

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:

- Give the X-ray symbols for the electronic levels: $4s$, $5p_{3/2}$, $3d_{5/2}$, $4f_{7/2}$, $6p_{1/2}$.
- Give the spectroscopic symbols for the electronic levels: N_2 , L_3 , O_4 , M_5 , N_6 .
- Give the spectroscopic and X-ray symbols for all levels in the $n = 4$ shell.
- Give the spectroscopic and X-ray symbols for all possible transitions from the $n = 3$ shell to the $n = 1$ shell.
- Give the spectroscopic and X-ray symbols for all possible transitions from the $n = 3$ shell to the $n = 2$ shell.

(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 $K\alpha_1:K\alpha_2 = 2:1$.

- What are the wavelengths (in Å) for each transition?
- What is the wavelength (in Å) of Cu $K\alpha$ radiation?
- Identify the spectroscopic symbols for the initial and final levels of each transition for each X-ray emission and explain the intensity ratio for $K\alpha_1:K\alpha_2$.
- 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?
- 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?

(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.

- Write the decay process for a free neutron.
- 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 $1/k$.)
- 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

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

- (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° .
- Decide the lattice type for the cubic cell and assign Miller indices to each peak.
 - Evaluate the cubic lattice constant a (in \AA).
 - If the density of the substance is 8.31 g/cm^3 , propose its formula weight. What are some possible compounds that fit this solution?
- (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° , 16.66° , 21.55° , 25.58° , and 27.92° .
- Most metals adopt FCC, BCC, or HCP structures. With this fact in mind, what is the crystal class of this structure?
 - Determine the Miller indices for each reflection.
 - Evaluate the lattice constant(s) (in \AA) of the unit cell.
 - The density of the element is 1.74 g/cm^3 . Identify the element.
- (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.
- 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.
- (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:
- $$\text{Cu } K\alpha_1 = 1.5408 \text{ \AA}; K\alpha_2 = 1.5443 \text{ \AA}.$$
- (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° |
- Identify the crystal structures of **A**, **B**, and **C**.
 - What is the length of the side of the conventional cubic cell in each case?
 - What would be the expected scattering angles if Mo $K\alpha$ radiation ($\lambda = 0.711 \text{ \AA}$) was used?
 - 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?

- (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 ($\lambda = 1.5418 \text{ \AA}$).

$$cP6: a = 4.211 \text{ \AA};$$

$$\text{Nb at } (\frac{1}{2}, 0, 0), (0, \frac{1}{2}, 0), (0, 0, \frac{1}{2})$$

$$\text{O at } (\frac{1}{2}, \frac{1}{2}, 0), (\frac{1}{2}, 0, \frac{1}{2}), (0, \frac{1}{2}, \frac{1}{2})$$

$$cF8: a = 4.211 \text{ \AA};$$

$$\text{Nb at } (\frac{1}{2}, 0, 0), (0, \frac{1}{2}, 0), (0, 0, \frac{1}{2}), (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$$

$$\text{O at } (0, 0, 0), (\frac{1}{2}, \frac{1}{2}, 0), (\frac{1}{2}, 0, \frac{1}{2}), (0, \frac{1}{2}, \frac{1}{2})$$

- (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 contains one Hg atom at the Wyckoff site (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:

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

- (b) Evaluate the parameters a^* and α^* of the rhombohedral unit cell in reciprocal space.
 (c) Transform the unit cell to the hexagonal setting. Determine the hexagonal unit cell parameters and re-index the reflections identified in (a).
 (d) Consider a distortion of the structure of α -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 α -Hg(*s*)?
 (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*)?

- (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 $32.23^\circ, 35.90^\circ, 46.22^\circ, 56.75^\circ, 59.87^\circ, 66.78^\circ, 67.43^\circ,$ and 76.10° .

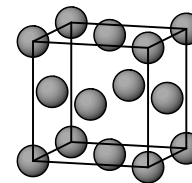
- (a) Determine the lattice type and index these eight reflections. The d -spacings for a tetragonal unit cell are:

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

- (b) Determine the lattice constants for this element.
 (c) What is the coordination environment of each metal atom in this structure?
 (d) The density of this element is 15.37 g/cm^3 . Identify the element.

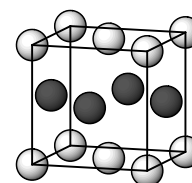
(12) Evaluate the geometrical structure factors S_{hkl} and 2θ values of the diffraction peaks predicted to be observed in an X-ray powder diffraction pattern for $2\theta < 90^\circ$ using Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) of five possible modifications of CuAu listed below. For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

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



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

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



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

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

(f) Discuss significant differences among these diffraction patterns.

(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 .

(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 $a = 3.75 \text{ \AA}$, $c = 3.75 \text{ \AA}$.

(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 $a = 3.75 \text{ \AA}$.

For each structure model, report your results in a table formatted as:

$\{hkl\}$	$d_{hkl} (\text{\AA}^{-1})$	$2\theta_{hkl}$	$ S_{hkl} $	LP_{hkl}	m_{hkl}

- (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 N₂ at ~50 GPa and ~2000 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 $a = 4.8041(2)$ Å. Subsequent theoretical studies suggested that a pyrite-type “PtN₂” with dinitrogen units was a better choice; this suggestion was later affirmed.

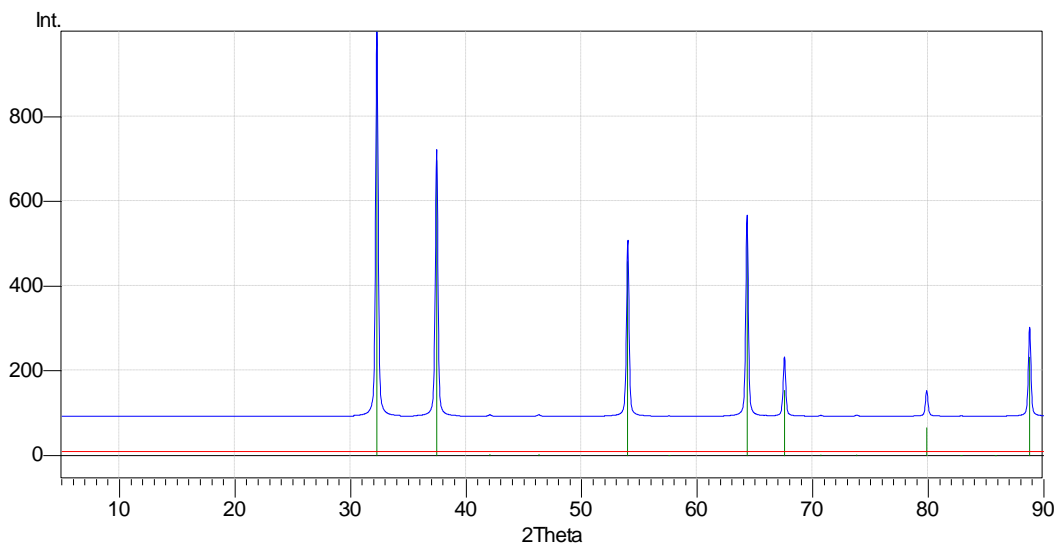
- (a) To examine the challenge of distinguishing different structure types for a Pt-N cubic phase with $a = 4.8041$ Å, calculate the $|S_{hkl}|^2$ values (use atomic numbers of the elements for their atomic structure factors), $2\theta_{hkl}$ values, and multiplicities for diffraction peaks observed for 2θ values below 85° using Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å) 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 ($-\frac{1}{4}$, $-\frac{1}{4}$, $-\frac{1}{4}$).

For each structure model, report your results in a table formatted as:

$\{hkl\}$	$2\theta_{hkl}$	$ S_{hkl} $	Multiplicity

- (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.
- (c) Here is a theoretical diffraction pattern for pyrite-type PtN₂ (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.



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

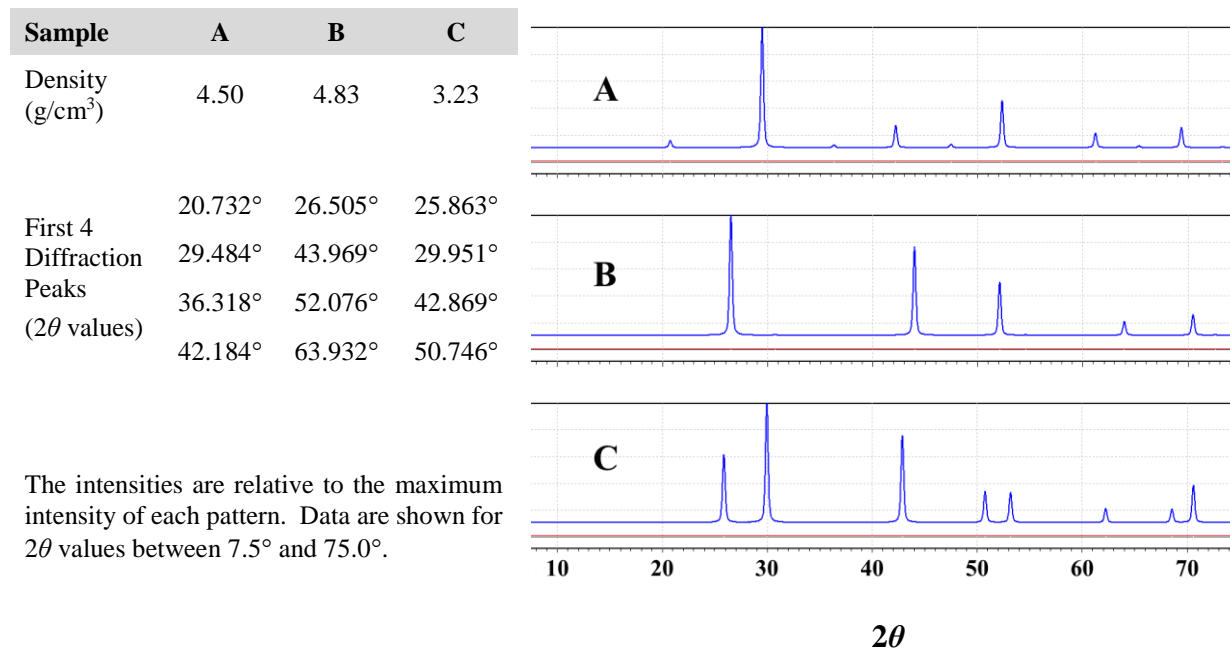
B: $42.97^\circ, 47.77^\circ, 52.23^\circ, 78.75^\circ$; $\rho = 7.43 \text{ g/cm}^3$

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.

- (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 made this assignment.
- (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**.
- (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 lattice constant of TiNiSn is 5.93 \AA . Determine the 2θ values and the 3 possible geometrical structure factors $|S_{hkl}|$ for the first six reflections using Cu $K\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$). Use atomic

numbers for the atomic form factors. How might an experimental powder pattern determine the arrangement of atoms in TiNiSn?

- (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:

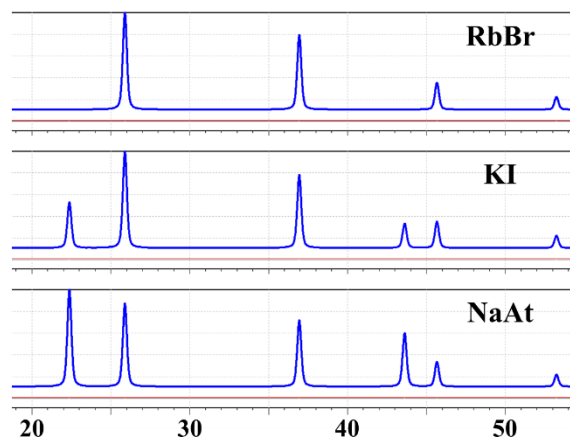
A: $37.185^\circ, 38.812^\circ, 43.250^\circ, 54.838^\circ$

B: $42.881^\circ, 49.932^\circ, 73.298^\circ, 88.845^\circ$

C: $43.342^\circ, 62.965^\circ, 79.525^\circ, 95.217^\circ$

- (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.
- (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.
- (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.

- (19) Here are three model X-ray powder diffraction patterns for rocksalt-type halides RbBr, KI, and "NaAt" calculated for lattice constant 6.877 \AA and Cu $K\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$). There are six possible reflections in this region at scattering angles $22.374^\circ, 25.891^\circ, 36.941^\circ, 43.616^\circ, 45.662^\circ,$ 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.

- (20) SrSnO_3 and Sr_3SnO 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° .

SrSnO_3 : $a = 4.0254 \text{ \AA}$; Sr at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, Sn at $(0,0,0)$, O at $(\frac{1}{2}, 0, 0)$, $(0, \frac{1}{2}, 0)$, $(0, 0, \frac{1}{2})$

Sr_3SnO : $a = 5.1394 \text{ \AA}$; 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.

- (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 $(0,0,0)$, $(0,0,\frac{1}{2})$, $(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$, and $(\frac{2}{3}, \frac{1}{3}, \frac{3}{4})$; In at $(\frac{1}{3}, \frac{2}{3}, \frac{3}{4})$ and $(\frac{2}{3}, \frac{1}{3}, \frac{1}{4})$

II: Ni at $(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$, $(\frac{2}{3}, \frac{1}{3}, \frac{1}{4})$, $(\frac{2}{3}, \frac{1}{3}, \frac{3}{4})$, and $(\frac{1}{3}, \frac{2}{3}, \frac{3}{4})$; In at $(0,0,0)$ and $(0,0,\frac{1}{2})$

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?

- (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 $(0,0,\frac{1}{2})$; Be at $(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$ and $(\frac{2}{3}, \frac{1}{3}, \frac{3}{4})$; Si at $(\frac{1}{3}, \frac{2}{3}, \frac{3}{4})$ and $(\frac{2}{3}, \frac{1}{3}, \frac{1}{4})$

II: Zr at $(0,0,0)$ and $(0,0,\frac{1}{2})$; Be/Si $(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$, $(\frac{2}{3}, \frac{1}{3}, \frac{1}{4})$, $(\frac{2}{3}, \frac{1}{3}, \frac{3}{4})$, and $(\frac{1}{3}, \frac{2}{3}, \frac{3}{4})$

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?

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

(a) Estimate the lattice constant of $\text{InSb}(s)$.

(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, $\lambda = 1.5418 \text{ \AA}$.

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

- (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.
- Estimate the lattice constants of AgI(s) assuming ideal tetrahedral coordination.
 - 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.
 - There are some unexpected extinctions among these reflections. Identify which ones are not observed and explain why.
- (25) CaC₂ and MoSi₂ 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 Cu $K\alpha_1$ radiation ($\lambda = 1.5406$ Å), index each peak and determine the lattice constants.

CaC₂: 26.798°, 27.858°, 32.526°, 43.343°, 46.662°, 48.637°

MoSi₂: 22.607°, 30.129°, 39.806°, 44.665°, 46.159°, 46.260°

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 CaC₂, the two most intense peaks are the third (100%) and fourth (~46%) peaks. Estimate z_C .

In the diffraction pattern of MoSi₂, the two most intense peaks are the third (~75%) and fourth (100%) peaks. Estimate z_{Si} .

- (26) $\text{AgTe}_3(s)$ 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 $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$;

Te: $(\frac{1}{2}, 0, 0)$, $(0, \frac{1}{2}, 0)$, $(0, 0, \frac{1}{2})$, $(\frac{1}{2}, \frac{1}{2}, 0)$, $(\frac{1}{2}, 0, \frac{1}{2})$, and $(0, \frac{1}{2}, \frac{1}{2})$.

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

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>

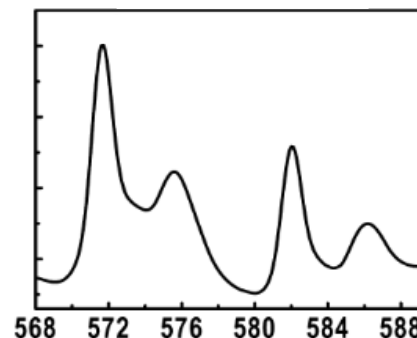
- Determine the Miller indices $\{hkl\}$ and 2θ values of the expected observed reflections for scattering angles less than 70° when using Cu $K\alpha$ X-radiation, $\lambda = 1.5418 \text{ \AA}$.
- Evaluate the relative intensities, with respect to the most intense peak, of these observed reflections.
- 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?
- Describe the structure of $\text{AgTe}_3(s)$.

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.

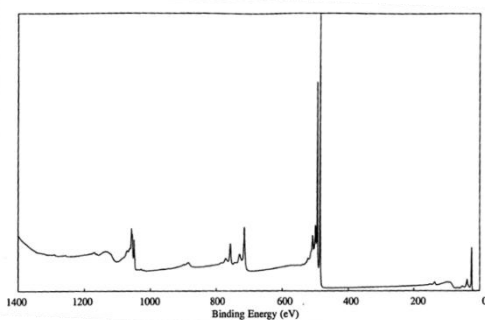
- (a) The band at 12 eV is Te 5s. Which of these bands arise from the $n = 3$ shell? Consider spin-orbit coupling, if necessary.
- (b) If Mg $K\alpha$ radiation is used (1253.6 eV), what are the maximum kinetic energies of the photoelectrons emitted from the $n = 3$ shell of Te?
- (c) Here is a spectrum collected for a rare-earth tellurium compound R_2Te_3 . 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).



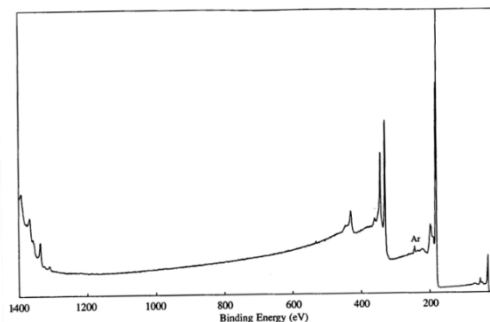
(28) During a laboratory clean-up, a box was found with five glass vials, but the individual labels were detached. According to these labels, the five compounds are AsI_3 (orange-dark red), As_2O_5 (white) GaAs (gray), $KAsF_6$ (white), and $NaAsO_2$ (white-light gray). To determine their identities, 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 $3d_{5/2}$ band using Mg $K\alpha$ 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.

(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.

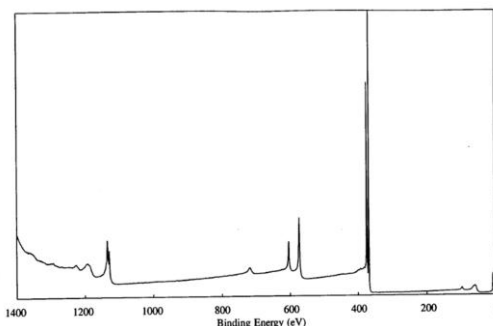
Source: Handbook of X-ray Photoelectron Spectroscopy, 1995.



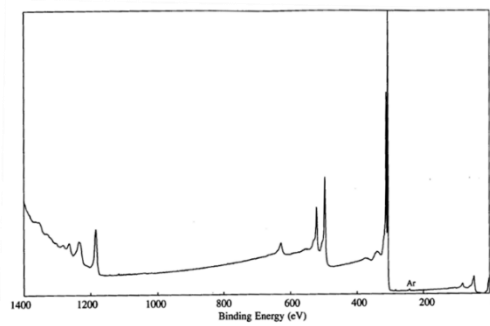
(A)



(B)

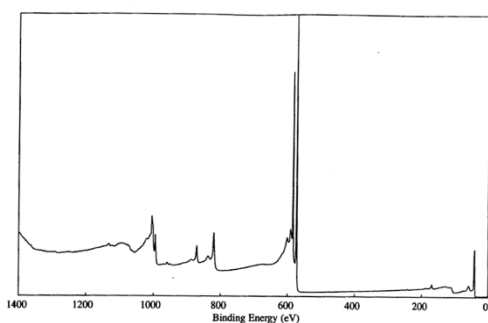


(C)

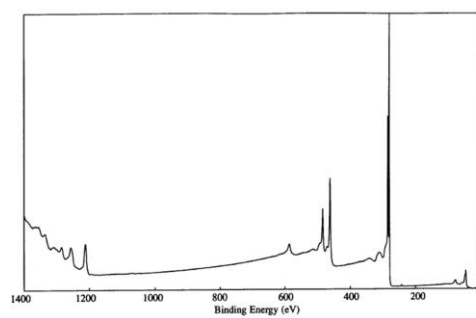


(D)

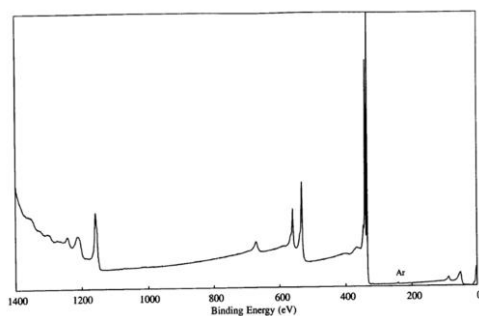
- (a) Assign each spectrum to its element. Explain your reasoning.
 (b) For the single photoionization processes on the spectra, write the level in both spectroscopic and X-ray notation.
- (30)** Each of these unlabeled XPS spectra, measured using Al $K\alpha$ radiation, corresponds to one of the following 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.



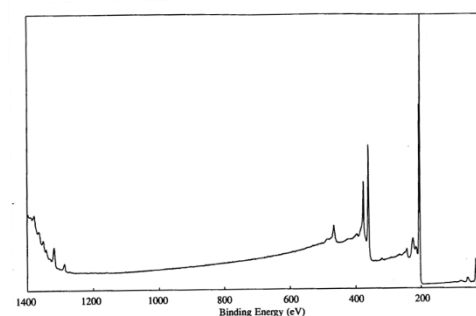
(A)



(B)

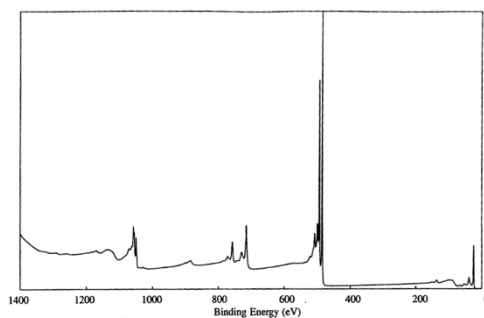


(C)

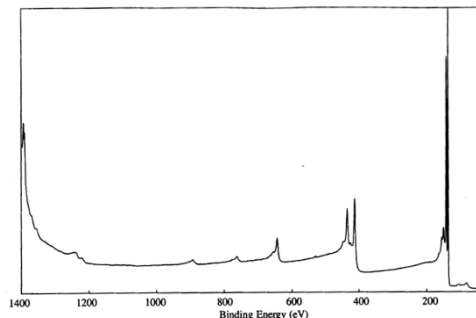


(D)

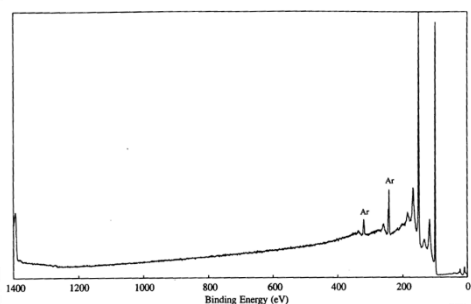
- (a) Assign each spectrum to its element. Explain your reasoning.
 (b) For the single photoionization processes on the spectra, write the level in both spectroscopic and X-ray notation.
- (31)** Each of these unlabeled XPS spectra, measured using Al $K\alpha$ radiation, corresponds to one of the following Group 14 elements: Si, Ge, Sn, or Pb.
Source: Handbook of X-ray Photoelectron Spectroscopy, 1995.



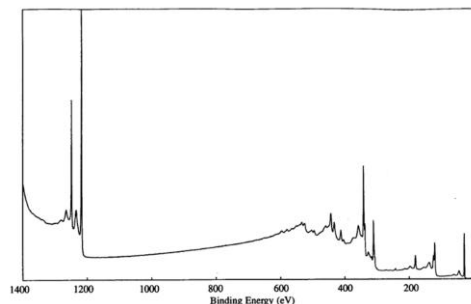
(A)



(B)



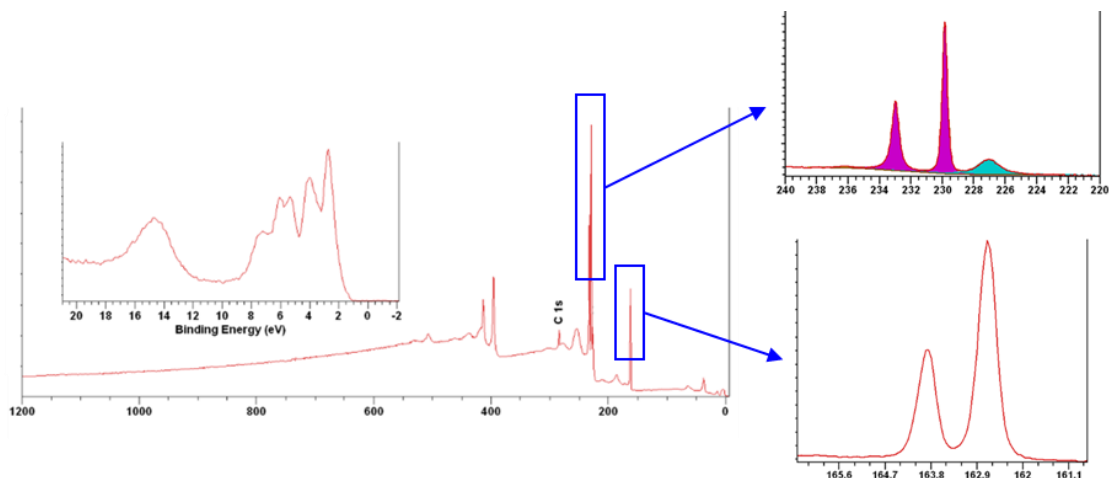
(C)



(D)

- (a) Assign each spectrum to its element. Explain your reasoning.
 (b) Identify the peaks for the highest energy core levels.

- (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.



- (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).

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:

	X-ray Powder Diffraction (Cu $K\alpha = 1.5418 \text{ \AA}$)	Density	XPS BEs (eV)
	23.8° 27.5° 39.3° 46.5° 48.7° 56.8° 62.5° 64.3°		
A		6.2 g/cm ³	405.1, 411.8 572.5, 582.9 576.0, 586.4 (low)
B		6.1 g/cm ³	526.2, 535.6 528.7, 538.1 (low) 837.2, 853.9
C		5.8 g/cm ³	484.9, 493.3 (sharp) 486.9, 495.2 (low)
D		5.8 g/cm ³	444.2, 451.7 526.0, 535.4 528.7, 538.1 (low)
	20 30 40 50 60		

Identify each sample and account for the observations.

- (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. Specimens 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

- (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). Determine the chemical formula of the red-orange solid.
- (b) Using the results in part (a), deduce the empirical formula of the orange-yellow solid.
- (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?
- (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.)
- (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.)
- (c) What is the likely reduction product of the reaction described above? Explain your choice.

This problem is based on an article by Köllisch and Schnick published in *Angew. Chem.* 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 density. The results are:

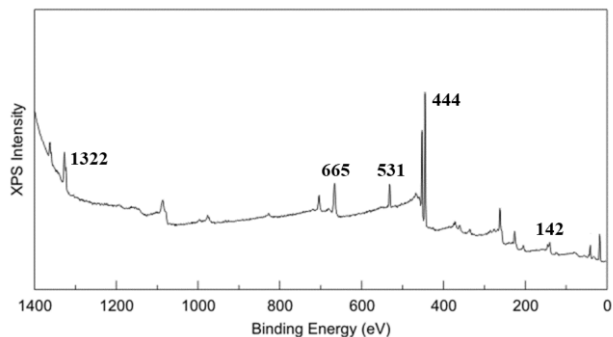
Thermal Analysis: Sample melts congruently at $\sim 940^\circ\text{C}$.

XRD: 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 $\text{Cu } K\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$).

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

XPS: A spectrum measured using $\text{Al } K\alpha$ radiation is shown here. Certain line positions are indicated (no Auger peaks are labeled).

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



Photoelectron Line Positions (eV) by Element for Al $K\alpha$ 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.