult.	SrSnO ₃					Sr ₃ SnO				
		2θ	LP	S_{hkl}	I_{rel}		2θ	LP	S_{hkl}	I_{rel}	
{100}	6	22.06	25.86	14.44	7.89		17.24	43.05	-4.68	0.50	
{110}	12	31.40	12.26	52.80	100.00		24.47	20.82	13.68	4.11	
{111}	8	38.71	7.76	-1.22	0.02		30.09	13.43	-102.87	100.00	
{200}	6	45.00	5.54	53.24	22.99		34.89	9.76	102.09	53.65	
{210}	24	50.67	4.24	7.76	1.49		39.16	7.57	-4.28	0.29	
{211}	24	55.90	3.39	38.46	29.31		43.08	6.12	8.94	1.03	
{220}	12	65.54	2.38	41.55	12.01		50.17	4.33	82.87	31.39	
{300}	6	70.07	2.07	6.77	0.14		53.44	3.75	-3.46	0.02	
{310}	24	74.48	1.84	31.85	10.91		56.58	3.29	7.19	0.36	
{311}	24	78.79	1.67	0.65	0.00		59.62	2.93	-70.48	30.70	
{222}	8	83.04	1.54	35.55	3.80		62.56	2.63	71.74	9.52	
{320}	24	87.25	1.45	6.89	0.40		65.42	2.39	-3.39	0.06	
{321}	48						68.22	2.18	6.78	0.42	
{400}	6						73.67	1.88	63.78	4.02	
{410}	24						76.34	1.76	-3.65	0.05	

{411}	24							78.97	1.66	6.81	0.16
{330}	12							78.97	1.66	6.81	0.08
{331}	24							81.58	1.58	-56.01	10.46
{420}	24							84.18	1.52	57.63	10.62
{421}	48							86.76	1.46	-3.95	0.10
{332}	24							89.34	1.42	6.91	0.14

SrSnO₃: Having the smaller lattice constant means that there are fewer possible Bragg reflections within a certain range of scattering angles than for Sr₃SnO. The geometrical structure factors are greatest for all even indices, but their amplitudes decrease with increasing scattering angles. The calculation of relative intensities suggests there will be 5 or 6 observable peaks in the pattern.



Sr₃SnO: There are more possible Bragg reflections than for SrSnO₃. The geometrical structure factors are dominated by Sr. The calculation of relative intensities suggests there will be 7 or 8 observable peaks in the pattern.



(21) The hexagonal structures of AlB_2 and InNi_2 are closely related and differ by the arrangements of atoms in their respective unit cells. Consider two possible arrangements of Ni and In atoms in InNi_2 , which has lattice parameters $a \sim 4.2 \text{ \AA}$ and $c \sim 5.1 \text{ \AA}$:

I: Ni at $(0,0,0)$, $(0,0,1/2)$, $(1/3,2/3,1/4)$, and $(2/3,1/3,3/4)$; In at $(1/3,2/3,3/4)$ and $(2/3,1/3,1/4)$

II: Ni at $(1/3,2/3,1/4)$, $(2/3,1/3,1/4)$, $(2/3,1/3,3/4)$, and $(1/3,2/3,3/4)$; In at $(0,0,0)$ and $(0,0,1/2)$

Determine all reflections using Cu $K\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$) with scattering angles less than 60° . For each possible reflection, determine the indices, the multiplicity, and the geometrical structure factor (in terms of the atomic form factors f_{In} and f_{Ni}).

How would you distinguish between the two arrangements of atoms?

For a hexagonal structure, $\frac{\lambda^2(h^2+hk+k^2)}{3a^2} + \frac{\lambda^2l^2}{4c^2} = \sin^2 \theta_{hkl}$. Therefore, for $2\theta_{hkl} < 60^\circ$

$$0.04485(h^2 + hk + k^2) + 0.02281 l^2 < 0.25; \text{ or } h^2 + hk + k^2 < 5.6 \text{ and } l^2 < 10.9.$$

Possible indices include $\{001\}, \{002\}, \{003\}; \{100\}, \{200\}, \{110\}; \{101\}, \{102\}, \{201\}, \{111\}, \{112\}$.

The geometrical structure factors S_{hkl} for these unit cells are:

$$\text{I: } S_{hkl} = f_{\text{Ni}} \left[1 + (-1)^l + \exp\left(\frac{2\pi ih}{3} + \frac{4\pi ik}{3} + \frac{\pi il}{2}\right) + \exp\left(\frac{4\pi ih}{3} + \frac{2\pi ik}{3} + \frac{3\pi il}{2}\right) \right] \\ + f_{\text{In}} \left[\exp\left(\frac{4\pi ih}{3} + \frac{2\pi ik}{3} + \frac{\pi il}{2}\right) + \exp\left(\frac{2\pi ih}{3} + \frac{4\pi ik}{3} + \frac{3\pi il}{2}\right) \right]$$

$$\text{II: } S_{hkl} = f_{\text{In}} \left[1 + (-1)^l \right] + f_{\text{Ni}} \left[\exp\left(\frac{2\pi ih}{3} + \frac{4\pi ik}{3} + \frac{\pi il}{2}\right) + \exp\left(\frac{4\pi ih}{3} + \frac{2\pi ik}{3} + \frac{3\pi il}{2}\right) + \exp\left(\frac{4\pi ih}{3} + \frac{2\pi ik}{3} + \frac{\pi il}{2}\right) + \exp\left(\frac{2\pi ih}{3} + \frac{4\pi ik}{3} + \frac{3\pi il}{2}\right) \right]$$

The multiplicities and S_{hkl} expressions for each structure, listing in order of increasing 2θ are:

$\{hkl\}$	Mult.	2θ	$S_{hkl}(\text{I})$	$S_{hkl}(\text{II})$
$\{001\}$	2	17.37	0	0
$\{100\}$	6	24.45	$-f_{\text{In}} + f_{\text{Ni}}$	$2f_{\text{In}} - 2f_{\text{Ni}}$
$\{101\}$	12	30.15	$\sqrt{3}f_{\text{In}} - \sqrt{3}f_{\text{Ni}}$	0
$\{002\}$	2	35.16	$-2f_{\text{In}}$	$2f_{\text{In}} - 4f_{\text{Ni}}$
$\{110\}$	6	43.04	$2f_{\text{In}} + 4f_{\text{Ni}}$	$2f_{\text{In}} + 4f_{\text{Ni}}$
$\{102\}$	12	43.30	$f_{\text{In}} + 3f_{\text{Ni}}$	$2f_{\text{In}} + 2f_{\text{Ni}}$
$\{111\}$	12	46.74	0	0
$\{200\}$	6	50.12	$-f_{\text{In}} + f_{\text{Ni}}$	$2f_{\text{In}} - 2f_{\text{Ni}}$
$\{201\}$	12	53.45	$-\sqrt{3}f_{\text{In}} + \sqrt{3}f_{\text{Ni}}$	0
$\{003\}$	2	53.89	0	0
$\{112\}$	12	56.74	$-2f_{\text{In}}$	$2f_{\text{In}} - 4f_{\text{Ni}}$

For structure I, there are 8 expected reflections below 60° . There is a 6_3 screw axis, which creates extinctions for $\{00l\}$ reflections with odd l .

For structure II, there are 8 expected reflections below 60° . The actual unit cell has $c \sim 2.55 \text{ \AA}$, so all reflections with odd l are extinct.

Distinguishing between the two models is best determined by the $\{101\}$ and $\{201\}$ reflections, which are expected to have observable intensities for Model I but to be totally extinct for Model II. Also, their intensities are expected to be larger, respectively, than the two immediately preceding reflections $\{100\}$ and $\{200\}$.

(22) Hexagonal structures related to ZrBeSi show either ordered or random arrangements of atoms on the main group atom sites. Consider two possible arrangements of Be and Si atoms in ZrBeSi, which has lattice parameters $a \sim 3.7 \text{ \AA}$ and $c \sim 7.2 \text{ \AA}$:

I: Zr at (0,0,0) and (0,0,1/2); Be at (1/3, 2/3, 1/4) and (2/3, 1/3, 3/4); Si at (1/3, 2/3, 3/4) and (2/3, 1/3, 1/4)

II: Zr at (0,0,0) and (0,0,1/2); Be/Si (1/3, 2/3, 1/4), (2/3, 1/3, 1/4), (2/3, 1/3, 3/4), and (1/3, 2/3, 3/4)

Determine all reflections using Cu $K\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$) with scattering angles less than 60° . For each possible reflection, determine the indices, the multiplicity, and the geometrical structure factor (in terms of the atomic form factors f_{Zr} , f_{Be} , and f_{Si}).

How would you distinguish between the two arrangements of atoms?

For a hexagonal structure, $\frac{\lambda^2(h^2+hk+k^2)}{3a^2} + \frac{\lambda^2l^2}{4c^2} = \sin^2 \theta_{hkl}$. Therefore, for $2\theta_{hkl} < 60^\circ$

$$0.05779(h^2 + hk + k^2) + 0.01145 l^2 < 0.25; \text{ or } h^2 + hk + k^2 < 4.3 \text{ and } l^2 < 21.8.$$

Possible indices include:

{001}, {002}, {003}, {004}; {100}, {200}, {110}; {101}, {102}, {103}, {104}, {201}, {111}, {112}.

The Lorentz-polarization factor for a powder diffraction pattern varies as $\frac{1+\cos^2 2\theta}{\sin \theta \sin 2\theta}$.

The geometrical structure factors S_{hkl} for these unit cells are:

$$\text{I: } S_{hkl} = f_{\text{Zr}} [1 + (-1)^l] + f_{\text{Be}} \left[\exp\left(\frac{2\pi ih}{3} + \frac{4\pi ik}{3} + \frac{\pi il}{2}\right) + \exp\left(\frac{4\pi ih}{3} + \frac{2\pi ik}{3} + \frac{3\pi il}{2}\right) \right] \\ + f_{\text{Si}} \left[\exp\left(\frac{4\pi ih}{3} + \frac{2\pi ik}{3} + \frac{\pi il}{2}\right) + \exp\left(\frac{2\pi ih}{3} + \frac{4\pi ik}{3} + \frac{3\pi il}{2}\right) \right]$$

$$\text{II: } S_{hkl} = f_{\text{Zr}} [1 + (-1)^l] + f_{\text{Be/Si}} \left[\exp\left(\frac{2\pi ih}{3} + \frac{4\pi ik}{3} + \frac{\pi il}{2}\right) + \exp\left(\frac{4\pi ih}{3} + \frac{2\pi ik}{3} + \frac{3\pi il}{2}\right) + \right. \\ \left. \exp\left(\frac{4\pi ih}{3} + \frac{2\pi ik}{3} + \frac{\pi il}{2}\right) + \exp\left(\frac{2\pi ih}{3} + \frac{4\pi ik}{3} + \frac{3\pi il}{2}\right) \right]$$

$$f_{\text{Be/Si}} = (f_{\text{Be}} + f_{\text{Si}})/2$$

The multiplicities and S_{hkl} expressions for each structure, listing in order of increasing 2θ are:

{hkl}	Mult.	2θ	$S_{hkl}(\text{I})$	$S_{hkl}(\text{II})$	
{001}	2	12.28	0	0	<p>For structure I, there are 11 expected reflections below 60°. There is a 6_3 screw axis, which creates extinctions for {00l} reflections with odd l.</p> <p>For structure II, there are 8 expected reflections below 60°. The actual unit cell has $c \sim 3.6 \text{ \AA}$, so all reflections with odd l are extinct.</p>
{002}	2	24.71	$2f_{\text{Zr}} - 2f_{\text{Be}} - 2f_{\text{Si}}$	$2f_{\text{Zr}} - 2f_{\text{Be}} - 2f_{\text{Si}}$	
{100}	6	27.82	$2f_{\text{Zr}} - f_{\text{Be}} - f_{\text{Si}}$	$2f_{\text{Zr}} - f_{\text{Be}} - f_{\text{Si}}$	
{101}	12	30.51	$-\sqrt{3}f_{\text{Be}} + \sqrt{3}f_{\text{Si}}$	0	
{003}	2	37.44	0	0	
{102}	12	37.55	$2f_{\text{Zr}} + f_{\text{Be}} + f_{\text{Si}}$	$2f_{\text{Zr}} + f_{\text{Be}} + f_{\text{Si}}$	
{103}	12	47.28	$\sqrt{3}f_{\text{Be}} - \sqrt{3}f_{\text{Si}}$	0	
{110}	6	49.21	$2f_{\text{Zr}} + 2f_{\text{Be}} + 2f_{\text{Si}}$	$2f_{\text{Zr}} + 2f_{\text{Be}} + 2f_{\text{Si}}$	
{004}	2	50.67	$2f_{\text{Zr}} + 2f_{\text{Be}} + 2f_{\text{Si}}$	$2f_{\text{Zr}} + 2f_{\text{Be}} + 2f_{\text{Si}}$	
{111}	12	50.92	0	0	
{112}	12	55.83	$2f_{\text{Zr}} - 2f_{\text{Be}} - 2f_{\text{Si}}$	$2f_{\text{Zr}} - 2f_{\text{Be}} - 2f_{\text{Si}}$	
{200}	6	57.47	$2f_{\text{Zr}} - f_{\text{Be}} - f_{\text{Si}}$	$2f_{\text{Zr}} - f_{\text{Be}} - f_{\text{Si}}$	
{104}	12	58.79	$2f_{\text{Zr}} - f_{\text{Be}} - f_{\text{Si}}$	$2f_{\text{Zr}} - f_{\text{Be}} - f_{\text{Si}}$	
{201}	12	59.02	$\sqrt{3}f_{\text{Be}} - \sqrt{3}f_{\text{Si}}$	0	

Distinguishing between the two models is best determined by the {101}, {103}, and {201} reflections, which are expected to have observable intensities for Model I but to be totally extinct for Model II.

- (23) InSb(s) is a narrow-gap semiconductor adopting the cubic sphalerite-type structure. The covalent radii of In and Sb are, respectively, 1.42 Å and 1.39 Å.

- (a) Estimate the lattice constant of InSb(s).

In–Sb distance ~2.81 Å. The sphalerite-type structure has space group $F\bar{4}3m$ with Sb atoms at (0, 0, 0) and In atoms at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$.

In the sphalerite-type structure, this distance is one-quarter of the body-diagonal of the cubic unit cell. This distance is 11.24 Å. Therefore, the lattice constant is ~6.49 Å.

The experimental value is 6.48 Å.

- (b) Determine the Miller indices $\{hkl\}$ and 2θ values of the expected observed reflections for scattering angles less than 90° when using Cu $K\alpha$ X-radiation, $\lambda = 1.5418$ Å.

For cubic structures, $(h^2 + k^2 + l^2)\lambda^2 = 4a^2 \sin^2 \theta_{hkl}$. For $\theta_{\max} = 45^\circ$, $h^2 + k^2 + l^2 < 35.4$.

For an FCC structure, h, k, l are either all even or all odd integers. Therefore, the peaks that fulfill both restrictions are:

$$\{hkl\} = \{111\}, \{200\}, \{220\}, \{311\}, \{222\}, \{400\}, \{331\}, \{420\}, \{422\}, \{333\}, \{511\}, \{440\}, \{531\}$$

The geometrical structure factor is

$$S_{hkl} = f_{\text{Sb}}e^{i0} + f_{\text{In}}e^{i\pi(h+k+l)/2} = f_{\text{Sb}} + f_{\text{In}}(i)^{h+k+l}$$

The following table lists the predicted reflections with their 2θ values and S_{hkl} expressions:

$\{hkl\}$	2θ	S_{hkl}	$ S_{hkl} ^2$
{111}	23.75	$f_{\text{Sb}} - if_{\text{In}}$	$f_{\text{Sb}}^2 + f_{\text{In}}^2$
{200}	27.49	$f_{\text{Sb}} - f_{\text{In}}$	$(f_{\text{Sb}} - f_{\text{In}})^2 \sim 0$
{220}	39.26	$f_{\text{Sb}} + f_{\text{In}}$	$(f_{\text{Sb}} + f_{\text{In}})^2$
{311}	46.40	$f_{\text{Sb}} + if_{\text{In}}$	$f_{\text{Sb}}^2 + f_{\text{In}}^2$
{222}	48.60	$f_{\text{Sb}} - if_{\text{In}}$	$(f_{\text{Sb}} - f_{\text{In}})^2 \sim 0$
{400}	56.74	$f_{\text{Sb}} + f_{\text{In}}$	$(f_{\text{Sb}} + f_{\text{In}})^2$
{331}	62.36	$f_{\text{Sb}} - if_{\text{In}}$	$f_{\text{Sb}}^2 + f_{\text{In}}^2$

$\{hkl\}$	2θ	S_{hkl}	$ S_{hkl} ^2$
{420}	64.17	$f_{\text{Sb}} - f_{\text{In}}$	$(f_{\text{Sb}} - f_{\text{In}})^2 \sim 0$
{422}	71.17	$f_{\text{Sb}} + f_{\text{In}}$	$(f_{\text{Sb}} + f_{\text{In}})^2$
{333}	76.23	$f_{\text{Sb}} + if_{\text{In}}$	$f_{\text{Sb}}^2 + f_{\text{In}}^2$
{511}	76.23	$f_{\text{Sb}} - if_{\text{In}}$	$f_{\text{Sb}}^2 + f_{\text{In}}^2$
{440}	84.43	$f_{\text{Sb}} - if_{\text{In}}$	$f_{\text{Sb}}^2 + f_{\text{In}}^2$
{531}	89.29	$f_{\text{Sb}} + if_{\text{In}}$	$f_{\text{Sb}}^2 + f_{\text{In}}^2$

- (c) There are some unexpected extinctions among these reflections. Identify which ones are not observed and explain why.

The table summarizes the results. Because the atomic scattering factors for In and Sb are close to each other, their difference is close to 0. These reflections will appear to be missing from the pattern.

- (24) AgI(s) is a yellow solid adopting the hexagonal wurtzite-type structure. The covalent radii of Ag and I are, respectively, 1.45 Å and 1.39 Å.

- (a) Estimate the lattice constants of AgI(s) assuming ideal tetrahedral coordination.

Ag–I distance ~2.84 Å. The wurtzite-type structure has space group $P6_3mc$ with I atoms at $(\frac{2}{3}, \frac{1}{3}, 0)$ and $(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$ and Ag atoms at $(\frac{2}{3}, \frac{1}{3}, \frac{3}{8})$ and $(\frac{1}{3}, \frac{2}{3}, \frac{7}{8})$.

In the wurtzite-type structure, each tetrahedron has one contact parallel to the c -axis with the opposite triangular face setting the a -axis length. By geometry,

$$a \sim \sqrt{8/3} d(\text{Ag} - \text{I}) = 4.64 \text{ Å and } c \sim \sqrt{8/3} a = 7.57 \text{ Å.}$$

The experimental values are $a = 4.59$ Å and $c = 7.51$ Å.

- (b) Determine the Miller indices $\{hkl\}$ and 2θ values of the expected observed reflections for scattering angles less than 90° when using Cu $K\alpha$ X-radiation, $\lambda = 1.5418$ Å.

For a hexagonal structure, $\frac{\lambda^2(h^2+hk+k^2)}{3a^2} + \frac{\lambda^2l^2}{4c^2} = \sin^2 \theta_{hkl}$. Therefore, for $2\theta_{hkl} < 90^\circ$

$$0.03761(h^2 + hk + k^2) + 0.01054 l^2 < 0.50; \text{ or } h^2 + hk + k^2 < 13.3 \text{ and } l^2 < 47.4.$$

Possible indices include:

{001}, {002}, {003}, {004}, {005}, {006}; {100}, {200}, {300}, {110}, {210}, {220}, {310};
 {101}, {102}, {103}, {104}, {105}, {106}, {201}, {202}, {203}, {204}, {205}, {301}, {302}, {303}, {304},
 {111}, {112}, {113}, {114}, {115}, {116}, {211}, {212}, {213}, {214}, {221}, {222}, {311}

The geometrical structure factor is

$$S_{hkl} = f_I \left[\exp\left(\frac{2\pi i(2h+k)}{3}\right) + (-1)^l \exp\left(\frac{2\pi i(h+2k)}{3}\right) \right] + f_{Ag} \left[\exp\left(\frac{2\pi i(2h+k)}{3} + \frac{3\pi i l}{4}\right) + \exp\left(\frac{2\pi i(h+2k)}{3} + \frac{7\pi i l}{4}\right) \right]$$

The following table lists the predicted reflections with their 2θ values and $|S_{hkl}|^2$ expressions. Certain geometrical structure factors are exactly 0; these correspond to extinctions in $P6_3mc$.

{hkl}	2θ	$ S_{hkl} ^2$
{001}	11.69	0
{100}	22.12	$f_I^2 + f_{Ag}^2 + 2f_{Ag}f_I$
{002}	23.50	$4f_I^2 + 4f_{Ag}^2$
{101}	25.09	$3f_I^2 + 3f_{Ag}^2 - \sqrt{18}f_{Ag}f_I$
{102}	32.50	$f_I^2 + f_{Ag}^2$
{003}	35.58	0
{110}	38.81	$4f_I^2 + 4f_{Ag}^2 + 8f_{Ag}f_I$
{111}	40.67	0
{103}	42.29	$3f_I^2 + 3f_{Ag}^2 + \sqrt{18}f_{Ag}f_I$
{200}	45.12	$f_I^2 + f_{Ag}^2 + 2f_{Ag}f_I$
{112}	45.88	$4f_I^2 + 4f_{Ag}^2$
{201}	46.78	$3f_I^2 + 3f_{Ag}^2 - \sqrt{18}f_{Ag}f_I$
{004}	48.08	$4f_I^2 + 4f_{Ag}^2 - 8f_{Ag}f_I \sim 0$
{202}	51.49	$f_I^2 + f_{Ag}^2$
{104}	53.52	$f_I^2 + f_{Ag}^2 - 2f_{Ag}f_I \sim 0$
{113}	53.67	0
{203}	58.74	$3f_I^2 + 3f_{Ag}^2 + \sqrt{18}f_{Ag}f_I$
{210}	61.00	$f_I^2 + f_{Ag}^2 + 2f_{Ag}f_I$
{005}	61.22	0
{211}	62.35	$3f_I^2 + 3f_{Ag}^2 - \sqrt{18}f_{Ag}f_I$
{114}	63.43	$4f_I^2 + 4f_{Ag}^2 - 8f_{Ag}f_I \sim 0$

{hkl}	2θ	$ S_{hkl} ^2$
{105}	65.93	$3f_I^2 + 3f_{Ag}^2 + \sqrt{18}f_{Ag}f_I$
{212}	66.31	$f_I^2 + f_{Ag}^2$
{204}	68.06	$f_I^2 + f_{Ag}^2 - 2f_{Ag}f_I \sim 0$
{300}	70.27	$4f_I^2 + 4f_{Ag}^2 + 8f_{Ag}f_I$
{301}	71.53	0
{213}	72.66	$3f_I^2 + 3f_{Ag}^2 + \sqrt{18}f_{Ag}f_I$
{115}	74.89	0
{302}	75.25	$4f_I^2 + 4f_{Ag}^2$
{006}	75.33	$4f_I^2 + 4f_{Ag}^2$
{205}	79.22	$3f_I^2 + 3f_{Ag}^2 + \sqrt{18}f_{Ag}f_I$
{106}	79.65	$f_I^2 + f_{Ag}^2$
{214}	81.21	$f_I^2 + f_{Ag}^2 - 2f_{Ag}f_I \sim 0$
{303}	81.32	0
{220}	83.30	$4f_I^2 + 4f_{Ag}^2 + 8f_{Ag}f_I$
{221}	84.49	0
{310}	87.53	$f_I^2 + f_{Ag}^2 + 2f_{Ag}f_I$
{222}	88.07	$4f_I^2 + 4f_{Ag}^2$
{116}	88.14	$4f_I^2 + 4f_{Ag}^2$
{311}	88.72	$3f_I^2 + 3f_{Ag}^2 - \sqrt{18}f_{Ag}f_I$
{304}	89.68	$4f_I^2 + 4f_{Ag}^2 - 8f_{Ag}f_I \sim 0$

There are 41 possible reflections with the proper indices. The space group produces 9 extinctions among these, which leaves 32 observable reflections with scattering angles less than 90° .

- (c) There are some unexpected extinctions among these reflections. Identify which ones are not observed and explain why.

The table summarizes the results. Because the atomic scattering factors for Ag and I are close to each other, some of the $|S_{hkl}|^2$ values are nearly nullified. These reflections, all of which have $l = 4$, will appear to be missing from the pattern.

- (25) CaC_2 and MoSi_2 are isopointal tetragonal structures with different networks of the carbon and silicon atoms. Carbon atoms form dicarbide anions whereas silicon atoms form a 3-d 3-connected network. The unit cells contain two Ca or Mo atoms at $(0,0,0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and four C or Si atoms at $(0,0,z)$, $(0,0,-z)$, $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2} + z)$, $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2} - z)$. Using the first six observed diffraction peaks in X-ray powder diffraction patterns using $\text{Cu } K\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$), index each peak and determine the lattice constants.

$$\text{CaC}_2: \quad 26.798^\circ, 27.858^\circ, 32.526^\circ, 43.343^\circ, 46.662^\circ, 48.637^\circ$$

$$\text{MoSi}_2: \quad 22.607^\circ, 30.129^\circ, 39.806^\circ, 44.665^\circ, 46.159^\circ, 46.260^\circ$$

The atomic form factors may be evaluated using the following approximation:

$$f_Z(d_{hkl}) = a_1 \exp\left(-\frac{b_1}{d_{hkl}^2}\right) + a_2 \exp\left(-\frac{b_2}{d_{hkl}^2}\right) + a_3 \exp\left(-\frac{b_3}{d_{hkl}^2}\right) + a_4 \exp\left(-\frac{b_4}{d_{hkl}^2}\right) + c$$

Element	a_1	b_1	a_2	b_2	a_3	b_3	a_4	b_4	c
C	2.31	20.8439	1.02	10.2075	1.5886	0.5687	0.865	51.6512	0.2156
Ca	8.6266	10.4421	7.3873	0.6599	1.5899	85.7484	1.0211	178.437	1.3751
Si	6.2915	2.4386	3.0353	32.3337	1.9891	0.6785	1.541	81.6937	1.1407
Mo	3.7025	0.2772	17.2356	1.0958	12.8876	11.004	3.7429	61.6584	4.3875

Source: <https://lampz.tugraz.at/~hadley/ss1/crystaldiffraction/atomicformfactors/formfactors.php>

Using your results, how would you determine the z-coordinate of C or Si in each case?

In the diffraction pattern of CaC_2 , the two most intense peaks are the third (100%) and fourth (~46%) peaks. Estimate $z(\text{C})$.

In the diffraction pattern of MoSi_2 , the two most intense peaks are the third (~75%) and fourth (100%) peaks. Estimate $z(\text{Si})$.

For tetragonal structures, $\frac{1}{d_{hkl}^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2} = \frac{4 \sin^2 \theta_{hkl}}{\lambda^2}$.

The geometrical structure factors for these AX_2 structures are:

$$S_{hkl} = f_A [e^{i0} + e^{i\pi(h+k+l)}] + f_X [e^{2\pi ilz} + e^{-2\pi ilz} + e^{i\pi(h+k+l+2lz)} + e^{i\pi(h+k+l-2lz)}]$$

$$= (f_A + 2f_X \cos 2\pi lz) [1 + (-1)^{h+k+l}]$$

Therefore, there are extinctions when $h + k + l = \text{odd integer}$; the structure is body-centered tetragonal.

As a result, the indices for the first few observed reflections would be $\{002\}$, $\{110\}$, $\{200\}$, and $\{101\}$. From the d -spacing equation, $\{00l\}$ reflections will provide the c -axis length and $\{hk0\}$ reflections will provide the a -axis length. Therefore, using the body-centered lattice restriction, we must examine the data for either $\{002\}$ and $\{004\}$ or $\{110\}$ and $\{200\}$. The $\sin^2 \theta_{004}/\sin^2 \theta_{002}$ ratio equals 4 and $\sin^2 \theta_{200}/\sin^2 \theta_{110}$ ratio equals 2, so we need to look for these ratio within the first 6 reflections. Once either pair of reflections is identified, then we look to assign the other axis length.

CaC₂ Results:

n	$2\theta_n$	$\sin \theta_n$	$\left(\frac{\sin \theta_n}{\sin \theta_1}\right)^2$	$\left(\frac{\sin \theta_n}{\sin \theta_2}\right)^2$	$\left(\frac{\sin \theta_n}{\sin \theta_3}\right)^2$	Conclusions	Assignment
1	26.798°	0.2317	1	0.9267	0.6847	Either $\{101\}$ or $\{002\}$	$\{101\}$
2	27.858°	0.2407	1.0791	1	0.7389	Either $\{002\}$ or $\{101\}$	$\{002\}$
3	32.526°	0.2800	1.4605	1.3534	1	$\{110\}$: $a = 3.890 \text{ \AA}$	$\{110\}$
4	43.343°	0.3693	2.5395	2.3534	1.7389		$\{112\}$
5	46.662°	0.3960	2.9209	2.7068	2.0000	$\{200\}$: $a = 3.890 \text{ \AA}$	$\{200\}$
6	48.637°	0.4118	3.1581	2.9266	2.1624		$\{103\}$

Since $\sin^2 \theta_5 / \sin^2 \theta_3 = 2$, then #3 = {110} and #5 = {200} and the *a*-axis length can be calculated. We may assume that reflections #1 and #2 must be either {101} or {002}. We determine the assignment by trial-and-error:

If #1 = {101}, then $c = 6.400 \text{ \AA}$ and $2\theta_2 = 2\theta_{002} = 27.858^\circ$; this agrees with experiment.

If #1 = {002}, then $c = 6.648 \text{ \AA}$ and $2\theta_2 = 2\theta_{101} = 26.527^\circ$; this does not agree with experiment.

Now that reflections #1, #2, #3, and #5 are assigned, the indices for reflections #4 and #6 can be worked out from the *d*-spacing equation, which requires solving the following equation for {*hkl*}:

$$0.039212 (h^2 + k^2) + 0.014486 l^2 = \sin^2 \theta_n.$$

$n = 4$: $0.039212 (h^2 + k^2) + 0.014486 l^2 = 0.136371$ which is solved by {112}.

$n = 6$: $0.039212 (h^2 + k^2) + 0.014486 l^2 = 0.169586$ which is solved by {103}.

Therefore, $a = 3.890 \text{ \AA}$ and $c = 6.400 \text{ \AA}$.

MoSi₂ Results:

<i>n</i>	$2\theta_n$	$\sin \theta_n$	$\left(\frac{\sin \theta_n}{\sin \theta_1}\right)^2$	$\left(\frac{\sin \theta_n}{\sin \theta_2}\right)^2$	$\left(\frac{\sin \theta_n}{\sin \theta_3}\right)^2$	Conclusions	Assignment
1	22.607°	0.1960	1	0.5687	0.3315	{002}: $c = 7.860 \text{ \AA}$	{002}
2	30.129°	0.2599	1.7583	1	0.5829	Either {110} or {101}	{101}
3	39.806°	0.3404	3.0166	1.7156	1	Either {110} or {101}	{110}
4	44.665°	0.3800	3.7583	2.1374	1.2459		{103}
5	46.159°	0.3920	4.0000	2.2749	1.3260	{004}: $c = 7.860 \text{ \AA}$	{004}
6	46.260°	0.3928	4.0165	2.2843	1.3315		{112}

Since $\sin^2 \theta_5 / \sin^2 \theta_1 = 4$, then #1 = {002} and #5 = {004} and the *c*-axis length can be calculated. We may assume that reflections #2 and #3 must be either {110} or {101}. We determine the assignment by trial-and-error:

If #2 = {110}, then $a = 4.191 \text{ \AA}$ and $2\theta_3 = 2\theta_{101} = 41.102^\circ$; this does not agree with experiment.

If #2 = {101}, then $a = 3.200 \text{ \AA}$ and $2\theta_3 = 2\theta_{110} = 39.806^\circ$; this agrees with experiment.

Now that reflections #1, #2, #3, and #5 are assigned, the indices for reflections #4 and #6 can be worked out from the *d*-spacing equation, which requires solving the following equation for {*hkl*}:

$$0.057946 (h^2 + k^2) + 0.009604 l^2 = \sin^2 \theta_n.$$

$n = 4$: $0.057946 (h^2 + k^2) + 0.009604 l^2 = 0.144385$ which can be solved by {103}.

$n = 6$: $0.057946 (h^2 + k^2) + 0.009604 l^2 = 0.154307$ which can be solved by {112}.

Therefore, $a = 3.200 \text{ \AA}$ and $c = 7.860 \text{ \AA}$.

In a powder diffraction pattern, the peak positions (2θ values) provide the lattice constants and assignment of the lattice type. To evaluate the *z*-coordinate of C or Si, an analysis of the structure factors or diffraction peak intensities are necessary. These are determined by integrating the area under each peak by some form of peak-fitting routine. We can estimate these intensities by their peak heights, which are proportional to (Multiplicity)(LP Factor) $|S_{hkl}|^2$.

Peak multiplicity considers inversion (Friedel's law) and the tetragonal symmetry of the lattice.

The Lorentz-polarization factor for a powder diffraction pattern varies as $\frac{1 + \cos^2 2\theta}{\sin \theta \sin 2\theta}$.

For observed reflections, $S_{hkl} = 2(f_A + 2f_X \cos 2\pi lz_X)$

CaC₂ Results:

$2\theta_n$	{ <i>hkl</i> }	$d_{hkl} (\text{\AA})$	Multiplicity	LP Factor	$ S_{hkl} $	Intensity Ratio
32.526°	{110}	2.7506	4	11.3623	20.6306 + 8.4068	1.00

43.343°	{112}	2.0859	8	6.0320	17.0110 + 6.9057 cos 4πz _c	0.46
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Using the intensity ratio, the following equation involving z_c arises:

$$0.46 \cdot (4)(11.3623)(20.6306 + 8.4068)^2 = (8)(6.0320)(17.0110 + 6.9057 \cos 4\pi z_c)^2 \text{ or}$$

$$132.7702 = 118.1702 + 47.9718 \cos 4\pi z_c$$

Then $\cos 4\pi z_c = 0.3043$, which has two solutions within the range $0 \leq 4\pi z_c \leq 2\pi$:

$$z_c \sim 0.100 \quad (4\pi z_c = 0.4016\pi) \text{ and } z_c \sim 0.400 \quad (4\pi z_c = 1.5984\pi).$$

Only $z_c \sim 0.400$ gives reasonable Ca–C distances. The experimental value $z_c \sim 0.399$. In actual refinements, the intensities of several peaks are needed to refine the positional parameter.

MoSi₂ Results:

2θ _n	{hkl}	d _{hkl} (Å)	Multiplicity	LP Factor	S _{hkl}	Intensity Ratio
39.806°	{110}	2.2627	4	7.2963	17.9827 + 27.1838	0.75
44.665°	{103}	2.0272	8	5.6375	16.6925 + 25.2158 cos 6πz _c	1.00

Using the intensity ratio, the following equation involving z_{si} arises:

$$(4)(7.2963)(17.9827 + 27.1838)^2 = 0.70 \cdot (8)(5.6375)(16.6925 + 25.2158 \cos 6\pi z_c)^2 \text{ or}$$

$$244.0051 = 97.0824 + 146.6538 \cos 6\pi z_c$$

Then $\cos 6\pi z_c = 1.$, which has two solutions within the range $0 \leq 6\pi z_c \leq 2\pi$:

$$z_{si} \sim 0 \quad (6\pi z_c = 0\pi) \text{ and } z_{si} \sim 0.333 \quad (6\pi z_c = 2\pi).$$

Only $z_{si} \sim 0.333$ gives reasonable Mo–Si distances. The experimental value $z_{si} \sim 0.333$.

- (26) AgTe₃(s) was prepared using high pressure techniques (see K.J. Range, M. Zabel, F. Rau, F. von Krziwanik, F. Marx, B. Panzer, *Angew. Chem.* **1982**, *94*, 717-718). The unit cell is rhombohedral, $a = 6.13 \text{ \AA}$; $\alpha = 90.15^\circ$. The atoms are assigned the following positions:

Ag: (0,0,0) and (½, ½, ½);

Te: (½, 0,0), (0, ½, 0), (0,0, ½), (½, ½, 0), (½, 0, ½), and (0, ½, ½).

$$f_z(d_{hkl}) = a_1 \exp\left(-\frac{b_1}{d_{hkl}^2}\right) + a_2 \exp\left(-\frac{b_2}{d_{hkl}^2}\right) + a_3 \exp\left(-\frac{b_3}{d_{hkl}^2}\right) + a_4 \exp\left(-\frac{b_4}{d_{hkl}^2}\right) + c$$

Element	a ₁	b ₁	a ₂	b ₂	a ₃	b ₃	a ₄	b ₄	c
Ag	19.2808	0.6446	16.6885	7.4726	4.8045	24.6605	1.0463	99.8156	5.179
Te	19.9644	4.81742	19.0138	0.420885	6.14487	28.5284	2.5239	70.8403	4.352

Source: <https://lampz.tugraz.at/~hadley/ss1/crystalldiffraction/atomicformfactors/formfactors.php>

- (a) Determine the Miller indices {hkl} and 2θ values of the expected observed reflections for scattering angles less than 70° when using Cu Kα X-radiation, λ = 1.5418 Å.
- (b) Evaluate the relative intensities, with respect to the most intense peak, of these observed reflections.

$$\text{For rhombohedral structures, } \frac{1}{d_{hkl}^2} = \frac{(h^2 + k^2 + l^2) \sin^2 \alpha + 2(kl + hl + hk)(\cos^2 \alpha - \cos \alpha)}{a^2(1 - 3 \cos^2 \alpha + 2 \cos^3 \alpha)} = \frac{4 \sin^2 \theta_{hkl}}{\lambda^2}.$$

In AgTe₃, the relationship between Miller indices and the maximum scattering angle $\theta_{hkl} < 35^\circ$ is

$$0.015815(h^2 + k^2 + l^2) + 0.000083(kl + hl + hk) < 0.3290.$$

Accordingly, the magnitude of any single index can be no larger than 4.

There may be extinctions based upon the geometrical structure factor:

$$S_{hkl} = f_{\text{Ag}}[1 + (-1)^{h+k+l}] + f_{\text{Te}}[(-1)^h + (-1)^k + (-1)^l + (-1)^{h+k} + (-1)^{h+l} + (-1)^{k+l}]$$

$$= [f_{\text{Ag}} + f_{\text{Te}}((-1)^h + (-1)^k + (-1)^l)][1 + (-1)^{h+k+l}]$$

Extinctions occur for $h + k + l = \text{odd integers}$. If the indices are all even, $S_{hkl} = 2f_{\text{Ag}} + 6f_{\text{Te}}$; if two indices are odd, $S_{hkl} = 2f_{\text{Ag}} - 2f_{\text{Te}}$.

Therefore, there are 24 possible reflections, and the information is summarized here:

$\{hkl\}$	2θ	Mult.	LP	S_{hkl}	I_{rel}
$\{1\bar{1}0\}$	20.4617	6	30.2427	-6.96	0.14
$\{110\}$	20.5161	6	30.0770	-6.96	0.14
$\{200\}$	29.1344	6	14.3971	270.83	100.00
$\{2\bar{1}\bar{1}\}$	35.8339	6	9.2018	-7.44	0.05
$\{2\bar{1}\bar{1}\}$	35.8663	12	9.1835	-7.43	0.10
$\{211\}$	35.9636	6	9.1292	-7.43	0.05
$\{2\bar{2}0\}$	41.6150	6	6.6080	224.46	31.53
$\{220\}$	41.7295	6	6.5676	224.10	31.23
$\{3\bar{1}0\}$	46.8274	12	5.0660	-6.37	0.04
$\{310\}$	46.9056	12	5.0469	-6.36	0.04
$\{22\bar{2}\}$	51.6032	6	4.0624	196.51	14.86
$\{222\}$	51.7971	2	4.0278	196.04	4.89

$\{hkl\}$	2θ	Mult.	LP	S_{hkl}	I_{rel}
$\{3\bar{2}\bar{1}\}$	56.0588	12	3.3647	-5.11	0.02
$\{3\bar{2}1\}$	56.0817	12	3.3616	-5.10	0.02
$\{3\bar{2}\bar{1}\}$	56.1505	12	3.3523	-5.10	0.02
$\{321\}$	56.2649	12	3.3368	-5.08	0.02
$\{400\}$	60.4014	6	2.8441	177.93	8.53
$\{3\bar{3}0\}$	64.3957	6	2.4697	-4.16	0.00
$\{4\bar{1}\bar{1}\}$	64.4168	6	2.4680	-4.16	0.00
$\{41\bar{1}\}$	64.4800	12	2.4627	-4.16	0.01
$\{330\}$	64.5854	6	2.4540	-4.15	0.00
$\{411\}$	64.5854	6	2.4540	-4.15	0.00
$\{4\bar{2}0\}$	68.3628	12	2.1752	164.99	11.21
$\{420\}$	68.5264	12	2.1645	164.75	11.13

There are 8 “observable” reflections for all even indices. Because Ag and Te are close on the periodic table, their atomic scattering factors are nearly equal. Therefore, the allowed reflections with 2 odd indices are nearly extinct because S_{hkl} is nearly zero.

- (c) The rhombohedral angle of the unit cell is very close to 90° . How would you be able to distinguish the X-ray diffraction pattern from a cubic cell?

The 8 “observable” reflections occur in 5 groups: $\{200\}$ at 29.13° ; $\{2\bar{2}0\}$ and $\{220\}$ at 41.62° and 41.73° ; $\{22\bar{2}\}$ and $\{222\}$ at 51.60° and 51.80° ; $\{400\}$ at 60.40° ; and $\{4\bar{2}0\}$ and $\{420\}$ at 68.36° and 68.53° .

If the rhombohedral angle would be 90° , then the pairs $\{2\bar{2}0\}$ and $\{220\}$, $\{22\bar{2}\}$ and $\{222\}$, and $\{4\bar{2}0\}$ and $\{420\}$ each coalesce into single scattering angles.

So, the diffractometer must be able to resolve diffraction peaks separated by $0.1\text{--}0.2^\circ$ in 2θ .

- (d) Describe the structure of $\text{AgTe}_3(s)$.

AgTe_3 is closely related to the simple cubic structure of polonium. One-quarter of the sites are occupied by Ag atoms that are positioned at maximum relative separation with respect to each other. The unit cell is very nearly cubic. The Ag atoms form a body-centered cubic pattern. The Te atoms occupy the centers of each face and each edge. Therefore, each Ag atom is coordinated by 6 Te atoms in a nearly octahedral environment; each Te atom is coordinated by 4 Te atoms in a nearly square planar arrangement and 2 Ag atoms above and below the distorted square. All near-neighbor Ag–Te and Te–Te distances are 3.065 \AA .

X-Ray Photoelectron Spectroscopy

(27) The binding energies for bands in the XPS spectrum of elemental Te(*s*) are (in eV):

1009, 871, 820, 583, 573, 170, 111, 42, 41, and 12.

(a) The band at 12 eV is Te 5*s*. Which of these bands arise from the *n* = 3 shell? Consider spin-orbit coupling, if necessary.

Bands from the *n* = 4 shell occur at 170 eV (4*s*), 111 eV (4*p*), and 42 eV, 41 eV (4*d*_{3/2}, 4*d*_{5/2}). The 4*d* band exhibits small spin-orbit splitting. As a result of these assignments, the remaining observed bands arise from the *n* = 3 shell:

1009 eV = 3*s*

871, 820 eV = 3*p*_{1/2}, 3*p*_{3/2}

583, 573 eV = 3*d*_{3/2}, 3*d*_{5/2}

(b) If Mg *K*α radiation is used (1253.6 eV), what are the maximum kinetic energies of the photoelectrons emitted from the *n* = 3 shell of Te?

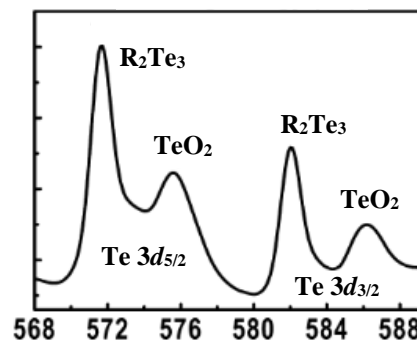
$$KE_{MAX} = h\nu - BE = 1253.6 \text{ eV} - BE$$

3*s*: KE_{MAX} = 244.6 eV

3*p*_{1/2}: KE_{MAX} = 382.6 eV; 3*p*_{3/2}: KE_{MAX} = 433.6 eV

3*d*_{3/2}: KE_{MAX} = 670.6 eV; 3*d*_{5/2}: KE_{MAX} = 680.6 eV

(c) Here is a spectrum collected for a rare-earth tellurium compound R₂Te₃. The researchers concluded that there was also a tellurium oxide impurity in the sample. Explain the occurrence and binding energies of the four peaks in this spectrum. The horizontal axis is binding energy (in eV).



These binding energies fall within the range for Te 3*d* bands, where the spin-orbit splitting is 10 eV. The two sharper peaks, which fall at binding energies slightly below those for elemental Te, correspond to the 3*d*_{3/2} and 3*d*_{5/2} Te levels of R₂Te₃ because Te is slightly reduced. The two slightly broader peaks, which fall at binding energies slightly above those for elemental Te, correspond to the 3*d*_{3/2} and 3*d*_{5/2} Te levels of TeO₂, an impurity in the sample. Surface Te in the rare-earth telluride will be susceptible to oxidation by oxygen.

(28) During a laboratory clean-up, a box was found with five glass vials, but the individual labels were detached. According to these labels, the five compounds are AsI₃ (orange-dark red), As₂O₅ (white) GaAs (gray) KAsF₆ (white), and NaAsO₂ (white-light gray). To determine their identities, the glass vials are marked *A*, *B*, *C*, *D*, and *E*, and samples of each are examined using X-ray photoelectron spectroscopy. The measured kinetic energies of the As 3*d*_{5/2} band using Mg *K*α radiation (1253.6 eV) are: *A* (1205.6 eV) *B* (1210.1 eV), *C* (1212.8 eV), *D* (1208.7 eV), and *E* (1207.4 eV). Assign each compound to the labeled vial.

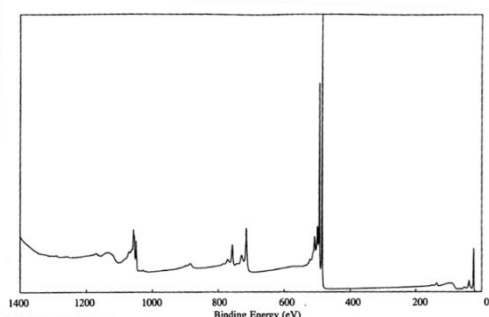
The simplest model to rationalize XPS binding energies relies on oxidation states and the relative ionicity of bonds formed with the element. Increasing oxidation states generally lead to higher binding energies; for a given oxidation state, increasing bond ionicities also lead to higher binding energies. Among the 5 compounds, the lowest As oxidation state occurs for GaAs (most reduced). AsI₃ and NaAsO₂ both involve As(III) with sodium arsenite showing larger ionicities for As–O bonds than for As–I bonds. Lastly, As₂O₅ and KAsF₆ both involve As(V) with KAsF₆ having larger ionicities for As–F bonds than for As–O bonds. Therefore, we expect the binding energies for the As 3*d*_{5/2} band will increase according to the sequence:



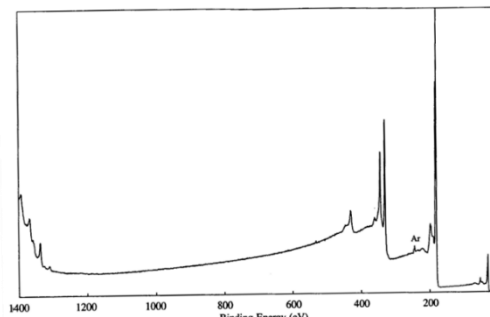
- | | | |
|------------|--|--------------------------------|
| <i>A</i> : | BE = 1253.6 eV – 1205.6 eV = 48.0 eV (highest value) | KAsF ₆ |
| <i>B</i> : | BE = 1253.6 eV – 1210.1 eV = 43.5 eV | AsI ₃ |
| <i>C</i> : | BE = 1253.6 eV – 1212.8 eV = 40.8 eV (lowest value) | GaAs |
| <i>D</i> : | BE = 1253.6 eV – 1208.7 eV = 44.9 eV | NaAsO ₂ |
| <i>E</i> : | BE = 1253.6 eV – 1207.4 eV = 46.2 eV | As ₂ O ₅ |

- (29) Each of these unlabeled XPS spectra, measured using Al $K\alpha$ radiation, corresponds to one of the following 5th period elements: Zr, Rh, Ag, or Sn. All peaks with binding energies below 1000 eV originate from single photoionization processes, whereas those above 1000 eV are Auger transitions.

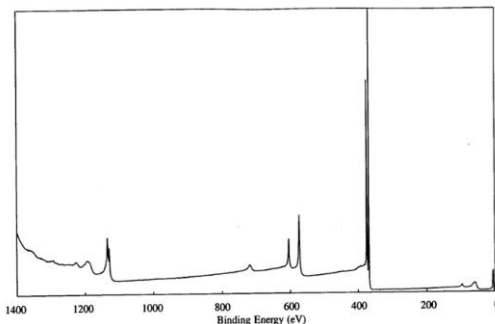
Source: Handbook of X-ray Photoelectron Spectroscopy, 1995.



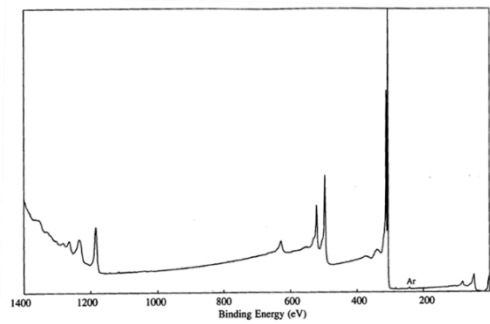
(A)



(B)



(C)



(D)

- (a) Assign each spectrum to its element. Explain your reasoning.

Across a period as atomic number increases, the effective nuclear charge of core and valence electrons increases, so that the binding energies of core states increases. For these 5th period elements, the most intense peaks occur for the $n = 3$ shell of electrons. The peaks of the $3d$ bands increase along the sequence $B < D < C < A$. Therefore,

A = Sn B = Zr C = Ag D = Rh

- (b) For the single photoionization processes involving core electrons in the spectra, write the level(s) in both spectroscopic and X-ray notation.

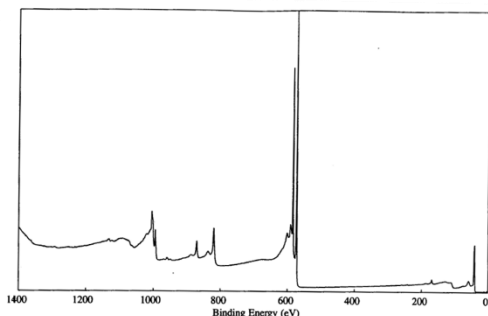
All elements of the 5th period show single photoionization processes for the $n = 3, 4,$ and 5 shells. Processes of the $n = 5$ shell involve valence electrons and have the lowest binding energies. Processes of the $n = 3$ and 4 shells involve core electrons. Therefore, the following core levels show single photoionization processes in the spectra of Zr, Rh, Ag, and Sn:

$n = 3$ shell: $3s = M_1$; $3p_{1/2} = M_2$; $3p_{3/2} = M_3$; $3d_{3/2} = M_4$; $3d_{5/2} = M_5$

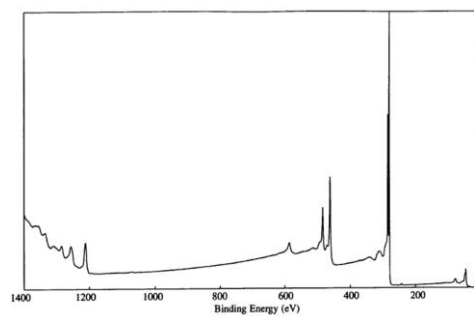
$n = 4$ shell: $4s = N_1$; $4p_{1/2} = N_2$; $4p_{3/2} = N_3$; $4d_{3/2} = N_4$; $4d_{5/2} = N_5$

- (30) Each of these unlabeled XPS spectra, measured using Al $K\alpha$ radiation, corresponds to one of the following 5th period elements: Nb, Ru, Pd, or Te. All peaks with binding energies below 1000 eV originate from single photoionization processes, whereas those above 1000 eV are Auger transitions.

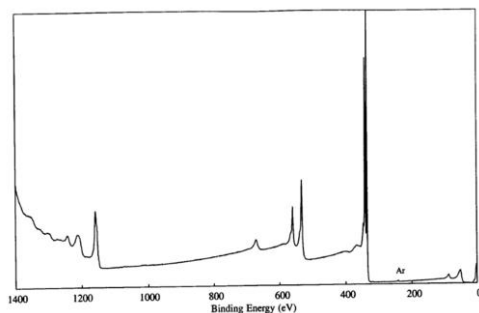
Source: Handbook of X-ray Photoelectron Spectroscopy, 1995.



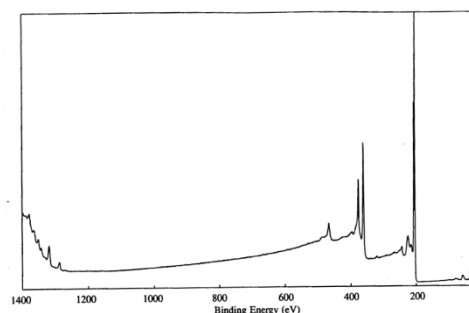
(A)



(B)



(C)



(D)

- (a) Assign each spectrum to its element. Explain your reasoning.

Across a period as atomic number increases, the effective nuclear charge of core and valence electrons increases, so that the binding energies of core states increases. For these 5th period elements, the most intense peaks occur for the $n = 3$ shell of electrons. The peaks of the $3d$ bands increase along the sequence $D < B < C < A$. Therefore,

A = Te B = Ru C = Pd D = Nb

- (b) For the single photoionization processes involving core electrons in the spectra, write the level(s) in both spectroscopic and X-ray notation.

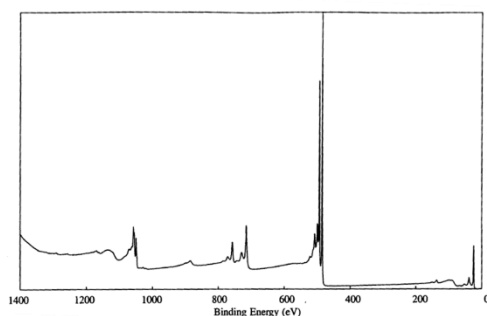
All elements of the 5th period show single photoionization processes for the $n = 3, 4,$ and 5 shells. Processes of the $n = 5$ shell involve valence electrons and have the lowest binding energies. Processes of the $n = 3$ and 4 shells involve core electrons. Therefore, the following core levels show single photoionization processes in the spectra of Zr, Rh, Ag, and Sn:

$n = 3$ shell: $3s = M_1$; $3p_{1/2} = M_2$; $3p_{3/2} = M_3$; $3d_{3/2} = M_4$; $3d_{5/2} = M_5$

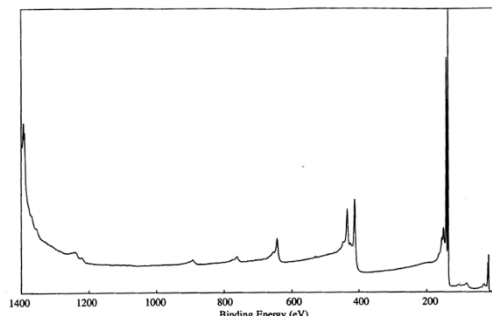
$n = 4$ shell: $4s = N_1$; $4p_{1/2} = N_2$; $4p_{3/2} = N_3$; $4d_{3/2} = N_4$; $4d_{5/2} = N_5$

- (31) Each of these unlabeled XPS spectra, measured using Al $K\alpha$ radiation, corresponds to one of the following Group 14 elements: Si, Ge, Sn, or Pb.

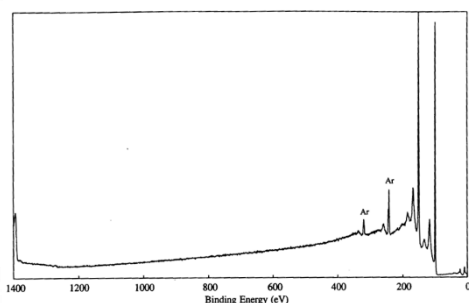
Source: Handbook of X-ray Photoelectron Spectroscopy, 1995.



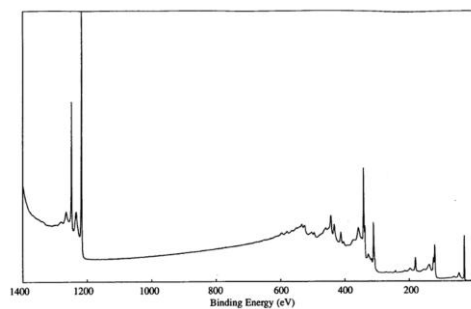
(A)



(B)



(C)



(D)

- (a) Assign each spectrum to its element. Explain your reasoning.

As the atomic number increases within a group, the number of core electrons and the spin-orbit splitting of p , d , etc. shells steadily increase. Therefore,

A = Sn B = Pb C = Si D = Ge

- (b) Identify the peaks for the highest energy core levels.

A = Sn: 885 eV ($3s$) – low intensity single peak

757 eV ($3p_{1/2}$), 715 eV ($3p_{3/2}$) – clear doublet with the peak at 715 eV having about $2\times$ intensity of the peak at 757 eV. The spectrum includes two smaller peaks shifted to slightly higher binding energies, which presumably arise from a surface oxide, e.g., SnO or SnO₂.

493 eV ($3d_{3/2}$), 485 eV ($3d_{5/2}$) – intense doublet with the peak at 485 eV having about $1.5\times$ intensity of the peak at 493 eV.

Peaks below 200 eV arise from the $n = 4$ shell.

B = Pb: 893 eV ($4s$) – low intensity single peak

762 eV ($4p_{1/2}$), 644 eV ($4p_{3/2}$) – the spin-orbit splitting is sufficiently large that these peaks seem to be weak singlets.

434 eV ($4d_{3/2}$), 412 eV ($4d_{5/2}$) – moderate doublet.

142 eV ($4f_{5/2}$), 137 eV ($4f_{7/2}$) – intense doublet.

Peaks below 150 eV arise from the $n = 5$ shell.

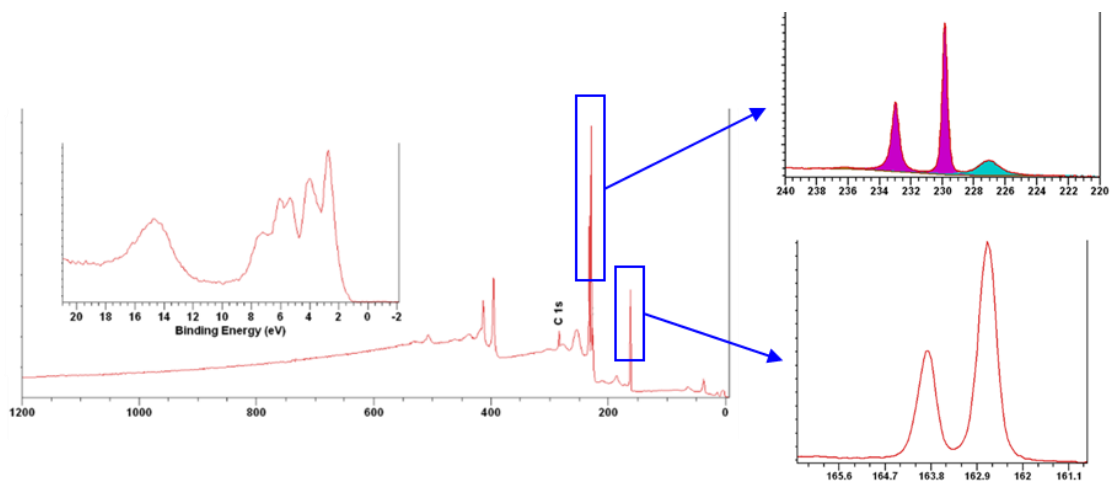
C = Si: 151 eV ($2s$) – intense single peak

100 eV ($2p_{1/2}$), 99 eV ($2p_{3/2}$) – intense peak.

The spectrum includes smaller peaks shifted to slightly higher binding energies than these two core levels, which may arise from a surface oxide, e.g., SiO₂.

- D = Ge:** 1248 eV ($2p_{1/2}$), 1217 eV ($2p_{3/2}$) – clear intense doublet with the peak at 1217 eV having about 2× intensity of the peak at 1248 eV. The spectrum includes two smaller peaks shifted to slightly higher binding energies, which presumably arise from a surface oxide, e.g., GeO or GeO₂.
~300–550 eV – Auger peaks, not associated with single photoionization processes.
160 eV ($3s$) – intense single peak
126 eV ($3p_{1/2}$), 122 eV ($3p_{3/2}$) – weak doublet.

- (32) What are the elements in the binary compound that give the following XPS spectrum using Al $K\alpha$ incident radiation? According to the spectrum near the Fermi level, is the compound metallic or semiconducting? From this answer, propose a chemical formula for the compound.



According to the two highlighted regions of the XPS spectrum, we must identify elements with p or d core states. One of these states occurs near a binding energy of 230 eV with a spin-orbit splitting of 3-4 eV; the other state occurs near a binding energy of 163 eV with a spin-orbit splitting of ~1.5 eV.

Scanning the table of photoelectron line positions reveals that the elements Mo and S can account for this spectrum. The two peaks near 230 eV are Mo $3d_{3/2}$ and $3d_{5/2}$ bands. The single broad peak at 227 eV is S $2s$. The doublet near 163 eV arises from S $2p_{1/2}$ and $2p_{3/2}$ bands.

The spectrum near the Fermi level indicates zero density of states, which suggests the compound to be semiconducting. Therefore, the compound is likely MoS₂.

- (33) Read the article “Core Photoelectron Shifts in Reduced Zirconium Halides. Relaxation Effects and Delocalized Metal-Metal Bonding,” by J.D. Corbett in *Inorganic Chemistry*, **1983**, *22*, 2269-2672. Discuss trends in Zr $3d_{5/2}$ and Cl $2p_{3/2}$ core level binding energies among Zr, $ZrCl_n$ ($n = 1-4$) and $ZrClH_x$ ($x = 0.5$ and 1).

Figure 1 of this article provides the useful data to answer this question by plotting binding energies vs. Zr oxidation state. Obviously, the oxidation state of Zr in Zr metal is 0. For the binary chloride $ZrCl_n$, the Zr oxidation state is $+n$. For the ternary hydride halides, the Zr oxidation states are +1.5 for $ZrClH_{0.5}$ and +2 for $ZrClH$. According to the article, the binding energy values are referenced with respect to either adventitious carbon (1s), silver ($3d_{5/2}$) mounted on the sample probe, or overlaid gold ($4f_{7/2}$).

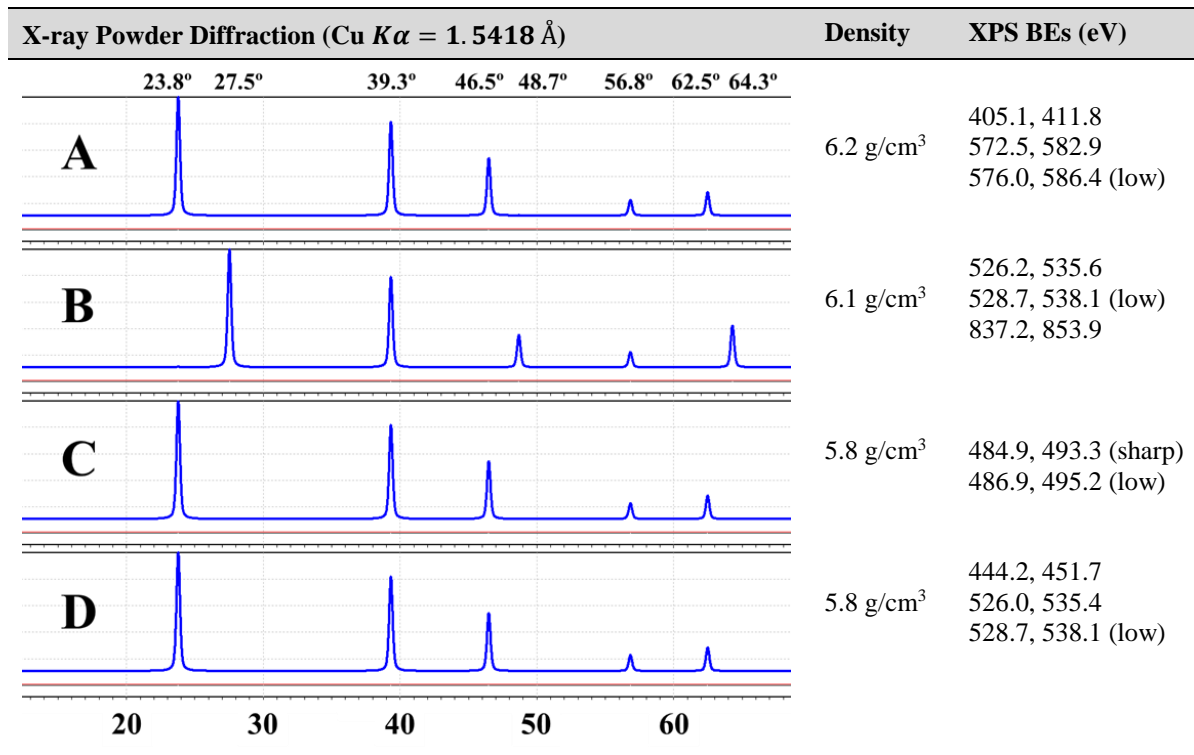
The Cl $2p_{3/2}$ binding energies lie slightly above 199 eV for $n = 1-3$ in $ZrCl_n$ and $ZrClH_x$, but it is close to 198.5 eV for $ZrCl_4$. Except for the smaller value for $ZrCl_4$, the trend of Cl $2p_{3/2}$ binding energies with increasing Zr oxidation state reveals very little change. Since Cl orbitals contribute relatively little to Zr-Zr bonding orbitals in these reduced zirconium chlorides, this outcome is deemed to be “reasonable”.

The Zr $3d_{5/2}$ binding energies increase linearly from ~178.5–180 eV from $n = 0$ to $n = 2$, then they increase abruptly to 182 eV and 183.8 eV for +3 and +4, respectively. Although relaxation can play a role in these values, the structural and electronic features of the various compounds:

- Zr metal is hcp.
- $ZrCl$, $ZrClH_x$ are metallic based on Zr bilayers sandwiched between Cl planes. For the hydride halides, H atoms occupy tetrahedral voids within the Zr bilayers.
- $ZrCl_2$ is a small-gap semiconductor consisting of single Zr planes, isotypic with MoS_2 . Another polytype, Zr_6Cl_{12} consists of octahedral clusters.
- $ZrCl_3$ is a 1-d compound consisting of chains of face-sharing $ZrCl_{6/2}$ octahedra. Shifting of Zr atoms in the chains localize valence electron pairs, unlike the more delocalized nature of the valence electrons for the more-reduced examples.
- $ZrCl_4$ is d^0 with valence electrons used of Zr-Cl bonding.

Combined Analyses

- (34) Four unknown gray-colored solid samples were found during a lab clean-up. To identify each substance, lab technicians performed various analyses which included X-ray diffraction, density measurements, and X-ray photoelectron spectroscopy. The observed powder patterns, density values, and binding energies are listed below:



Identify each sample and account for the observations.

According to the X-ray diffraction patterns, samples A, C, and D adopt identical structure types, but they are different substances based upon densities (A) and XPS binding energies.

We can start with either the X-ray diffraction patterns or the XPS binding energies. Since each X-ray diffraction pattern shows only 5 visible peaks, we can consider that the structures are cubic. Also, the patterns for samples A, C, and D are essentially identical in appearance, so their lattice constants must be nearly equal. We can also scan the photoelectron line positions for the possible elements in each sample, but we can use the X-ray diffraction patterns and densities to narrow possible compositions, and then use the XPS binding energies to substantiate these conclusions:

For cubic structures, $\left(\frac{\lambda^2}{4}\right) \frac{h^2+k^2+l^2}{a^2} + \frac{l^2}{c^2} = \sin^2 \theta_{hkl}$. Therefore, taking ratios of this equation for each observed reflection with respect to the first one will reveal the pattern of observed reflection indices:

A, C, D:

n	2θ	$\frac{\sin^2 \theta_n}{\sin^2 \theta_1}$	$\{hkl\}$	a (Å)
1	23.8°	1	{111}	6.48
2	39.3°	2.66 ~ 8/3	{220}	6.48
3	46.5°	3.66 ~ 11/3	{311}	6.48
4	56.8°	5.33 ~ 16/3	{400}	6.48
5	62.5°	6.33 ~ 19/3	{331}	6.48

B:

n	2θ	$\frac{\sin^2 \theta_n}{\sin^2 \theta_1}$	$\{hkl\}$	a (Å)	$\{h'k'l'\}$	a' (Å)
1	27.5°	1	{100}	3.24	{200}	6.49
2	39.3°	2.03 ~ 2/1	{110}	3.24	{220}	6.48
3	48.7°	3.05 ~ 3/1	{111}	3.24	{222}	6.48
4	56.8°	4.06 ~ 4/1	{200}	3.24	{400}	6.48
5	64.3°	5.08 ~ 5/1	{210}	3.24	{420}	6.48

The indices for samples A, C, and D are either all even or all odd, which is the extinction condition for a face-centered cubic lattice. The ratios involve integers divided by 3, which implies the first observed reflection is {111}. According to the scattering angles, the lattice constants are approximately 6.48 Å.

Using the densities and the fact that an FCC unit cell contains 4 formula units, the formula weights for A, C, and D are, respectively, 254 g/mol, 238 g/mol, and 238 g/mol. These values are too large to be elemental structures, so let's divide these numbers by 2 to obtain average atomic weights of "127 g/mol", "119 g/mol", and "119 g/mol", which are values close to Te and Sn. An examination of the photoelectron line positions indicates that the elements at and around Sn are reasonable candidates to be found in these samples. We suggest that sample C is elemental Sn, which adopts the diamond structure. Samples A and D should be binary compounds adopting the zinc blende structure type. Using the photoelectron line positions, we can assign sample A as CdTe and sample D as InSb.

On the other hand, according to its X-ray diffraction pattern, sample B seems to be primitive cubic with a lattice constant of 3.24 Å, which would be a cell holding no more than 1 atom. Using the observed density, the formula weight is 125 g/mol, which corresponds to either I or Te, which is unlikely. The XPS spectrum suggests the substance to be a binary compound. We can re-index the pattern, which gives new indices that are only even integers. So, this structure is also face-centered cubic and the formula unit is 250 g/mole. Examination of the XPS binding energies indicate that Sb is one component. Using the density, the other component is likely La, which agrees with the XPS data.

To summarize:

Sample A = CdTe.

Sample B = LaSb.

Sample C = Sn.

Sample D = InSb.

- (35) A mineral sample is analyzed to give mostly arsenic and sulfur, with trace amounts of antimony. Under an optical microscope, the sample contains orange-yellow crystals and orange-red crystals. Samples of both crystals are studied by X-ray diffraction (XRD), density measurements, and X-ray photoelectron spectroscopy (XPS). The results are

Measurement	Orange-Yellow Crystals	Orange-Red Crystals
Unit Cell (XRD)	$a = 11.475 \text{ \AA}$, $b = 9.577 \text{ \AA}$, $c = 4.256 \text{ \AA}$; $\beta = 90.68^\circ$	$a = 9.325 \text{ \AA}$, $b = 13.571 \text{ \AA}$, $c = 6.587 \text{ \AA}$; $\beta = 106.38^\circ$
Density	$\sim 3.49 \text{ g/cm}^3$	$\sim 3.55 \text{ g/cm}^3$
XPS	S 2s 227.1 eV S 2p 162.3 eV As 3p 142.7 eV As 3d 43.5 eV	226.8 eV 162.6 eV 142.1 eV 43.0 eV

- (a) The orange-red substance sublimes, and a mass spectrum derived from a sample heated under reduced pressure to 400 K shows the following most intense mass peaks, in amu (relative intensity): 428 (100); 396 (30); 321 (47); 300 (39); 257 (19); 150 (30); 107 (11). Identify the chemical formula of the red-orange solid.

We can assume that the compound consists of arsenic (AW = 75 amu) and sulfur (32 amu). Since the orange-red substance sublimes, we may conclude that it is composed of molecules that are held together by weaker intermolecular forces than polar-covalent bonds. Thus, we must identify the subscripts m and n in the formula As_mS_n .

Using the mass spectrum, assume that the molecular peak occurs at 428 amu. So, what combination of integers m and n gives $75m + 32n = 428$. Clearly, $m < 6$, so by trial-and-error, we find that $m = 4$ and $n = 4$. Therefore, the chemical formula is As_4S_4 , which is the mineral *realgar*.

We can assign the other mass spectrum peaks as $As_4S_3^+$ (396); $As_3S_3^+$ (321); As_4^+ (300); As_3S^+ (257); As_2^+ (150); and AsS^+ (107).

- (b) Using the results in part (a), deduce the empirical formula of the orange-yellow solid.

In this case, the data in the table will help. Let's first use the XRD and density data to determine the mass of the unit cell contents of the orange-yellow solid.

$$\text{Volume (Å}^3\text{)} = abc \sin \beta = (11.475 \text{ Å})(9.577 \text{ Å})(4.256 \text{ Å}) \sin(90.68^\circ) = 467.685 \text{ Å}^3$$

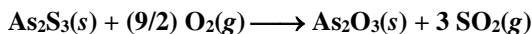
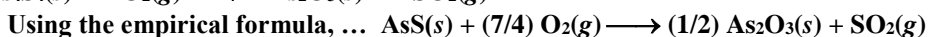
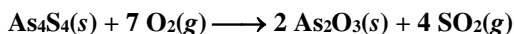
$$\text{Mass of contents in one unit cell} = (3.49 \text{ g/cm}^3)(467.685 \times 10^{-24} \text{ cm}^3) = 1.632 \times 10^{-21} \text{ g}$$

$$\text{Converting to amu: } 1.632 \times 10^{-21} \text{ g} / 1.67 \times 10^{-24} \text{ g/amu} \sim 977 \text{ amu.}$$

So, we now see which integers best fit $75m + 32n = 977$. At this point, let's use a bit of chemical knowledge. The red-orange solid is As_4S_4 , which means that this is As(II) sulfide. Since As belongs to the same group as N, P, Sb, and Bi, common oxidation states of arsenic, in the presence of sulfur, will be +3 and +5. Let's try As(III) sulfide = As_2S_3 , which has molar mass of 246 amu. $977/246 = 3.97$, or approximately 4 formula units per unit cell. If we try As(V) sulfide = As_2S_5 , which has a molar mass of 310, then $977/310 = 3.15$, which is not as close to an integer as 3.97. Note, a purely numerical solution could also give $m = 10$, $n = 7$, i.e., As_{10}S_7 (molar mass = 974 amu).

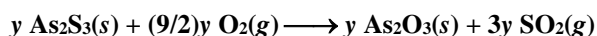
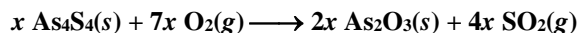
Now, use the XPS information. The binding energies for the 3p and 3d shells of As are greater in the orange-yellow solid than in the red-orange solid. Since both involve sulfides, we can infer that the oxidation state of arsenic should be higher in the orange-yellow solid than in the orange-red solid. Therefore, the data point toward an empirical formula of As_2S_3 for the orange-yellow solid, which is the mineral *orpiment*.

- (c) Each substance, when heated in air, forms arsenic(III) oxide and sulfur dioxide. Write the two balanced chemical equations describing these reactions.



- (d) If a 100.00 g sample of the mineral (mixture) yields 85.00 g of arsenic(III) oxide after the sample is heated in air, what was the original composition by mass of the mixture?

Use the two equations in part (c), noting that x moles of $\text{As}_4\text{S}_4(\text{s})$ and y moles of $\text{As}_2\text{S}_3(\text{s})$ are present in the 100.00 g mixture. Then,



$\text{FW}(\text{As}_2\text{O}_3) = 198 \text{ g/mol}$; $\text{FW}(\text{As}_4\text{S}_4) = 428 \text{ g/mol}$; $\text{FW}(\text{As}_2\text{S}_3) = 246 \text{ g/mol}$; then

$$428x + 246y = 100.00 \text{ g} \quad (\text{total amount of mineral sample})$$

$$198(2x) + 198y = 85.00 \text{ g} \quad (\text{total amount of arsenic(III) oxide})$$

Solving, gives $x = 0.08759 \text{ mol}$ (37.49 g; 37.49%) $\text{As}_4\text{S}_4(\text{s})$ and $y = 0.2541 \text{ mol}$ (62.51 g; 62.51%) $\text{As}_2\text{S}_3(\text{s})$ in the original sample.

- (36) Transparent ruby-red crystals are obtained from a high-temperature reaction of a mixture of cerium metal, silicon diimide $\text{Si}(\text{NH})_2$, and silica SiO_2 under a purified N_2 atmosphere. This product forms alongside yellow and yellow-orange crystals. Infra-red spectroscopy indicates no hydrogen in any of the solids. The ruby-red solid is characterized as follows: chemical analysis yields 69.90% Ce and 13.13% Si by mass; an X-ray diffraction study gives a cubic unit cell with $a = 1540.36 \text{ pm}$; its density is measured to be 5.83 g/cm^3 ; and magnetic susceptibility suggests that cerium occurs as Ce(III).

For the ruby-red solid:

- (a) What is the Ce:Si molar ratio using closest integer values? (HINT: it is not 1:1.)

Take 100.00 g of the sample. Then, the sample contains

$$69.90 \text{ g Ce} / 140.116 \text{ g/mol} = 0.49887 \text{ mol Ce}$$

$$13.13 \text{ g Si} / 28.086 \text{ g/mol} = 0.46749 \text{ mol Si.}$$

The ratio $0.49887 / 0.46749 = 1.06717$, which we can express as $1 + x$. Since x is small, we can assume that $1 + x = 1 + 1/N$ for some integer N .

$1 / 0.06717 = 14.89 \sim 15$, so that $1.06717 \sim 16 / 15$.

Therefore, # moles Ce / # moles Si $\sim 16 / 15$.

- (b) In this case, X-ray diffraction may not be able to unequivocally distinguish N and O atoms in the crystal. Therefore, use the physical information to determine the empirical formula of the compound using integer subscripts. (HINT: it may be helpful to evaluate the mass percentages of nitrogen and oxygen in the compound.)

We use charge and mass balance concepts applied to a formula $Ce_{0.49887}Si_{0.46749}N_xO_y$:

Charge Balance: All Ce is Ce^{3+} and all Si is Si^{4+} . Let's assume that there are no anion-anion bonds in the structure for such high oxidation state metals. Then, one equation for x and y is

$$(0.49887)(3) + (0.46749)(4) = 3x + 2y = 3.36657.$$

Mass Balance: For the 100.00 g sample, the remaining mass is 16.97 g, which would be divided into portions from N and O:

$$(14.007 \text{ g/mol})x + (15.999 \text{ g/mol})y = 16.97$$

These are two linear equations with two unknowns. Solving this system of equations gives

$$x = 0.996935 \text{ and } y = 0.187882.$$

To obtain a chemical formula using only integer subscripts, then we must multiply each of these values by $(15 / 0.46749)$: $Ce_{16}Si_{15}N_{32}O_6$

- (c) What is the likely reduction product of the reaction described above? Explain your choice.

The reaction is certainly a reduction-oxidation reaction because Ce metal is oxidized to Ce(III) in the compound. Among the substances present among the reactants, the only two substances that could be reduced are the H atoms in silicon diimide to H_2 (g) or nitrogen atoms in nitrogen gas to nitride N^{3-} in the solids. Since no hydrogen is evident in any solid, then H_2 (g) must be the reduction product.

This problem is based on an article by Köllisch and Schnick published in *Angew. Chem. Intl. Ed.* **1999**, 38, pp. 357-359. From this article:

- Comment on the synthesis. What ratio of reactants would be needed to achieve a "stoichiometric" single product of the title compound?
- Discuss problems concerning the structural solution.
- How can O and N be distinguished in such compounds?
- What are some coordination environments for O and N in this compound?

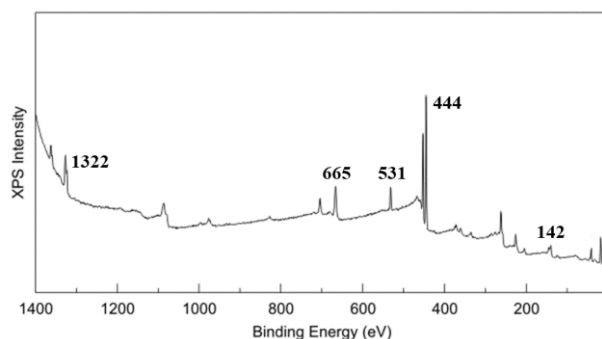
- (37) A sample of unknown gray crystals is analyzed by X-ray powder diffraction, X-ray photoelectron spectroscopy, thermal analysis, and a density measurement. The results are:

Thermal Analysis: sample melts congruently at $\sim 940^\circ C$.

X-ray powder diffraction: observed diffraction peaks at scattering angles 25.45° , 29.46° (very weak), 42.16° , 49.88° , 52.27° (very weak), 61.14° , 67.32° , 69.31° (very weak), 77.06° , and 82.70° using $Cu K\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$).

Density Measurement: $\sim 5.7 \text{ g/cm}^3$

X-ray photoelectron spectroscopy: A spectrum measured using $Al K\alpha$ radiation is shown here. Certain photoelectron line positions are indicated (no Auger peaks are labeled).



- (a) Determine the chemical identity of the unknown compound.
- (b) Explain the very weak intensities of the diffraction peaks at scattering angle values 29.46° , 52.27° , and 69.31° .
- (c) Identify the levels marked on the XPS spectrum.

Comparing information in the table of “Photoelectron Line Positions...” with the XPS spectrum identifies O, As, and In in the sample. It is possible the substance could be a binary compound (possibly InAs) or a ternary oxide such as InAsO₃.

Since InAs melts at 942°C, it is likely that the sample is InAs with surface oxide impurity.

To confirm this assignment, we can use the X-ray diffraction and density information:

InAs adopts the cubic sphalerite-type structure with a reported lattice constant $a \sim 6.058 \text{ \AA}$ and has a face-centered cubic lattice. Therefore, the observed diffraction peaks will fall at Bragg angles using Cu $K\alpha_1$ according to the following expression:

$$\sin^2 \theta_{hkl} = \frac{\lambda^2}{4a^2} (h^2 + k^2 + l^2) = 0.01617(h^2 + k^2 + l^2),$$

and h, k, l are either all even or all odd integers. The first 10 peaks of the diffraction pattern will have the indices:

$$\{hkl\} = \{111\}, \{200\}, \{220\}, \{311\}, \{222\}, \{400\}, \{331\}, \{420\}, \{422\}, \{333\}, \{511\}$$

The geometrical structure factor is

$$S_{hkl} = f_{\text{In}} e^{i0} + f_{\text{As}} e^{i\pi(h+k+l)/2} = f_{\text{In}} + f_{\text{As}}(i)^{h+k+l}$$

The following table lists the predicted and observed reflections with 2θ values and S_{hkl} expressions:

$\{hkl\}$	$2\theta_{hkl}(\text{the})$	$2\theta_{hkl}(\text{obs})$	S_{hkl}	$ S_{hkl} ^2$
$\{111\}$	25.45°	25.45°	$f_{\text{In}} - if_{\text{As}}$	$f_{\text{In}}^2 + f_{\text{As}}^2$
$\{200\}$	29.47°	29.46°	$f_{\text{In}} - f_{\text{As}}$	$(f_{\text{In}} - f_{\text{As}})^2$
$\{220\}$	42.16°	42.16°	$f_{\text{In}} + f_{\text{As}}$	$(f_{\text{In}} + f_{\text{As}})^2$
$\{311\}$	49.89°	49.88°	$f_{\text{In}} + if_{\text{As}}$	$f_{\text{In}}^2 + f_{\text{As}}^2$
$\{222\}$	52.27°	52.27°	$f_{\text{In}} - if_{\text{As}}$	$(f_{\text{In}} - f_{\text{As}})^2$
$\{400\}$	61.14°	61.14°	$f_{\text{In}} + f_{\text{As}}$	$(f_{\text{In}} + f_{\text{As}})^2$
$\{331\}$	67.32°	67.32°	$f_{\text{In}} - if_{\text{As}}$	$f_{\text{In}}^2 + f_{\text{As}}^2$
$\{420\}$	69.31°	69.31°	$f_{\text{In}} - f_{\text{As}}$	$(f_{\text{In}} - f_{\text{As}})^2$
$\{422\}$	77.06°	77.06°	$f_{\text{In}} + f_{\text{As}}$	$(f_{\text{In}} + f_{\text{As}})^2$
$\{333\}$	82.71°	82.70°	$f_{\text{In}} + if_{\text{As}}$	$f_{\text{In}}^2 + f_{\text{As}}^2$
$\{511\}$	82.71°	82.70°	$f_{\text{In}} - if_{\text{As}}$	$f_{\text{In}}^2 + f_{\text{As}}^2$

The first 10 X-ray diffraction peaks excellently fit the reported structure and lattice constant for InAs. The 3 very weak diffraction peaks, emphasized in the table by light gray shading, will have low intensities due to intracell interference between In ($Z = 49$) and As ($Z = 33$).

Lastly, using this information, the calculated density is:

$$\text{Mass in one unit cell} = (189.74 \text{ g/mol})(4 \text{ units}) / (6.022 \times 10^{23} \text{ units/mol}) = 1.2603 \times 10^{-21} \text{ g}$$

$$\text{Volume of one unit cell} = (6.058 \text{ \AA})^3 (10^{-24} \text{ cm}^3/\text{\AA}^3) = 2.223 \times 10^{-22} \text{ cm}^3$$

$$\text{Density} = 5.67 \text{ g/cm}^3$$

Therefore, this sample must be InAs. The peaks labeled in the XPS spectrum correspond to:

- 142 eV: Photoionization of As $3p_{3/2}$
- 444 eV: Photoionization of In $3d_{5/2}$
- 531 eV: Photoionization of O $1s$ (likely a surface impurity from oxidation)
- 665 eV: Photoionization of In $3p_{3/2}$
- 1322 eV: Photoionization of As $2p_{3/2}$

Photoelectron Line Positions (eV) by Element for Al K α X-radiation (1486.6 eV): Z = 3–54 (Li–Xe)

Source: Handbook of X-ray Photoelectron Spectroscopy, J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, Physical Electronics, Inc., Eden Prairie, MN, 1995.

At. No.		1s	2s	2p		3s	3p		3d		4s	4p		4d		5s
				1/2	3/2		1/2	3/2	3/2	5/2		1/2	3/2	3/2	5/2	
3	Li	56														
4	Be	112														
5	B	189														
6	C	285														
7	N	398														
8	O	531	23													
9	F	685	30													
10	Ne	863	41	14												
11	Na	1072	64	31												
12	Mg	1303	89	50												
13	Al		118	73												
14	Si		151	100	99											
15	P		188	131	130	14										
16	S		228	165	164	18										
17	Cl		271	201	199	17	6									
18	Ar		320	244	242	24										
19	K		380	297	294	35	19									
20	Ca		440	351	347	45	26									
21	Sc		499	404	399	51	29									
22	Ti		561	460	454	59	33									
23	V		626	520	512	66	37									
24	Cr		696	583	574	75	43									
25	Mn		769	650	639	83	48									
26	Fe		845	720	707	92	53									
27	Co		925	793	778	101	60									
28	Ni		1009	870	853	111	67									
29	Cu		1097	953	933	123	77	75								
30	Zn		1195	1045	1022	140	91	89	10							
31	Ga		1301	1144	1117	160	107	104	19							
32	Ge			1248	1217	181	126	122	30	29						
33	As			1359	1324	205	146	141	43	42						
34	Se					232	169	163	57	56						
35	Br					256	189	182	70	69	15	5				
36	Kr					287	216	208	88	87	21	8				
37	Rb					325	249	240	113	111	31	16				
38	Sr					369	281	270	136	134	39	21				
39	Y					394	311	299	158	156	45	24				
40	Zr					430	343	330	181	179	51	28				
41	Nb					467	376	361	205	202	56	31				
42	Mo					506	412	394	231	228	63	36				
43	Tc					544	445	425	257	253	68	39				
44	Ru					586	484	462	284	280	75	43				
45	Rh					629	521	497	312	307	81	48				
46	Pd					671	560	533	340	335	88	52				
47	Ag					719	604	573	374	368	98	60				
48	Cd					772	652	618	412	405	110	69		11		
49	In					828	703	665	452	444	123	78		17		
50	Sn					885	757	715	493	485	137	89		25		
51	Sb					944	813	767	537	528	153	99		33		
52	Te					1009	871	820	583	573	170	111	42	41	12	
53	I					1071	930	875	630	619	187	123	51	49	17	
54	Xe					1141	996	934	683	670	207	139	63	61	17	

Photoelectron Line Positions (eV) by Element for Al $K\alpha$ X-radiation (1486.6 eV): $Z = 55-83$ (Cs–Bi)

Source: Handbook of X-ray Photoelectron Spectroscopy, J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, Physical Electronics, Inc., Eden Prairie, MN, 1995.

At. No.		3s	3p		3d		4s	4p		4d		4f		5s	5p		5d	
			1/2	3/2	3/2	5/2		1/2	3/2	3/2	5/2	5/2	7/2		1/2	3/2	3/2	5/2
55	Cs	1219	1069	1002	740	726	234	173	161	80	77			25				
56	Ba	1292	1138	1064	796	781	254	193	179	93	90			31	15			
57	La		1208	1128	853	836	275	213	197	106	103			34	17			
58	Ce		1272	1184	902	884	290	223	207	112	109			36	18			
59	Pr		1339	1242	952	932	305	234	218	115*				38	18			
60	Nd			1301	1003	981	320	245	228	121*				39	19			
61	Pm				1060	1034	337	264	242	129*				38	22			
62	Sm				1108	1081	349	283	250	129*				41	19			
63	Eu				1155	1126	363	289	255	128*				39	19			
64	Gd				1218	1186	378	291	272	140*		8		43	21			
65	Tb				1276	1241	396	322	285	146*		8		45	22			
66	Dy				1333	1296	417	337	297	152*		8		48	23			
67	Ho				1393	1352	435	353	309	160*		9		49	30	24		
68	Er						451	368	321	167*		9		52	31	24		
69	Tm						470	384	333	175*		8		53	32	25		
70	Yb						482	389	341	182*		3		51	30	24		
71	Lu						509	413	360	206	196	9	7	57	34	27		
72	Hf						534	437	380	222	211	16	14	63	38	30		
73	Ta						563	463	401	238	226	24	22	69	43	33		
74	W						594	491	424	256	243	33	31	75	47	37		
75	Re						625	518	446	274	260	42	40	99				
76	Os						658	548	471	293	279	54	51	89**	44			
77	Ir						692	578	495	312	297	64	61	96**	48			
78	Pt						725	609	520	332	315	74	71	103**	52			
79	Au						763	643	547	353	335	88	84	110**	57	74		
80	Hg						805	682	579	381	361	105	101	125**	85	67	12	10
81	Tl						847	720	610	406	385	122	118	133**	95	74	15	13
82	Pb						893	762	644	434	412	142	137	150**	107	84	21	18
83	Bi						940	806	679	464	440	162	157	161**	119	93	27	24

* The 4d doublet for these elements is complex and variable with its chemical state because of multiplet splitting and multi-electron processes.

** The 5s band has low intensity and is often in the shake-up structure of the 4f lines. These values are estimates.