CHEM-E4205 - Crystallography Basics and Structural Characterization

Exam 27/10/2015

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.

1.

The following crystal structure was proposed for lanthanum oxyfluoride LaOF:

Space group $P4/nmm$; Lattice parameters: $a = b = 4.091$ Å, $c = 5.852$ Å.

Atomic positions:

F   (0,0,0) & (½,½,0)

O   (0,0,½) & (½,½,½)

La $(0,½;z)$ & $(½,0,\bar{z})$; $z = 0.778$

    a.   Draw the proposed unit cell both 2D and 3D representations with the atoms.

    b.   Assign Wyckoff sites

    c.   Experimentally the density of the LaOF sample was determined to be 5.90 g/cm³. Judge the correctness of the proposed structure model by comparing the experimental density value with the theoretical density value calculated based on the proposed crystal structure. ($N_A = 6.022 \times 10^{23}$ mol⁻¹; atomic weights (g/mol): La 138.91, O 15.999, F 18.998)

    d.   Describe the coordination of La in the proposed structure: site symmetry, coordination number and the La-O and La-F bond lengths.

    e.   Given that the coherent neutron scattering length of O is 5.803 fm and F is 5.654 fm and La 8.24 fm discuss the ability of both neutrons and x rays to distinguish between all the atoms in the compound.

2.

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

(1) Mössbauer spectroscopy

(2) EXAFS

(3) Raman spectroscopy

(4) SEM

(5) GIXRD

(6) ND

(7) RBS

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?

3.

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

b. Fe is by far the most studied element in Mössbauer spectroscopy. Why is this so?

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

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

e. Describe the effect of a magnetic field interacting with the sample.

4.

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 and neutron powder diffraction patterns of tetragonal palladium (II) oxide. Calculate lattice parameters

	dhkl (Å)	hkl	I(X –ray)	I(neutron)
1	3.04	100	4	94
2	2.64	101	261	133
3	2.15	110	37	0
4	2.005	102	0	92
5	1.672	112	67	211
6	1.520	200	63	128
7	1.318	211	45	72
8	1.209	212	0	63
9	1.080	213	26	44

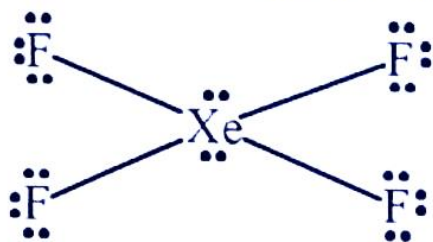c. If the density is 8.7×10^3 kg m^{-3} how many formula units are there per unit cell?

d. Describe how the variation of intensity between the X-Ray and the neuron pattern can give information on the positions of the Pd and O in the structure. Pay particular attention to 100, 102 and 212 drawings of the miller planes may help. Full structure factor treatment not required.

e. For NiO which has the sodium chloride structure (cubic Fm-3m), 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

RAM: Pd 106.4 O 16   Atomic number Pd46 O 8 Neutron scattering lengths 6.3 fm O 5.8fm N_A = 6.022×10^{23} mol^{-1}

5.

Square planar XeF_4 has the following structure

[Lewis structure of square planar XeF_4 with a central Xe bonded to four F atoms, each F and Xe shown with lone pairs.]

a. What is the point group?

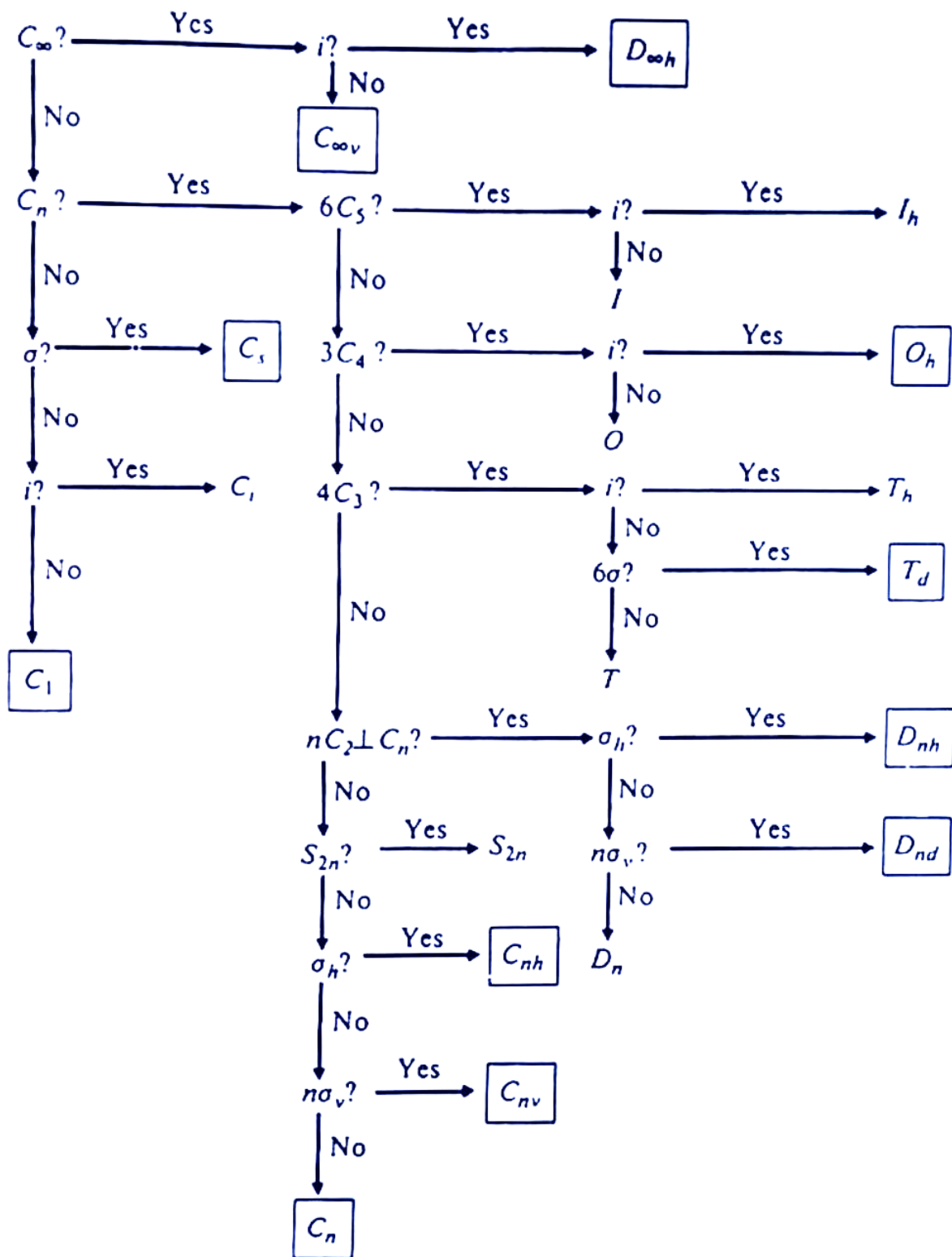b. Explain with diagrams the location of the rotation elements (including any improper) and the mirror planes.

Given the following character table and the reducible representation for an in plane stretch

	E	2C₄ (z)	C₂	2C'₂	2C''₂	i	2S₄	σₕ	2σᵥ	2σ_d	linears, rotations	quadratic
A_{1g}	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	R_z	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		x^2-y^2
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1		xy
E_g	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E_u	2	0	-2	0	0	-2	0	2	0	0	(x, y)	
Γ Stretch Xe-F	4	0	0	2	0	0	0	4	2	0		

c. Considering just the in plane stretch we can ignore the Eg and the ungerade A and B terms. Using the reduction formula for the rest calculate the irreps for the stretch.

d. Is the number of irreps consistent with the number of Xe-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.

6.

a. Consider an Atomic Force microscope. Compare and contrast the various modes of operation. You may want to make reference to a Lennard Jones potential diagram.

b. How would one alter a standard AFM to measure a polar material and which modes could be used?

c. Considering doped $BiFeO_3$ has the space group R3c. Films grown with 003 and 110 (hexagonal setting) are measured using the altered AFM. Which one would show the stronger response and why?

d. Doped $BiFeO_3$ is also magnetic. How could the AFM setup be further altered to investigate this? What limits the resolution?

e. Consider both SEM and STEM.

 1 Describe how the equipment differs from one another.

 2 The sample limitations for each technique.

 3 Which is better for studying bulk material and which for surface defects?

C_∞? —Yes→ i? —Yes→ $D_{\infty h}$
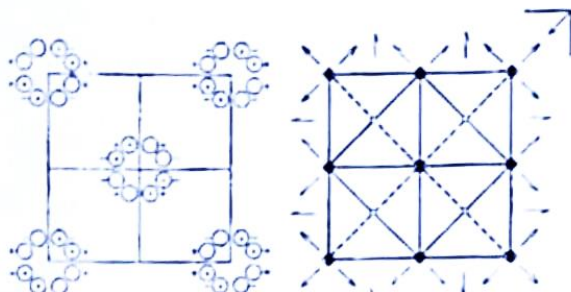
C_∞? —No↓

i? —No↓ $C_{\infty v}$

C_n? —Yes→ $6C_5$? —Yes→ i? —Yes→ I_h

$6C_5$? —No↓

i? —No↓ I

C_n? —No↓

σ? —Yes→ C_s

$3C_4$? —Yes→ i? —Yes→ O_h

$3C_4$? —No↓

i? —No↓ O

σ? —No↓

i? —Yes→ C_i

$4C_3$? —Yes→ i? —Yes→ T_h

$4C_3$? —No↓

i? —No↓ 6σ? —Yes→ T_d

6σ? —No↓ T

i? —No↓ C_1

$nC_2 \perp C_n$? —Yes→ σ_h? —Yes→ D_{nh}

$nC_2 \perp C_n$? —No↓

σ_h? —No↓

S_{2n}? —Yes→ S_{2n}

$n\sigma_v$? —Yes→ D_{nd}

S_{2n}? —No↓

$n\sigma_v$? —No↓ D_n

σ_h? —Yes→ C_{nh}

σ_h? —No↓

$n\sigma_v$? —Yes→ C_{nv}

$n\sigma_v$? —No↓

C_n

P 4/n m m D_{4h}^{7} 4/m m m   Tetragonal

No. 129 $P\,4/n\,2_1/m\,2/m$ Patterson symmetry $P\,4/m\,m\,m$

ORIGIN CHOICE 1

Origin at $\bar{4}m2$ at $\bar{4}/nm\,2/g$, at $-\frac{1}{4},\frac{1}{4},0$ from centre (2/m)

Asymmetric unit $0 \leq x \leq \frac{1}{2}$, $0 \leq y \leq \frac{1}{2}$, $0 \leq z \leq \frac{1}{2}$, $y \leq \frac{1}{2} - x$

Symmetry operations

(1) 1	(2) 2 0,0,z	(3) 4⁺ 0,½,z	(4) 4⁻ ½,0,z
(5) 2(0,½,0) ¼,y,0	(6) 2(½,0,0) x,¼,0	(7) 2̄ ¼,¼,0	(8) 2̄ x,x̄,0
(9) 1̄ ¼,¼,0	(10) n(½,½,0) x,y,0	(11) 4̄⁺ 0,0,z; 0,0,0	(12) 4̄⁻ 0,0,z; 0,0,0
(13) m ¼,0,z	(14) m 0,y,z	(15) m x+¼,x̄,z	(16) g(½,½,0) x,x,z

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

Generators selected   (1); $t(1,0,0)$; $t(0,1,0)$, $t(0,0,1)$;   (2);   (3);   (5);   (9)

Positions

Multiplicity, Wyckoff letter, Site symmetry	Coordinates				Reflection conditions

Reflection conditions

General:

16	k	1	(1) x,y,z	(2) $\bar{x},\bar{y},z$	(3) $\bar{y}+\tfrac{1}{2},x+\tfrac{1}{2},z$	(4) $y+\tfrac{1}{2},\bar{x}+\tfrac{1}{2},z$	$hk0:\ h+k=2n$
			(5) $\bar{x}+\tfrac{1}{2},y+\tfrac{1}{2},\bar{z}$	(6) $x+\tfrac{1}{2},\bar{y}+\tfrac{1}{2},\bar{z}$	(7) $y,x,\bar{z}$	(8) $\bar{y},\bar{x},\bar{z}$	$h00:\ h=2n$
			(9) $\bar{x}+\tfrac{1}{2},\bar{y}+\tfrac{1}{2},\bar{z}$	(10) $x+\tfrac{1}{2},y+\tfrac{1}{2},\bar{z}$	(11) $y,\bar{x},\bar{z}$	(12) $\bar{y},x,\bar{z}$	
			(13) $x,\bar{y},z$	(14) $\bar{x},y,z$	(15) $\bar{y}+\tfrac{1}{2},\bar{x}+\tfrac{1}{2},z$	(16) $y+\tfrac{1}{2},x+\tfrac{1}{2},z$	

Special: as above, plus

8	j	$..m$	$x,x+\tfrac{1}{2},z$	$\bar{x},\bar{x}+\tfrac{1}{2},z$	$\bar{x},x+\tfrac{1}{2},z$	$x,\bar{x}+\tfrac{1}{2},z$	no extra conditions
			$x+\tfrac{1}{2},x,\bar{z}$	$x+\tfrac{1}{2},\bar{x},\bar{z}$	$x+\tfrac{1}{2},x,\bar{z}$	$\bar{x}+\tfrac{1}{2},\bar{x},\bar{z}$	

8	i	$.m.$	$0,y,z$	$0,\bar{y},z$	$\bar{y}+\tfrac{1}{2},\tfrac{1}{2},z$	$y+\tfrac{1}{2},\tfrac{1}{2},z$	no extra conditions
			$\tfrac{1}{2},y+\tfrac{1}{2},\bar{z}$	$\tfrac{1}{2},\bar{y}+\tfrac{1}{2},\bar{z}$	$y,0,\bar{z}$	$\bar{y},0,\bar{z}$	

8	h	$..2$	$x,x,\tfrac{1}{2}$	$\bar{x},\bar{x},\tfrac{1}{2}$	$\bar{x}+\tfrac{1}{2},x-\tfrac{1}{2},\tfrac{1}{2}$	$x+\tfrac{1}{2},\bar{x}+\tfrac{1}{2},\tfrac{1}{2}$	$hkl:\ h+k=2n$
			$\bar{x}+\tfrac{1}{2},\bar{x}+\tfrac{1}{2},\tfrac{1}{2}$	$x-\tfrac{1}{2},x+\tfrac{1}{2},\tfrac{1}{2}$	$x,\bar{x},\tfrac{1}{2}$	$\bar{x},x,\tfrac{1}{2}$	

8	g	$..2$	$x,x,0$	$\bar{x},\bar{x},0$	$\bar{x}+\tfrac{1}{2},x+\tfrac{1}{2},0$	$x+\tfrac{1}{2},\bar{x}+\tfrac{1}{2},0$	$hkl:\ h+k=2n$
			$\bar{x}+\tfrac{1}{2},\bar{x}+\tfrac{1}{2},0$	$x+\tfrac{1}{2},x+\tfrac{1}{2},0$	$x,\bar{x},0$	$\bar{x},x,0$	

4	f	$2mm.$	$0,0,z$	$\tfrac{1}{2},\tfrac{1}{2},z$	$\tfrac{1}{2},\tfrac{1}{2},\bar{z}$	$0,0,\bar{z}$	$hkl:\ h+k=2n$

4	e	$..2/m$	$\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}$	$\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}$	$\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}$	$\bar{\tfrac{1}{2}},\tfrac{1}{2},\tfrac{1}{2}$	$hkl:\ h,k=2n$

4	d	$..2/m$	$\tfrac{1}{2},\tfrac{1}{2},0$	$\tfrac{1}{2},\tfrac{1}{2},0$	$\tfrac{1}{2},\tfrac{1}{2},0$	$\tfrac{1}{2},\tfrac{1}{2},0$	$hkl:\ h,k=2n$

2	c	$4mm$	$0,\tfrac{1}{2},z$	$\tfrac{1}{2},0,\bar{z}$			no extra conditions

2	b	$\bar{4}m2$	$0,0,\tfrac{1}{2}$	$\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}$			$hkl:\ h+k=2n$

2	a	$\bar{4}m2$	$0,0,0$	$\tfrac{1}{2},\tfrac{1}{2},0$			$hkl:\ h-k=2n$

Symmetry of special projections

Along [001] $p\,4mm$
$a'=\tfrac{1}{2}(a-b)$ $b'=\tfrac{1}{2}(a+b)$
Origin at $0,0,z$

Along [100] $p\,2mg$
$a'=b$ $b'=c$
Origin at $x,\tfrac{1}{4},0$

Along [110] $p\,2mm$
$a'=\tfrac{1}{2}(-a+b)$ $b'=c$
Origin at $x,x,0$

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:

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