Crystal Structure Analyses, **Take Home Exam-1**

Spring-2019, total 100 points, **Due Wednesday, April 10**

Instructions; Show all works. The answers should be in order (do not mix up the sequence of the answers). Answers should be organized and neat. Any book or computer programs may be used, but you may NOT consult with each other.

1. (12 points) Explain the followings.

(a) Laue group (b) Laue index (c) Friedel's law (d) mosaic structure

(e) systematic absence (f) primary extinction (g) microabsorption

(h) specimen displacement error and transparency error

(i) multiplicity in the International Tables for Crystallographers Volume A

(j) multiplicity which affects the intensity of diffraction peaks

(k) difference between X-ray diffraction and neutron diffraction

(l) atomic scattering factor & structure factor. Compare these two.

(m) θ should have a single value when d and wavelength are constant according to Bragg's law, but there is a range of θ which has appreciable intensity in real powder diffraction. Why? (see chapter 4-9, 5-2 of Cullity, chapter 3.9.2 of Jenkins & Snyder, ---)

2. (10 points) The space group of tungsten (W) is $I\frac{4}{m}\bar{3}\frac{2}{m}$.

(a) Explain what each symbol (4 parts) represents

(b) What is the crystal system?

(c) Indicate the crystallographic symmetry directions of $\frac{4}{m}$, $\bar{3}$ and $\frac{2}{m}$.

(d) What is the point group?

3. (12 points) Explain the reason the following lattices are not included in 14 Bravais lattices.

(a) cubic C lattice,

(b) tetragonal F lattice,

(c) tetragonal C lattice,

(d) monoclinic I lattice

4. (10 points) Determine the point group symmetry of the followings. How many, and which symmetry elements are present in this point group symmetry?

(a) tetrahedron, (b) octahedron, (c) H2O molecule

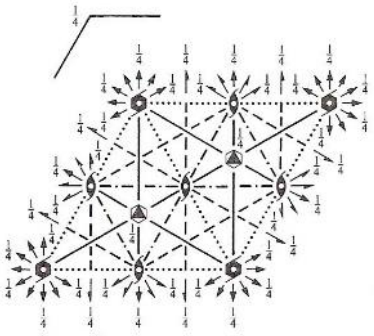
5. (10 points) The crystal structure of a material is described in space group symmetry $P\frac{6_3}{m}mc$ with the following atomic coordinates;

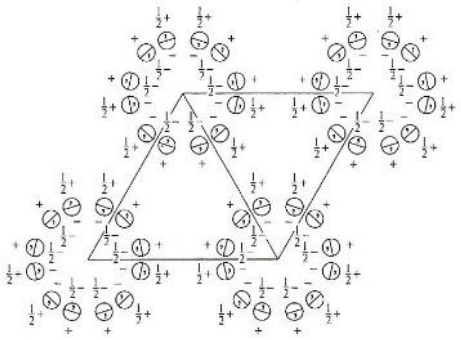
Atom	x	y	Z
Ba1	0	0	0.25
Ba2	0.3333	0.6667	0.9110
Ni	0	0	0
Sb	0.3333	0.6667	0.1510
O1	0.4816	-0.0368	0.25
O2	0.1685	0.3370	0.4169

Using the information in the International Tables for Crystallography which is given below, describe every atom in terms of the multiplicities and Wyckoff letters of their site positions and establish the content of the unit cell, the simplest chemical formula, and the number of formula units (Z) per unit cell. Usually, a formula unit corresponds to the simplest chemical formula or to the stoichiometry of the molecule of a material.

$P\,6_3/m\,m\,c$ D_{6h}^4 $6/m\,m\,m$ Hexagonal

No. 194 $P\,6_3/m\,2/m\,2/c$ Patterson symmetry $P\,6/m\,m\,m$





For $\bar{1}$ and $\bar{6}$ see $P6_3/m$ (No. 176)

Origin at centre $(\bar{3}m\,1)$ at $\bar{3}\,2/m\,c$

Asymmetric unit $0\le x\le\frac{1}{3}$; $0\le y\le\frac{1}{3}$; $0\le z\le\frac{1}{4}$; $x\le 2y$; $y\le\min(1-x,2x)$

Vertices $0,0,0$ $\frac{1}{3},\frac{1}{3},0$ $\frac{1}{3},\frac{2}{3},0$
$0,0,\frac{1}{4}$ $\frac{1}{3},\frac{1}{3},\frac{1}{4}$ $\frac{1}{3},\frac{2}{3},\frac{1}{4}$

Symmetry operations

(1) 1
(2) 3^+ $0,0,z$
(3) 3^- $0,0,z$
(4) $2(0,0,\frac{1}{2})$ $0,0,z$
(5) $6^-(0,0,\frac{1}{2})$ $0,0,z$
(6) $6^+(0,0,\frac{1}{2})$ $0,0,z$
(7) 2 $x,x,0$
(8) 2 $x,0,0$
(9) 2 $0,y,0$
(10) 2 $x,\bar{x},\frac{1}{4}$
(11) 2 $x,2x,\frac{1}{4}$
(12) 2 $2x,x,\frac{1}{4}$
(13) $\bar{1}$ $0,0,0$
(14) $\bar{3}^+$ $0,0,z$; $0,0,0$
(15) $\bar{3}^-$ $0,0,z$; $0,0,0$
(16) m $x,y,\frac{1}{4}$
(17) $\bar{6}^-$ $0,0,z$; $0,0,\frac{1}{4}$
(18) $\bar{6}^+$ $0,0,z$; $0,0,\frac{1}{4}$
(19) m $x,\bar{x},z$
(20) m $x,2x,z$
(21) m $2x,x,z$
(22) c x,x,z
(23) c $x,0,z$
(24) c $0,y,z$

CONTINUED **No. 194** $P\,6_3/m\,m\,c$

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (4); (7); (13)

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates			Reflection conditions
						General:
24	l	1	(1) x,y,z	(2) $\bar{y},x-y,z$	(3) $\bar{x}+y,\bar{x},z$	$hh\overline{2h}l$: $l=2n$
			(4) $\bar{x},\bar{y},z+\frac{1}{2}$	(5) $y,\bar{x}+y,z+\frac{1}{2}$	(6) $x-y,x,z+\frac{1}{2}$	$000l$: $l=2n$
			(7) $y,x,\bar{z}$	(8) $x-y,\bar{y},\bar{z}$	(9) $\bar{x},\bar{x}+y,\bar{z}$	
			(10) $\bar{y},\bar{x},\bar{z}+\frac{1}{2}$	(11) $\bar{x}+y,y,\bar{z}+\frac{1}{2}$	(12) $x,x-y,\bar{z}+\frac{1}{2}$	
			(13) $\bar{x},\bar{y},\bar{z}$	(14) $y,\bar{x}+y,\bar{z}$	(15) $x-y,x,\bar{z}$	
			(16) $x,y,\bar{z}+\frac{1}{2}$	(17) $\bar{y},x-y,\bar{z}+\frac{1}{2}$	(18) $\bar{x}+y,\bar{x},\bar{z}+\frac{1}{2}$	
			(19) $\bar{y},\bar{x},z$	(20) $\bar{x}+y,y,z$	(21) $x,x-y,z$	
			(22) $y,x,z+\frac{1}{2}$	(23) $x-y,\bar{y},z+\frac{1}{2}$	(24) $\bar{x},\bar{x}+y,z+\frac{1}{2}$	
						Special: as above, plus
12	k	$.m.$	$x,2x,z$	$2\bar{x},\bar{x},z$	$x,\bar{x},z$	$\bar{x},2\bar{x},z+\frac{1}{2}$	no extra conditions
			$2x,x,z+\frac{1}{2}$	$\bar{x},x,z+\frac{1}{2}$	$2x,x,\bar{z}$	$\bar{x},2\bar{x},\bar{z}$	
			$\bar{x},x,\bar{z}$	$2\bar{x},\bar{x},\bar{z}+\frac{1}{2}$	$x,2x,\bar{z}+\frac{1}{2}$	$x,\bar{x},\bar{z}+\frac{1}{2}$	
12	j	$m..$	$x,y,\frac{1}{4}$	$\bar{y},x-y,\frac{1}{4}$	$\bar{x}+y,\bar{x},\frac{1}{4}$	$\bar{x},\bar{y},\frac{3}{4}$	$y,\bar{x}+y,\frac{3}{4}$	$x-y,x,\frac{3}{4}$	no extra conditions
			$y,x,\frac{3}{4}$	$x-y,\bar{y},\frac{3}{4}$	$\bar{x},\bar{x}+y,\frac{3}{4}$	$\bar{y},\bar{x},\frac{1}{4}$	$\bar{x}+y,y,\frac{1}{4}$	$x,x-y,\frac{1}{4}$	
12	i	$.2.$	$x,0,0$	$0,x,0$	$\bar{x},\bar{x},0$	$\bar{x},0,\frac{1}{2}$	$0,\bar{x},\frac{1}{2}$	$x,x,\frac{1}{2}$	$hkil$: $l=2n$
			$\bar{x},0,0$	$0,\bar{x},0$	$x,x,0$	$x,0,\frac{1}{2}$	$0,x,\frac{1}{2}$	$\bar{x},\bar{x},\frac{1}{2}$	
6	h	$m\,m\,2$	$x,2x,\frac{1}{4}$	$2\bar{x},\bar{x},\frac{1}{4}$	$x,\bar{x},\frac{1}{4}$	$\bar{x},2\bar{x},\frac{3}{4}$	$2x,x,\frac{3}{4}$	$\bar{x},x,\frac{3}{4}$	no extra conditions
6	g	$.2/m.$	$\frac{1}{2},0,0$	$0,\frac{1}{2},0$	$\frac{1}{2},\frac{1}{2},0$	$\frac{1}{2},0,\frac{1}{2}$	$0,\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$	$hkil$: $l=2n$
4	f	$3m.$	$\frac{1}{3},\frac{2}{3},z$	$\frac{2}{3},\frac{1}{3},z+\frac{1}{2}$	$\frac{2}{3},\frac{1}{3},\bar{z}$	$\frac{1}{3},\frac{2}{3},\bar{z}+\frac{1}{2}$	$hkil$: $l=2n$ or $h-k=3n+1$ or $h-k=3n+2$
4	e	$3m.$	$0,0,z$	$0,0,z+\frac{1}{2}$	$0,0,\bar{z}$	$0,0,\bar{z}+\frac{1}{2}$	$hkil$: $l=2n$
2	d	$\bar{6}m\,2$	$\frac{1}{3},\frac{2}{3},\frac{3}{4}$	$\frac{2}{3},\frac{1}{3},\frac{1}{4}$			$hkil$: $l=2n$ or $h-k=3n+1$ or $h-k=3n+2$
2	c	$\bar{6}m\,2$	$\frac{1}{3},\frac{2}{3},\frac{1}{4}$	$\frac{2}{3},\frac{1}{3},\frac{3}{4}$			
2	b	$\bar{6}m\,2$	$0,0,\frac{1}{4}$	$0,0,\frac{3}{4}$			$hkil$: $l=2n$
2	a	$\bar{3}m.$	$0,0,0$	$0,0,\frac{1}{2}$			$hkil$: $l=2n$

Symmetry of special projections

Along [001] $p\,6m\,m$
$\boldsymbol{a}'=\boldsymbol{a}$ $\boldsymbol{b}'=\boldsymbol{b}$
Origin at $0,0,z$

Along [100] $p\,2g\,m$
$\boldsymbol{a}'=\frac{1}{2}(\boldsymbol{a}+2\boldsymbol{b})$ $\boldsymbol{b}'=\boldsymbol{c}$
Origin at $x,0,0$

Along [210] $p\,2m\,m$
$\boldsymbol{a}'=\frac{1}{2}\boldsymbol{b}$ $\boldsymbol{b}'=\frac{1}{2}\boldsymbol{c}$
Origin at $x,\frac{1}{2}x,0$

(*Continued on preceding page*)

6. (12 points)

The space group of the graphite is $P\frac{6_3}{m}mc$ (No. 194).

(a) The lattice constants of graphite are a = 2.46Å and c = 6.71Å. Carbon atoms occupy Wyckoff positions 2b and 2c in the space group. Using the hexahedron unit cell, illustrate the occupied positions in one unit cell of graphite.

(b) The c axis is normal to the basal plane of graphite. Draw the two-dimensional arrangement of carbon atoms in the basal plane of graphite, covering an area that includes nine unit cells.

(c) Calculate the center-to-center distance between the nearest-neighbor carbon atoms in the basal plane of graphite.

(d) Why is there no carbon atom at the origin of the unit cell in graphite.

(e) How many lattice points per unit cell are there in the graphite structure?

(f) On what axial combination of rotational symmetry axes is this space group based?

(g) Which of these symmetry operations is not present in the graphite structure: translation, rotation axis, reflection plane, inversion center, glide plane, screw axis, rotoinversion axis?

7. (12 points) Bragg's law: λ = 2d sinθ

(a) Suppose a Bragg reflection in a θ/2θ pattern to be observed at $2\theta_1$ when Cu Kα1 monochromatized radiation is applied. What would be the appropriate position of $2\theta_2$ for the Cu Kα2 line?

(b) What is the minimum value of d that can be measured for Cu Kα radiation (1.5418Å)?

(c) Derive an expression relating a small change in d (Δd) to a small change in θ (Δθ).

8. (10 points) In cubic substances two group of lattice planes may scatter simultaneously for the same scattering angle 2θ, because $\frac{1}{d^2} = \frac{(h^2+k^2+l^2)}{a^2}$ is not a one-to-one unique function of Miller indices hkl. Which are the first double reflections to occur in a θ/2θ scan? Give the first three of them for fcc and bcc structures.

9. (12 points)

(a) Plot the reciprocal lattice for a polycrystalline sample of a material with a simple tetragonal structure and lattice parameters a=4.0Å and c= 5.0Å. (Use a two-dimensional section through the three-dimensional space).

(b) Diffractometers typically can scan up to, but not beyond, 165° 2θ. For the sample in (a) what are the Miller indices of the highest angle reflection if (i) Cr Kα radiation is used, (ii) Cu Kα radiation is used? (λ(Cr Kα) radiation = 2.2910Å, λ(Cu Kα) radiation = 1.5418Å)