

CHEM-E4205 - Crystallography Basics and Structural Characterization

Exam 26/10/2017

Please answer **five questions** of the six. If you answer all six questions, the first five answers will be taken into account. If you do not want something to be marked cross out or put a line through the section not to be considered. Formulas and other useful material are at the end of the question sheet. *calculators are allowed.*

Q1.

- a. Explain how the Doppler phenomenon is related to Mössbauer spectroscopy. Why is Mössbauer sometimes called recoilless nuclear resonance fluorescence?

- b. What information about the compound can be deduced from Mössbauer spectroscopy?

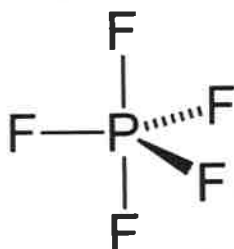
- c. Fe^{57} has $I=3/2$ with reference to schematic diagrams of energy levels show how this affects the resulting Mössbauer spectra.

- d. Compared to diffraction methods is the technique;
 - i a global or local probe?
 - ii higher in resolution?
 - iii Discuss the applicability to a wide range of material

Q2. Consider PF₅ shown below

a. What is the point group?

b. Explain with diagrams the location of the rotation elements (including any improper) and the mirror planes.



Given the following character table and the reducible representation for the 5F bonds

	E	σ_h	$2C_3$	$2S_3$	$3C_2$	$3\sigma_v$	linears, rotations	Linear	quadratic
A ₁ '	1	1	1	1	1	1			x^2+y^2, z^2
A ₂	1	1	1	1	-1	-1	R _z		
A ₁ ''	1	-1	1	-1	1	-1			x^2-y^2
A ₂ ''	1	-1	1	-1	-1	1		z	
E'	2	2	-1	-1	0	0		(x,y)	(xy, x ² -y ²)
E''	2	-2	-1	1	0	0	(R _x , R _y)		(xz, yz)
Γ P-F	5	3	2	0	1	3			

c. Using the reduction formula calculate the irreps for the 5P-F bond vibrations.

d. Is the number of irreps consistent with the number of P-F bonds used as the basis set? Explain your answer.

e. Which of the modes are IR active and which are Raman active? What needs to change in a system for a mode to be Raman or IR active?

f. With reference to diagrams explain the IR, Raman and Rayleigh transitions between energy levels.

Q3.

a. What kind of "radiation source" is used in the following characterization techniques:

- (1) Mössbauer spectroscopy
- (2) EXAFS / XANES
- (3) Raman spectroscopy
- (4) SEM
- (5) GIXRD
- (6) ND
- (7) μ SR

b. How XRD and ND techniques differ from each other in terms of the required sample amount? Why?

c. Why might XRD and ND may yield somewhat different lattice parameters for the same compound? Which of the two techniques gives more precise values?

d. Why do XRD and ND yield somewhat different values for the same O-H bond lengths? Which value you would consider more reliable?

e. Despite Zr lower neutron scattering length why do we use V sample cans for ND?

Q4.

a. What factors determine the intensity I_{hkl} of the Bragg reflection hkl in X-Ray and neutron diffraction? Are they angular dependent?

b. The following reflections are observed in the X-ray diffraction patterns for the isostructural K-X (X=I or F or Cl). Assign each pattern to its chemical explaining your reasoning? Could you do the same if it was a neutron pattern?

c Pick one of the three and index the pattern and give the lattice parameters and give centering.

	Pattern 1		Pattern 2		Pattern 3	
	dhkl (Å)	Intensity %	dhkl (Å)	Intensity %	dhkl (Å)	Intensity %
1	3.087	29	4.08	42	3.146	100
2	2.671	100	3.53	100	2.224	59
3	1.890	63	2.498	70	1.816	23
4	1.612	10	2.131	29	1.573	8
5	1.542	17	2.039	27		
6	1.337	8	1.767	15		

d For NiO which is also isostructural the powder neutron diffraction pattern below 250 °C corresponds to a cubic unit cell with a unit cell length twice that found by X-ray powder diffraction pattern. Discuss using diagrams to illustrate

Q5.

a. Consider scanning tunneling microscope (STM). Compare and contrast to non contact AFM.

b. How would one improve resolution of both instruments?

c. How would sample preparation differ for a metallic sample and an insulating sample?

d What are the other modes for an AFM and how to they operate?

e. Consider both Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM).

1 Describe how the equipment differs from one another.

2 The sample limitations for each technique.

3 Why is one better for studying surface defects?

Q6.

The following crystal structure was proposed for Zinc Oxide:

Space group $P63/mc$; Lattice parameters: $a = b = 3.253 \text{ \AA}$, $c = 5.213 \text{ \AA}$.

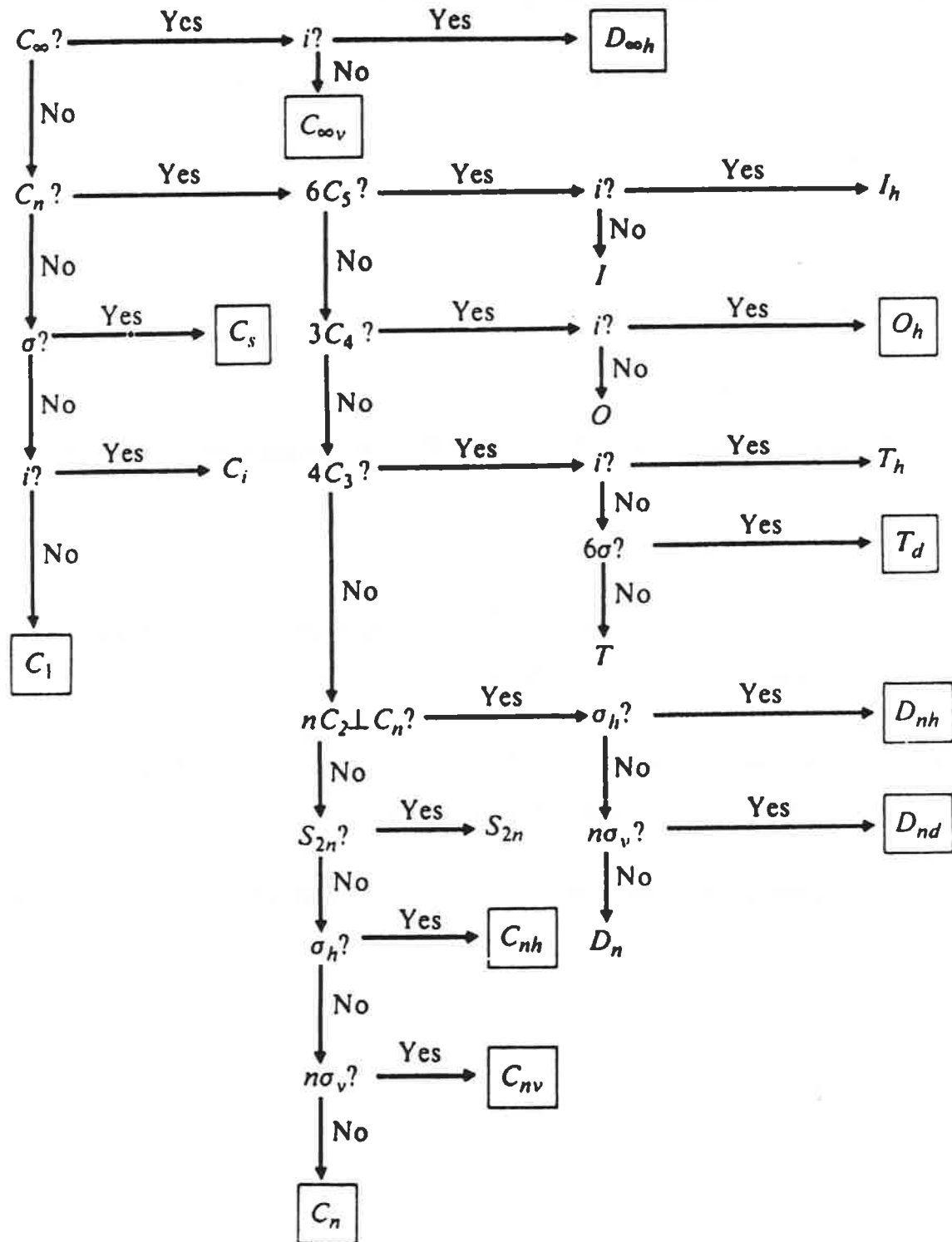
Atomic positions:

Zn $(1/3, 2/3, 0.1)$

O $(1/3, 2/3, 0.38)$

- a. Draw the proposed unit cell both 2D and 3D representations with the atoms.
- b. Assign Wyckoff sites
- c. Give Z and calculate the density of the ZnO sample. ($N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$; atomic weights (g/mol): Zn 65.4, O 15.999,)
- d. Describe the coordination of Zn in the proposed structure: site symmetry, coordination number and the Zn-O bond lengths.
- e. As ZnS forms the same structure discuss the expected differences in the two compounds X-Ray Diffraction patterns.

Material that may be of some use.



$$n(i) = \frac{1}{h} \sum_R \chi_r(R) \chi_i(R)$$

Cubic: $\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$

Tetragonal: $\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$

Hexagonal: $\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$

Rhombohedral:

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

Orthorhombic: $\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (4); (7)

Positions

Multiplicity,
Wyckoff letter,
Site symmetry

Coordinates

Reflection conditions

12	<i>d</i>	1	(1) x, y, z	(2) $\bar{y}, x-y, z$	(3) $\bar{x}+y, \bar{x}, z$
			(4) $\bar{x}, \bar{y}, z+\frac{1}{2}$	(5) $y, \bar{x}+y, z+\frac{1}{2}$	(6) $x-y, x, z+\frac{1}{2}$
			(7) \bar{y}, \bar{x}, z	(8) $\bar{x}+y, y, z$	(9) $x, x-y, z$
			(10) $y, x, z+\frac{1}{2}$	(11) $x-y, \bar{y}, z+\frac{1}{2}$	(12) $\bar{x}, \bar{x}+y, z+\frac{1}{2}$

General:

$$hh2hl: l = 2n$$

$$000l: l = 2n$$

Special: as above, plus

6	<i>c</i>	$.m.$	x, \bar{x}, z	$x, 2x, z$	$2\bar{x}, \bar{x}, z$	$\bar{x}, x, z+\frac{1}{2}$	$\bar{x}, 2\bar{x}, z+\frac{1}{2}$	$2x, x, z+\frac{1}{2}$
2	<i>b</i>	$3m.$	$\frac{1}{2}, \frac{1}{2}, z$	$\frac{1}{2}, \frac{1}{2}, z+\frac{1}{2}$				

no extra conditions

$$hkil: l = 2n$$

$$\text{or } h-k = 3n+1$$

$$\text{or } h-k = 3n+2$$

2	<i>a</i>	$3m.$	$0, 0, z$	$0, 0, z+\frac{1}{2}$
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$$hkil: l = 2n$$

Symmetry of special projections

Along [001] $p6mm$

$$a' = a \quad b' = b$$

Origin at $0, 0, z$ Along [100] $p1g1$

$$a' = \frac{1}{2}(a+2b) \quad b' = b$$

Origin at $x, 0, 0$ Along [210] $p1m1$

$$a' = \frac{1}{2}b \quad b' = \frac{1}{2}c$$

Origin at $x, \frac{1}{2}x, 0$

Maximal non-isomorphic subgroups

I	[2] $P6_311$ ($P6_3$)	1; 2; 3; 4; 5; 6
	[2] $P3m1$	1; 2; 3; 7; 8; 9
	[2] $P31c$	1; 2; 3; 10; 11; 12
	[3] $P2_1mc$ ($Cmc2_1$)	1; 4; 7; 10
	[3] $P2_1mc$ ($Cmc2_1$)	1; 4; 8; 11
	[3] $P2_1mc$ ($Cmc2_1$)	1; 4; 9; 12

IIa none

IIb [3] $H6_3mc$ ($a' = 3a, b' = 3b$) ($P6_3cm$)

Maximal isomorphic subgroups of lowest index

IIc [3] $P6_3mc$ ($c' = 3c$); [4] $P6_3mc$ ($a' = 2a, b' = 2b$)

Minimal non-isomorphic supergroups

I	[2] $P6_3/mmc$
II	[3] $H6_3mc$ ($P6_3cm$); [2] $P6mm$ ($2c' = c$)