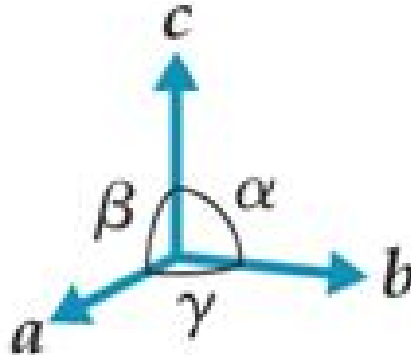


Problem Set 01

Analytical Techniques (July 2021)

1. Consider an unit cell (parallelepiped) represented using the lengths of the three sides (a, b, c) and the angles between the sides (α, β, γ) as shown:



Show that the separation between the (hkl) planes is given by:

$$\frac{1}{d_{hkl}^2} = \frac{S_{11}h^2 + S_{22}k^2 + S_{33}l^2 + 2S_{12}hk + 2S_{23}kl + 2S_{31}lh}{V^2}$$

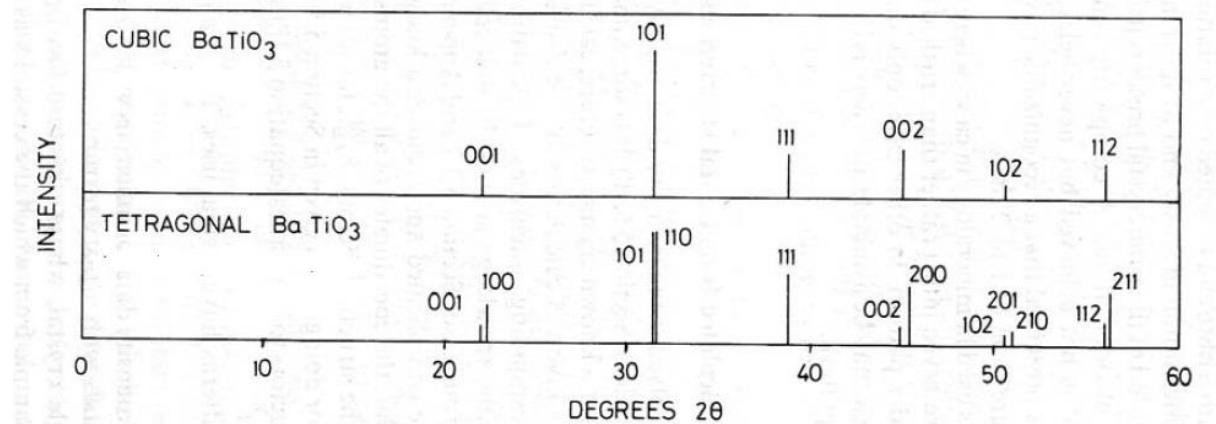
Where V is the volume of the unit cell and S_{ij} are as follows:

$$V = abc\sqrt{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma}$$

$$S = a^2b^2c^2 \begin{pmatrix} \frac{\sin^2 \alpha}{a^2} & \frac{\cos \alpha \cos \beta - \cos \gamma}{ab} & \frac{\cos \gamma \cos \alpha - \cos \beta}{ac} \\ \frac{\cos \alpha \cos \beta - \cos \gamma}{ba} & \frac{\sin^2 \beta}{b^2} & \frac{\cos \beta \cos \gamma - \cos \alpha}{bc} \\ \frac{\cos \gamma \cos \alpha - \cos \beta}{ca} & \frac{\cos \beta \cos \gamma - \cos \alpha}{ca} & \frac{\sin^2 \gamma}{c^2} \end{pmatrix}$$

2. Consider a material that has a BCC lattice. Let us assume that the material undergoes a phase transition and one of the edges of the unit cell (say c axis) gets longer than the other two. This is a cubic to tetragonal transition. The basis atoms still remain at $(0,0,0)$ & $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Describe what effect this will have on the diffraction pattern. Will some peaks disappear or appear?

Now consider a material BaTiO_3 which actually has a cubic-tetragonal transition at 120°C . The high temperature phase is cubic. From the data given below find the lattice constants of the two phases:

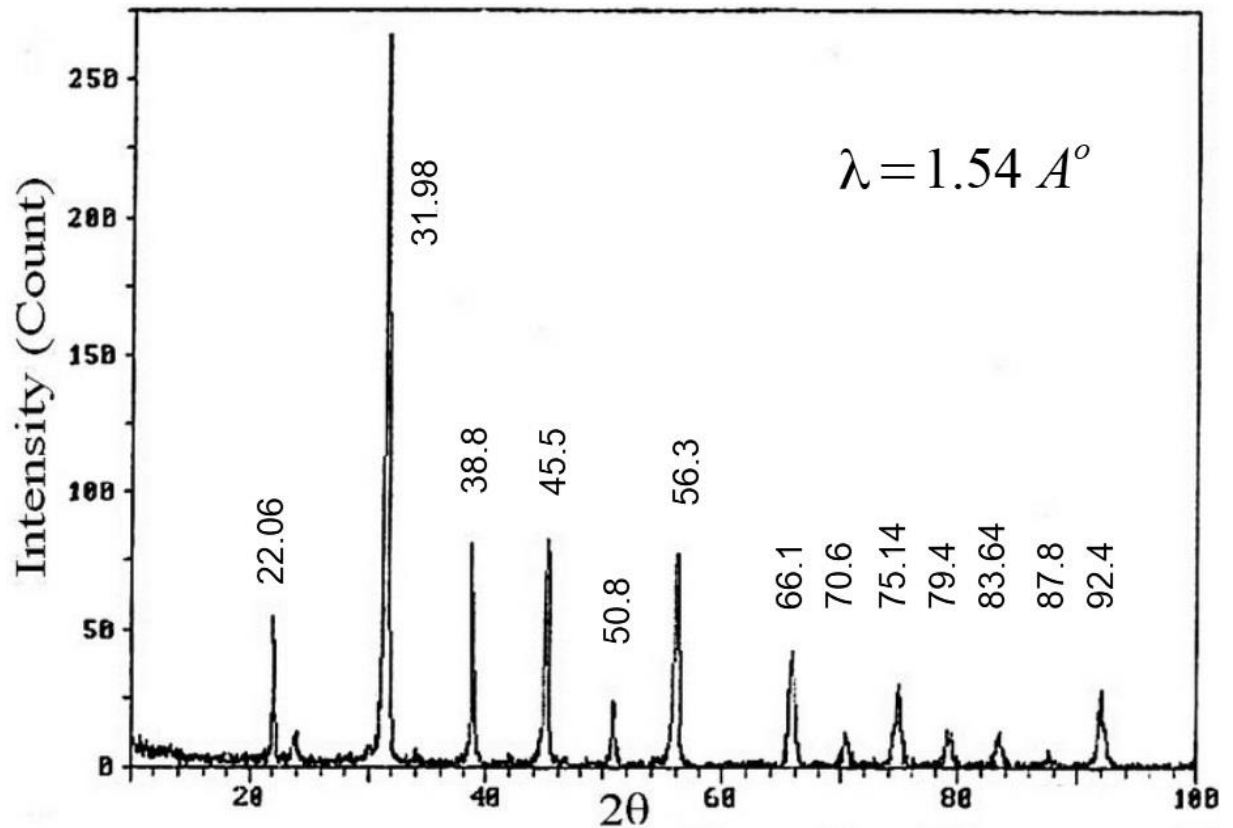


3. Consider the hexagonal system of writing directions with four indices $[hkil]$ rather than three indices $[hkl]$.
 - A. Show that $i = h + k$.
 - B. Suppose you are given the direction $[1\ 1\ \bar{2}\ 0]$. What are the six equivalent direction in the 4 index system and the 3 index system?
 - C. Can you now explain why we often use the four index system even though one index is redundant ?

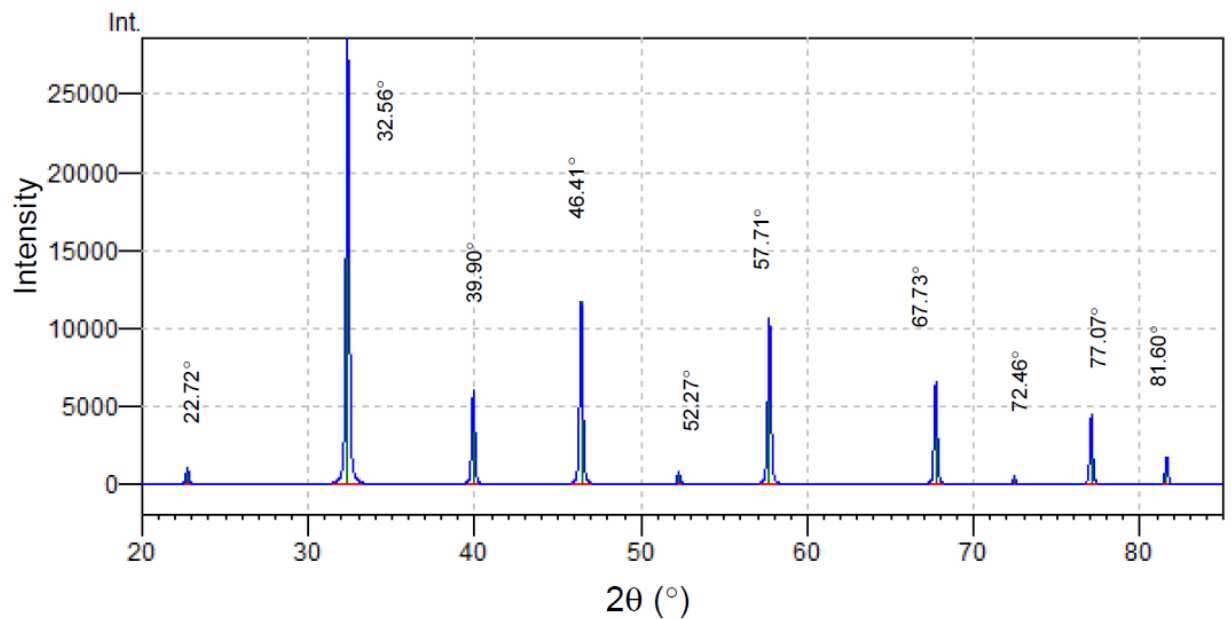
4. Consider the (100) and (111) planes in face centered cubic (FCC) lattice with lattice constant a . The (hkl) values are written using the conventional cubic axes $(\hat{i}, \hat{j}, \hat{k})$. It is also possible to describe the same system using the primitive unit vectors given by

$$\begin{aligned}\vec{A}_1 &= \frac{a}{2}(\hat{i} + \hat{j}) \\ \vec{A}_2 &= \frac{a}{2}(\hat{j} + \hat{k}) \\ \vec{A}_3 &= \frac{a}{2}(\hat{k} + \hat{i})\end{aligned}$$
 - A. What will be the new (HKL) indices of the planes (100) and (111) ?
 - B. What would be the general form of the “missing reflections” in the primitive system ?

5. Given the following powder diffraction data, determine the lattice type and the lattice constant after labelling all the peaks.



6. Analyse the following diffraction pattern and find out the type of lattice that can give rise to the pattern. The X-ray wavelength used was $\lambda = 1.5406 \text{ \AA}$.



- A) First construct a table and identify the hkl indices of the reflections.
- B) Determine the lattice constant *with reasoning*.
- C) From your list try to derive a conclusion about the lattice type *with reasoning*.
- D) Can you make an educated guess about the location of the heavy atoms in the basis from the intensity pattern of the lattice? (*Notice that the first & some of the other peaks are very weak. Does that give you a hint.....*)

7. Consider the two sets of (x, y) co-ordinates given in the two files

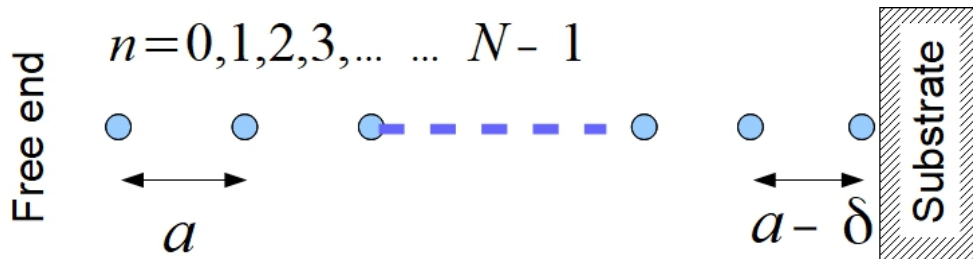
- a. ListOfVertices01.dat
- b. ListOfVertices02.dat

You may use any standard software like SciLab/MatLab/Mathematica/Octave/GNUPlot etc. You can write your own C/Python/any other language code. The first data set is trivial...but should help you to see if your codes etc are working correctly. The credit will be for doing the second one correctly ☺

Plot the points using any software of your choice. Try to find out what kind of symmetry the set of points have in the following way:

- A. In each case (a) and (b) what is the average nearest neighbor distance?
 - B. Make a plot of the pair distribution function $g(r)$ for $0 < r < 10$ with a resolution of at least 0.1 units.
 - C. Calculate the structure factor $S(\vec{q}) = \sum_n \exp[i \vec{q} \cdot \vec{r}_n]$ for $-4\pi < q_x, q_y < 4\pi$ where \vec{r}_n runs over all the points in the list.
 - D. Plot $|S(\vec{q})|$ as a 2D grayscale plot over the (q_x, q_y) range given. Adjust the scales etc so that all the features are clearly visible. What can you say about the symmetry of the two sets. Why is the range $\pm 4\pi$ given? Make sure you have about 1000 points along both the axes, otherwise the features may not show up correctly!
8. This question is meant to guide you through a very simple model of a strained lattice and the modification of the structure factor $S(q)$ resulting from this. Let us assume that a material in its "bulk" form has a cubic lattice constant a . Suppose a thin film of this material is deposited on a substrate due to which the lattice gets strained. We will ignore the "in-plane" direction and consider the relaxation of the lattice constant in the vertical direction only. So the problem is effectively reduced to a one-dimensional problem. Study the figure carefully:

At the left the "free end" has the same lattice constant as the bulk, a . But the other end of the chain of N atoms is attached to the substrate and is "strained". It is forced to have a lattice constant $a - \delta$. Assume that this relaxation happens linearly (from right to left)



- A. Suppose the first atom at the left (free) end has a co-ordinate $x = 0$. Write down the co-ordinate x_n , of the n th atom explicitly.
- B. Now you need to calculate $S(q)$. This has to be done numerically as the series cannot be summed explicitly in closed form. Obviously $q = \frac{2\pi}{a}$ is the reciprocal lattice vector. Now take $N = 100$ and use any numerical calculation and plotting software (Scilab/ Matlab/ Octave/ Gnuplot/ Mathematica/ Origin/ your own C/Fortran/Python/Basic code/any other favourite of yours...) and make a plot of $|S(q)|^2$ vs qa for the range $\left[2\pi - \frac{\pi}{4}$ to $2\pi + \frac{\pi}{4}\right]$ for three values of the maximum lattice strain $\frac{\delta}{a} = 0, 0.01, 0.02$. Obviously this corresponds to the unstrained, 1% strain and 2% strain. Plot a figure, it should bring out the important features of the strained and unstrained lattice clearly.

1. Analyse the data below and estimate the average grain size of the particles making up the sample, by using the Scherer formula. What is the likely reason the data from the crystal has split peaks? (The data is from <http://www.vanbokhoven.ethz.ch/education/XRDexercises>)

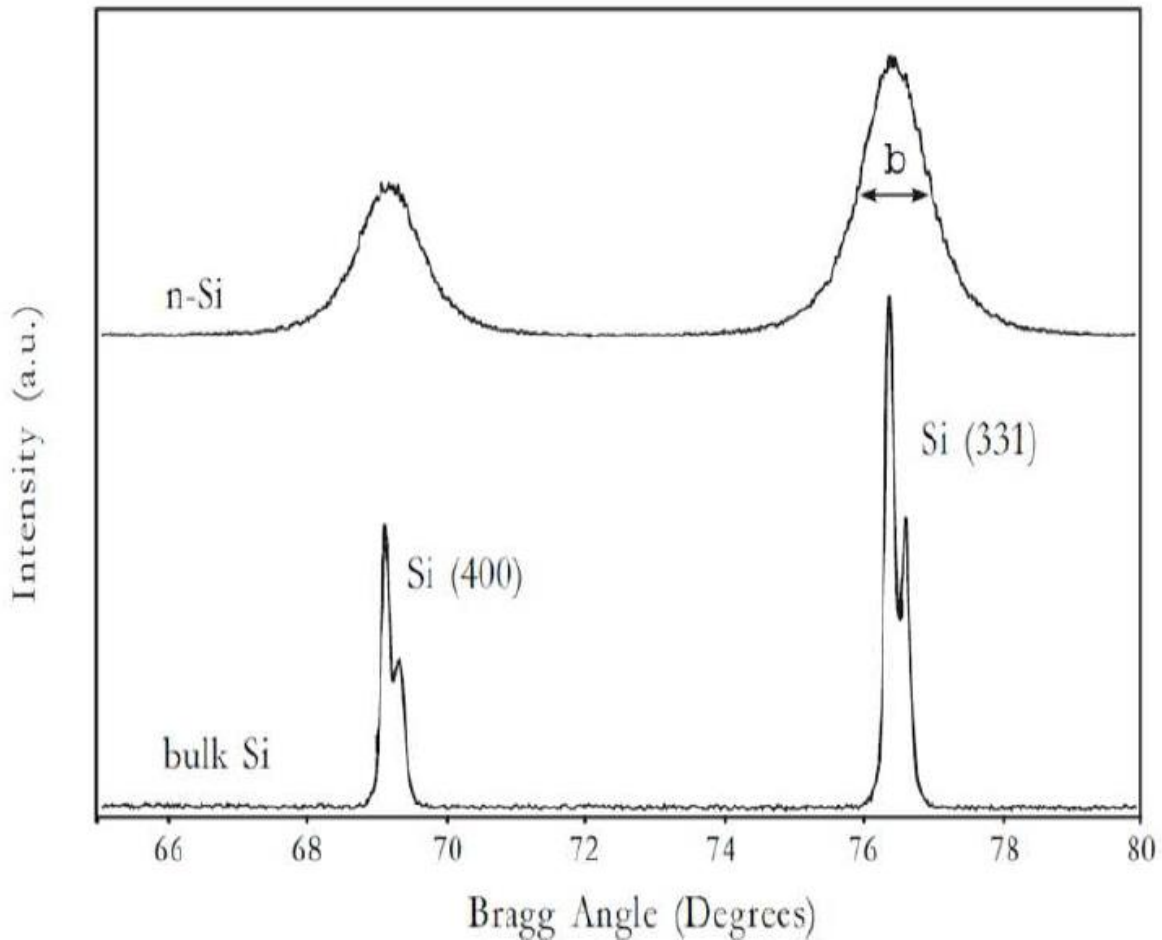


Figure 1 : X ray diffraction from bulk and nano-crystalline Silicon (Problem 1)

2. Consider a typical drawing of an Ewald sphere/reciprocal lattice, for a cubic lattice ($a = 5 \text{ \AA}$). Suppose on a piece of paper the dots appear 1 cm apart. What should be the width of each dot in same drawing if the crystallite size is about 100nm (a typical value) and the drawing is made to scale?
3. The figure shows the small angle X-ray reflectivity ($\lambda = 1.5406 \text{ \AA}$) obtained from a thin film of $\text{Ge}_{1-x}\text{Sn}_x$ alloy on a Ge substrate. Ignore the effect of the substrate. Calculate the approximate thickness of the film. If θ_c denotes the critical angle for total external reflection, then the maxima of the reflection (θ_m) are given by

$$\theta_m^2 - \theta_c^2 = m^2 \left(\frac{\lambda}{2d} \right)^2$$

Note that setting $\theta_c = 0$, reduces the expression to the simpler expression discussed in the class. How much difference does this make? Estimate the surface roughness of the film.

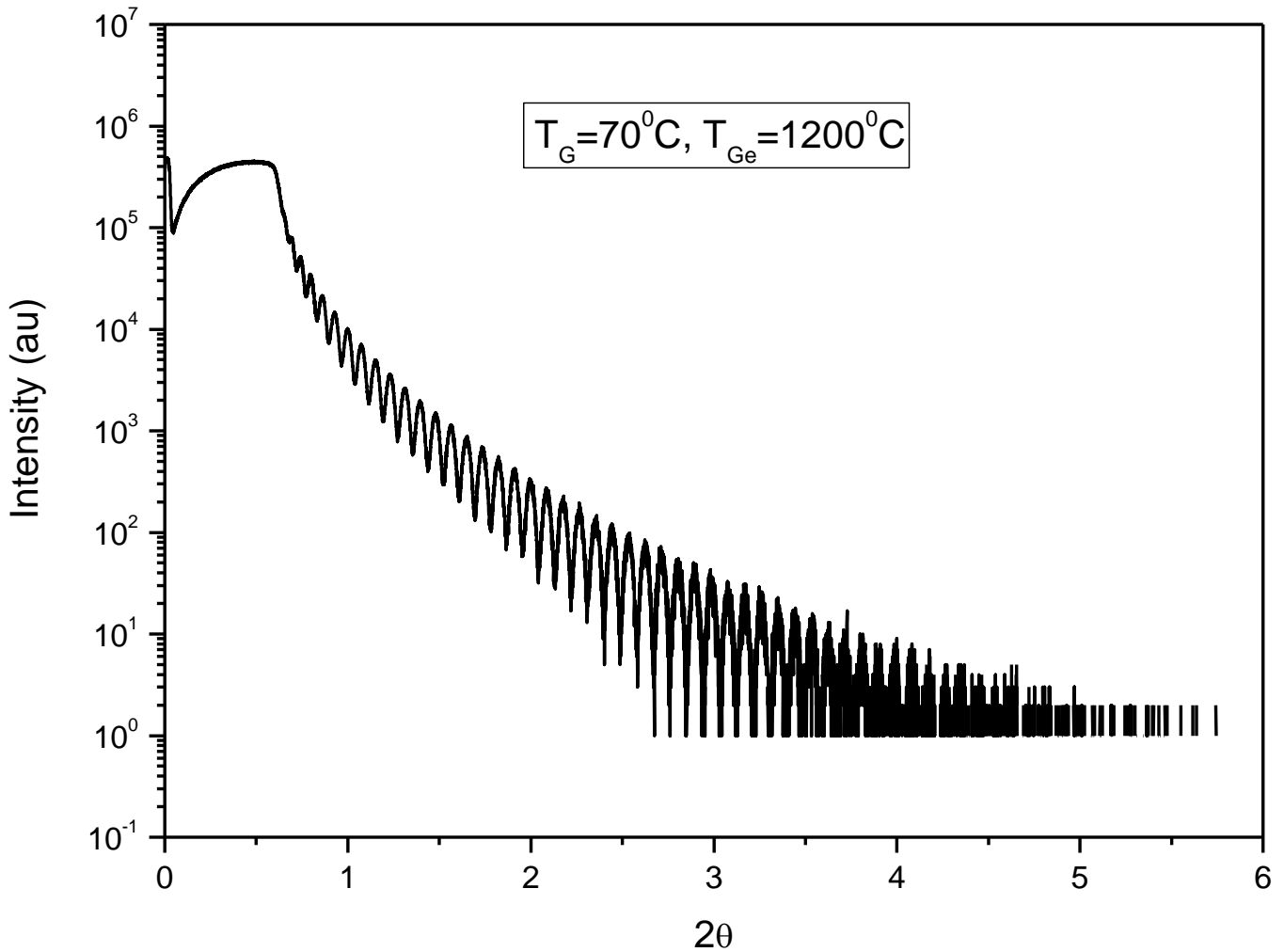


Figure 2 : X-ray reflectivity of a GeSn film (Problem 3). Data provided by S. Mahapatra & Krista R. The data is given in the file SmallAngleXRR.txt.

4. A film of GeSn alloy has been grown on Ge which is on a Silicon substrate. The figure shows the diffraction obtained from the sample. You are given the (004) and the (224) reflection data. The lattice constant of the GeSn alloy is slightly different from Ge. It is also a little different in the in-plane (a_{\parallel}) and the perpendicular direction (a_{\perp}) due to the effect of the substrate.
 - a. Calculate this difference from the data, the lattice of Si, Ge and GeSn are all FCC.
(To compute the lattice constants correctly to 3 decimal places, you would need to read off the data from the given origin file.)
 - b. Assume that the unit cell of GeSn distorts in such a way that the volume of the cell (when compared to the bulk value) remains same. If that is the case what is the value of the bulk lattice constant of GeSn? The bulk values are denoted by the superscript b.
 - c. Calculate a number for the degree of relaxation of the alloy film on the substrate, where relaxation is defined as

$$R = \frac{a_{GeSn}^{\parallel} - a_{Ge}^{\parallel}}{a_{GeSn}^b - a_{Ge}^b}$$

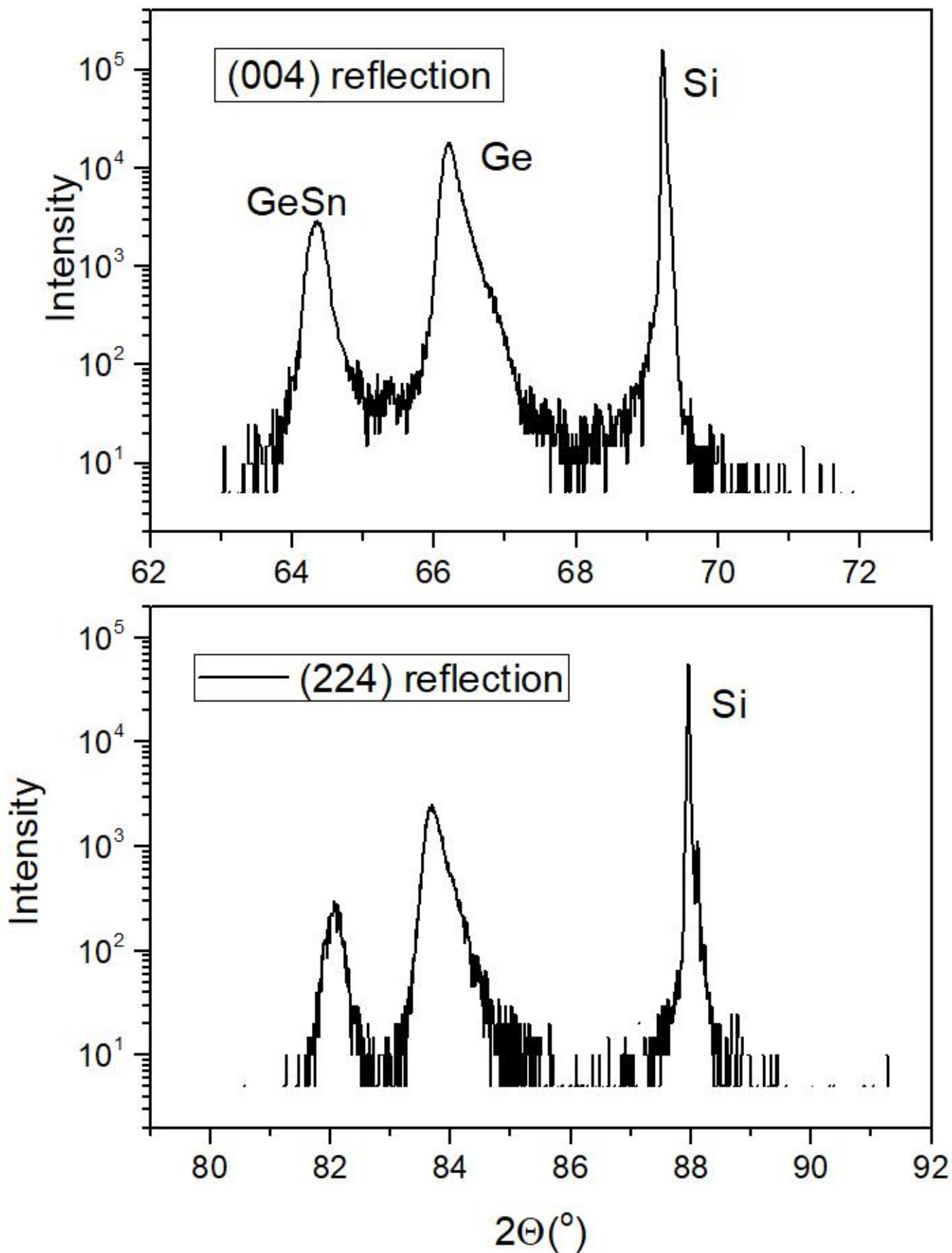
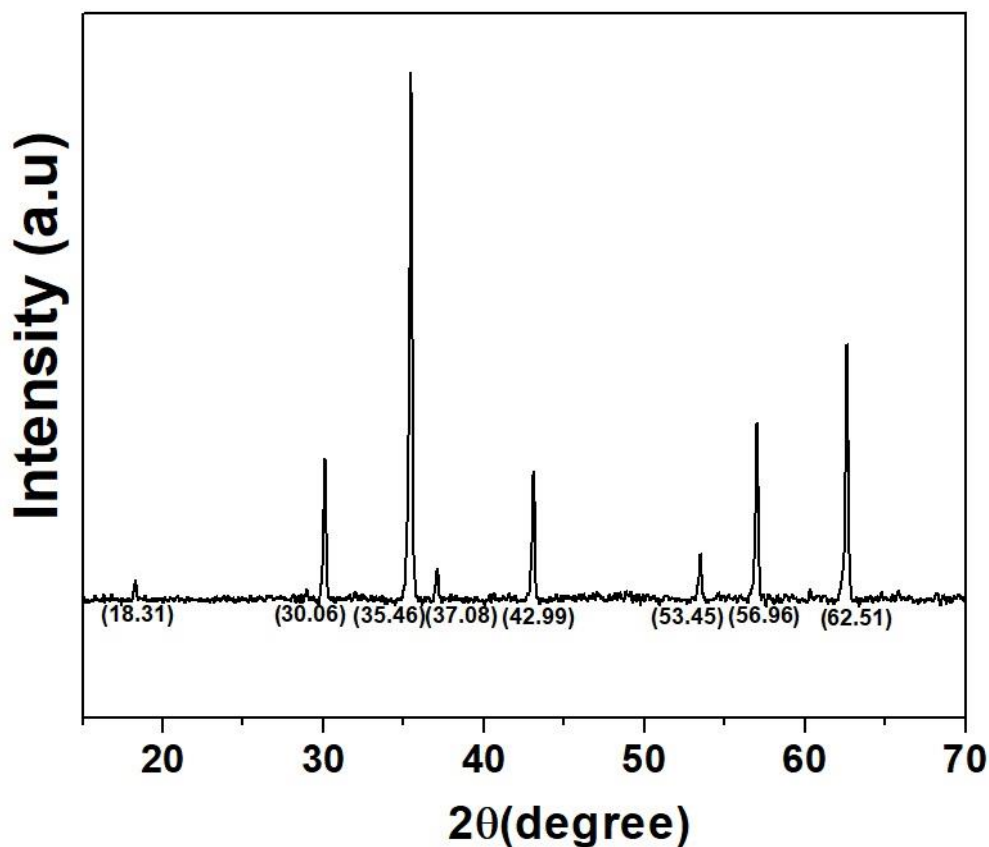
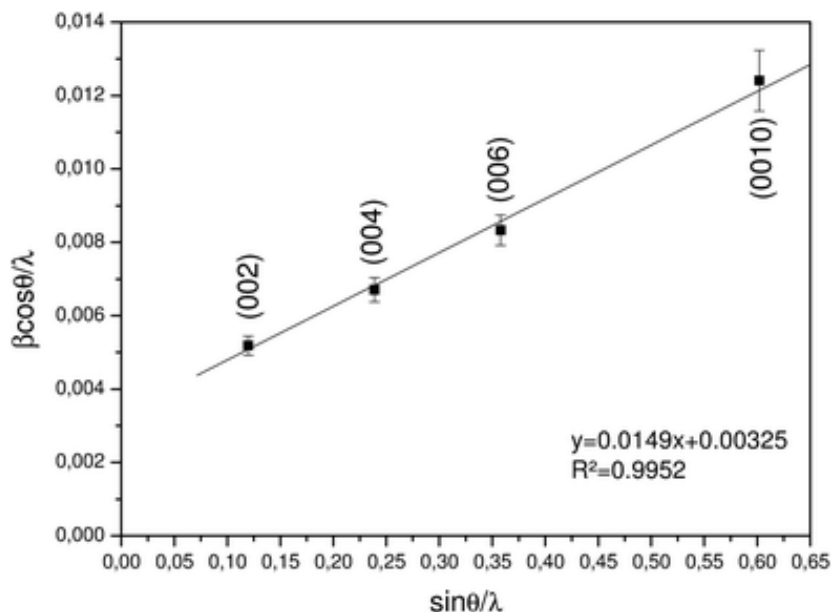


Figure 3 : (004) and (224) reflection of GeSn film (Data provided by S Mahapatra & Krista R.) The data are given in the files HRXRD_004_reflection.txt and HRXRD_224_reflection.txt.

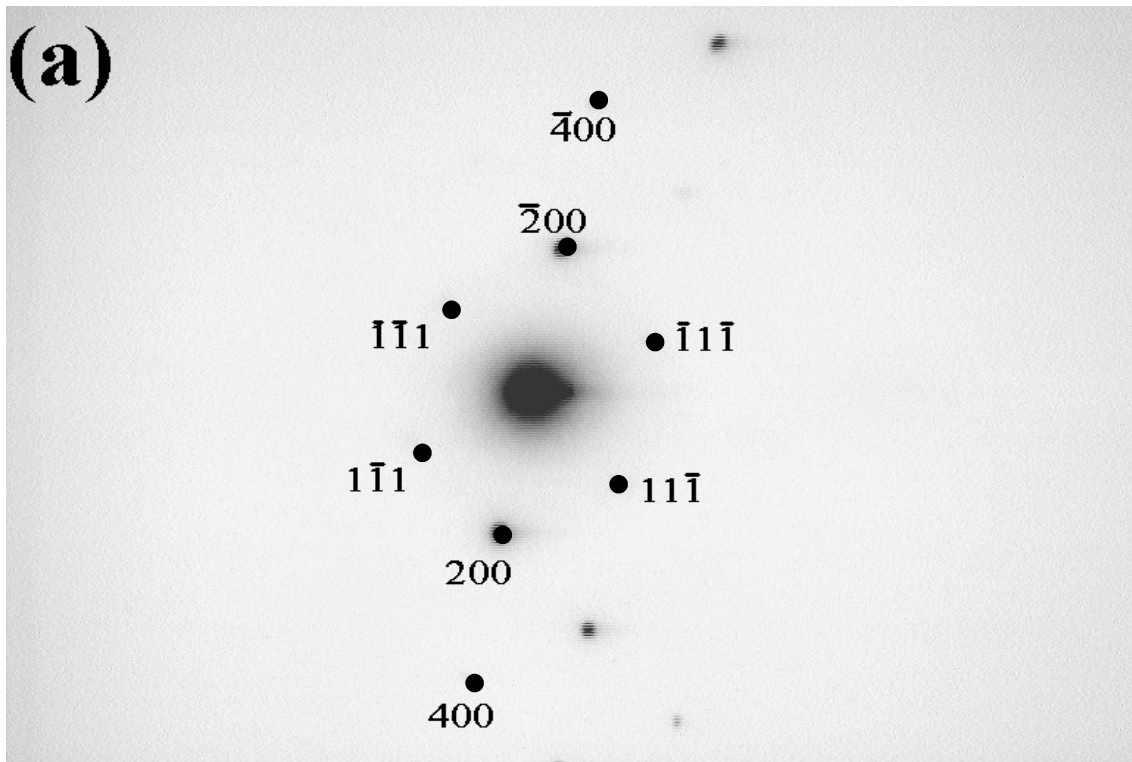
5. The figure below shows the XRD of a cubic powdered solid. The wavelength of X-ray used was $\lambda = 1.54 \text{ \AA}$. The 2θ values for all the peaks are given below each peak. The highest intensity peak is (311). Index all the peaks shown in this figure and find the lattice constant. Show all the calculations clearly. Guess the Bravais lattice type for this structure?



6. A certain material was analysed by X ray diffraction after growth and the quantity $\beta \frac{\cos \theta}{\lambda}$ was plotted against $\frac{\sin \theta}{\lambda}$ for a family of peaks. Here β is the FWHM. From the given plot estimate the grain size of the material. λ (\AA) is the wavelength of the X-ray used.

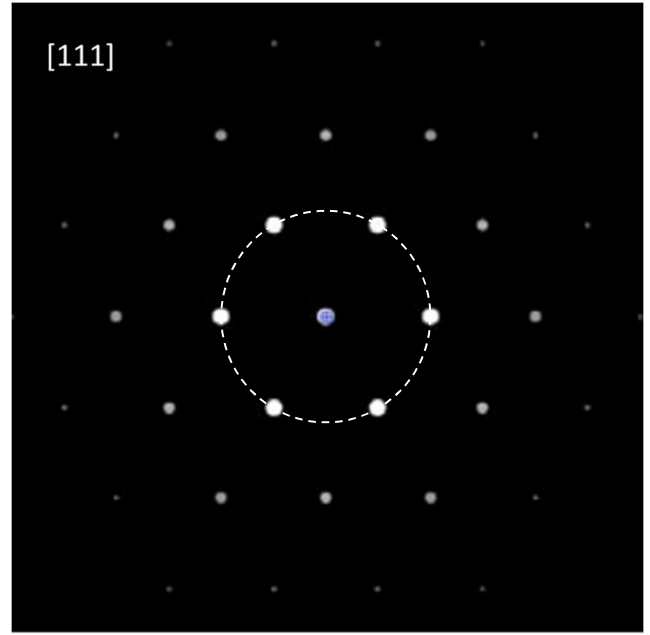
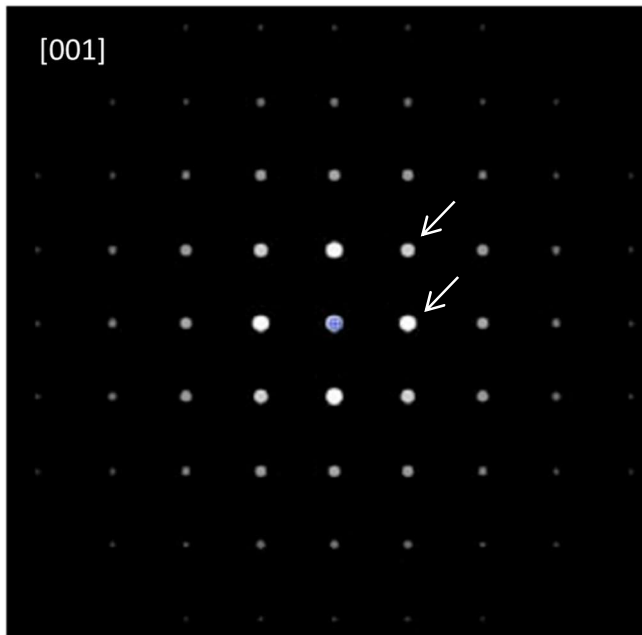


1. The figure gives the single crystal diffraction pattern of a material inside a carbon nanotube.
 - a) Given $d_{200} = 1.7723 \text{ \AA}$, find the d_{hkl} values corresponding to all the indexed spots. Compare with some standard data and identify the material. Also find the lattice constant.
 - b) Find the angle between $(\bar{2}00)$ and $(1\bar{1}1)$ and other similar pairs of planes and compare the values with the standard results.
 - c) Which is the plane to which electron beam is normally incident in this experiment?

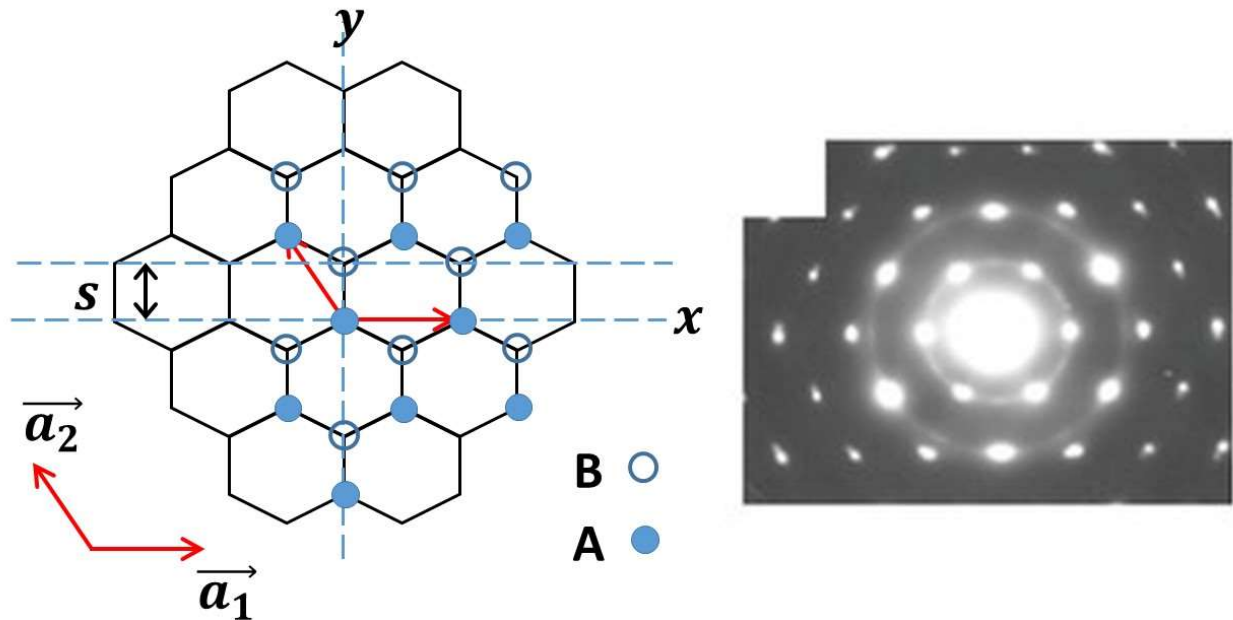


2. Calculate the radius of the first HOLZ ring for a material with planer spacing (parallel to the beam) of 0.6 nm when viewed in an instrument with camera constant $L\lambda = 3.0 \times 10^{-12} \text{ m}^2$.

3. Consider the electron diffraction patterns obtained from a sample of Aluminium (FCC). In the two figures the direction of incidence of the beam is given. The central spot is at the center of the pattern in each case.
- Write down the index of the two spots marked with arrows, for the [001] case, explaining the logic.
 - Identify the family of plane giving rise to the six spots, marked with a circle, for the [111] case.
 - Which spots in the [001] case, are from the First order Laue zone (FOLZ). You may use the grid points as (x, y) co-ordinates to designate the spots.
 - Why do you see more number of spots in the [001] case?



4. The given schematic (left) is that of a single layer of Graphite (Graphene). The two unit vectors of the direct lattice are denoted by the two arrows. The nearest neighbour distance is s and the sides of the hexagons are all equal. Also remember that the A and B sites are not equivalent. An electron beam (wavelength λ) is incident normally on this material. The figure on the right is the transmission electron diffraction pattern obtained. Study the figure carefully and answer the following:



- In terms of s , write down the components of the two unit vectors \vec{a}_1 and \vec{a}_2 , using the xy axes marked in the figure. Calculate the two reciprocal lattice vectors.
- What should be the two hkl families (3 index system) giving the set (ring) of spots nearest to the central spot? Answer with reason, not guesses!
- Index the six nearest spots in correct relative order. Then write the *same* indices in the four index ($hkil$) system.
- If the camera constant ($L\lambda$, where L is the distance from the sample to the screen) of the electron diffraction set up is $3 \times 10^{-12} \text{ m}^2$ what will be the radial distance of the nearest set of spots, if $s = 0.142 \text{ nm}$?

Appendix E: Parameter Tables of Crystals

This appendix lists in Tables E.1–E.3 the most common lattice types and corresponding lattice parameters of elemental crystals.

Table E.1 Lattices of elemental single crystals.

Element	Lattice	Element	Lattice	Element	Lattice	Element	Lattice	
1	H	hex	26	Fe	bcc	51	Sb	rhl
2	He	hex	27	Co	hex	52	Te	hex
3	Li	bcc	28	Ni	fcc	53	I	ort
4	Be	hex	29	Cu	fcc	54	Xe	fcc
5	B	tet	30	Zn	hex	55	Cs	bcc
6	C	dia	31	Ga	ort	56	Ba	bcc
7	N	hex	32	Ge	dia	57	La	hex
8	O	mcl	33	As	rhl	58	Ce	fcc
9	F	mcl	34	Se	hex	59	Pr	hex
10	Ne	fcc	35	Br	ort	60	Nd	hex
11	Na	bcc	36	Kr	fcc	61	Pm	—
12	Mg	hex	37	Rb	bcc	62	Sm	rhl
13	Al	fcc	38	Sr	fcc	63	Eu	bcc
14	Si	dia	39	Y	hex	64	Gd	hex
15	P	tcl	40	Zr	hex	65	Tb	hex
16	S	ort	41	Nb	bcc	66	Dy	hex
17	Cl	ort	42	Mo	bcc	67	Ho	hex
18	Ar	fcc	43	Tc	hex	68	Er	hex
19	K	bcc	44	Ru	hex	69	Tm	hex
20	Ca	fcc	45	Rh	fcc	70	Yb	fcc
21	Sc	hex	46	Pd	fcc	71	Lu	hex
22	Ti	hex	47	Ag	fcc	72	Hf	hex
23	V	bcc	48	Cd	hex	73	Ta	bcc
24	Cr	bcc	49	In	tet	74	W	bcc
25	Mn	cub	50	Sn	tet	75	Re	hex
						76	Os	hex
						77	Ir	fcc
						78	Pt	fcc
						79	Au	fcc
						80	Hg	rhl
						81	Tl	hex
						82	Pb	fcc
						83	Bi	rhl
						84	Po	cub
						85	At	—
						86	Rn	(fcc)
						87	Fr	(bcc)
						88	Ra	—
						89	Ac	fcc
						90	Th	fcc
						91	Pa	tet
						92	U	ort
						93	Np	ort
						94	Pu	mcl
						95	Am	—
						96	Cm	—
						97	Bk	—
						98	Cf	—
						99	Es	—
						100	Fm	—

Crystal types are abbreviated as: bcc, body-centered cubic; cub, cubic; dia, diamond; fcc, face-centered cubic; hex, hexagonal; mcl, monoclinic; ort, orthorhombic; rhl, rhombohedral; tcl, triclinic; tet, tetragonal.

Table E.2 Lattice constants of face- and body-centered cubic single crystals.

Element			Element		
<i>a</i> [Å]			<i>a</i> [Å]		
(a) Face centered cubic (fcc)^{a)}					
10	Ne	4.43	54	Xe	6.20
13	Al	4.05	58	Ce	5.16
18	Ar	5.26	70	Yb	5.49
20	Ca	5.58	77	Ir	3.84
28	Ni	3.52	78	Pt	3.92
29	Cu	3.61	79	Au	4.08
36	Kr	5.72	82	Pb	4.95
38	Sr	6.08	86	Rn	—
45	Rh	3.80	89	Ac	5.31
46	Pd	3.89	90	Th	5.08
47	Ag	4.09			
(b) Body-centered cubic (bcc)^{b)}					
3	Li	3.49	42	Mo	3.15
11	Na	4.23	55	Cs	6.05
19	K	5.23	56	Ba	5.02
23	V	3.02	63	Eu	4.61
24	Cr	2.88	73	Ta	3.31
26	Fe	2.87	74	W	3.16
37	Rb	5.59	87	Fr	—
41	Nb	3.30			

a) $\underline{R}_1^{\text{fcc}} = a/2 (0, 1, 1)$, $\underline{R}_2^{\text{fcc}} = a/2 (1, 0, 1)$, $\underline{R}_3^{\text{fcc}} = a/2 (1, 1, 0)$

b) $\underline{R}_1^{\text{bcc}} = a/2 (-1, 1, 1)$, $\underline{R}_2^{\text{bcc}} = a/2 (1, -1, 1)$, $\underline{R}_3^{\text{bcc}} = a/2 (1, 1, -1)$

Table E.3 Lattice constants of hexagonal single crystals.

Element				Element			
		<i>a</i> [Å]	<i>c/a</i>			<i>a</i> [Å]	<i>c/a</i>
1	H	3.75	1.731	52	Te	4.45	1.330
2	He	3.57	1.633	57	La	3.75	1.619
4	Be	2.29	1.567	59	Pr	3.67	1.614
7	N	4.039	1.651	60	Nd	3.66	1.614
12	Mg	3.21	1.624	64	Gd	3.64	1.588
21	Sc	3.31	1.594	65	Tb	3.60	1.581
22	Ti	2.95	1.588	66	Dy	3.59	1.573
27	Co	2.51	1.622	67	Ho	3.58	1.570
30	Zn	2.66	1.856	68	Er	3.56	1.570
34	Se	4.36	1.136	69	Tm	3.54	1.570
39	Y	3.65	1.571	71	Lu	3.51	1.585
40	Zr	3.23	1.593	72	Hf	3.20	1.582
43	Tc	2.74(?)	1.604(?)	75	Re	2.76	1.615
44	Ru	2.70	1.584	76	Os	2.74	1.579
48	Cd	2.98	1.886	81	Tl	3.46	1.599

The lattice definition is given in Cartesian coordinates below. Lattice constant ratios *c/a* may be compared with the ideal value $(c/a)^{\text{hcp}} = \sqrt{8/3} = 1.63299$ for a hexagonal close-packed (hcp) crystal. Note that some of the crystals may contain several atoms in the primitive unit cell, while two atoms for hcp crystals.

$\underline{R}_1^{\text{hex}} = a (1, 0, 0)$, $\underline{R}_2^{\text{hex}} = a (-1/2, \sqrt{3}/2, 0)$, $\underline{R}_3^{\text{hex}} = a (0, 0, c/a)$,

$\underline{r}_1^{\text{hcp}} = a (0, 0, 0)$, $\underline{r}_2^{\text{hcp}} = a (1/2, 1/\sqrt{12}, c/(2a))$

Problem Sheet 3 (Photoemission etc..) Analytical Techniques (July 2021)

1. The given figure (Fig 1) shows the XPS spectrum of a material obtained by using Al K_α radiation in a vacuum of 10⁻⁹ mbar.
 - a) Identify all the elements present and all the peaks. You can use the datafile (PeakIntelStd-2012.pdf) provided. You can also use some online database : <https://srdata.nist.gov/xps/EnergyTypeValSrch.aspx> . But make sure you understand what you are doing! You can ignore the small Carbon (1s) peak at 285 eV.
 - b) Which set of peaks may be significantly chemically shifted?
 - c) Try to calculate the relative concentrations of the significant atoms. Remember the area under the peak is not a direct measure of the concentration, since not all electron states will have identical cross sections for the process. The atomic percentage of the elements concerned can be determined by dividing the peak area by the sensitivity factor and expressing it as a fraction of the summation of all normalized intensities:

$$\text{atomic \% of [A]} = \frac{\left(\frac{I_A}{F_A}\right)}{\sum \frac{I}{F}} \times 100$$

Where I and F are integrated intensity (peak area) and sensitivity factor of the element of interest from the tabulated values in the file.

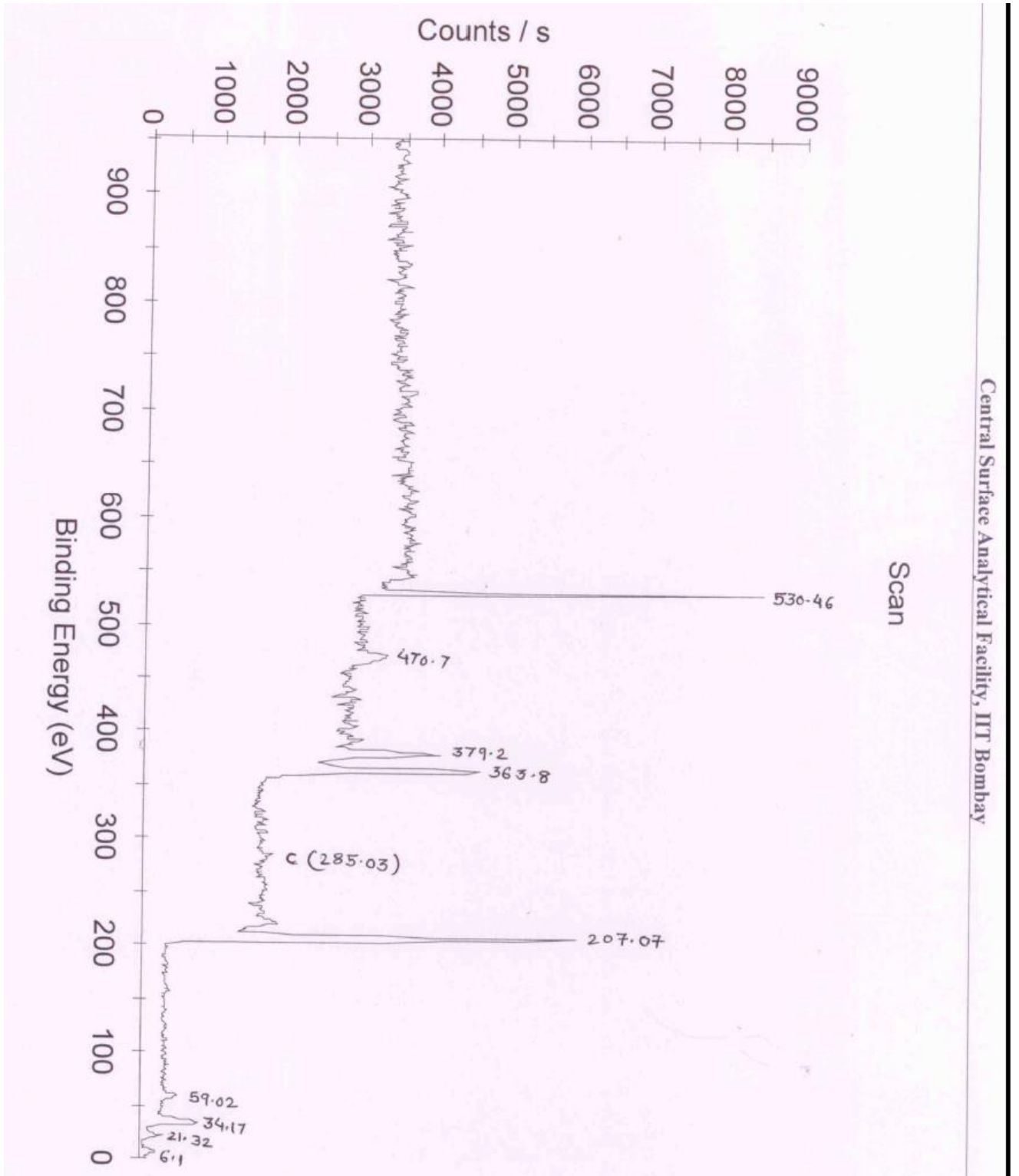


Figure 1 Spectrum obtained with Al K-alpha line.

2. The next figures shows two Auger Electron Spectra (AES) and some relevant data.
- a) Spectrum 1 (Figure 2) belongs to stainless steel (Containing Fe, Cr and Ni). Identify all the Auger lines belonging to these elements and tabulate them. In the Table give the observed energy, Standard values of energy and the peak to peak intensity. Calculate the atomic concentration of these elements. Use the two given files:
[AugerPrincipalEnergies.pdf](#)
[RelativeSensitivitiesOfAugerElectrons.pdf](#)
 - b) Spectrum 2 (Figure 3) belongs to Ga P. This spectrum also contains Auger lines of some standard impurities. Carry out the same analysis as in (a). In addition, identify the impurities and find their relative concentrations. Find the relative concentration of the main compound also.

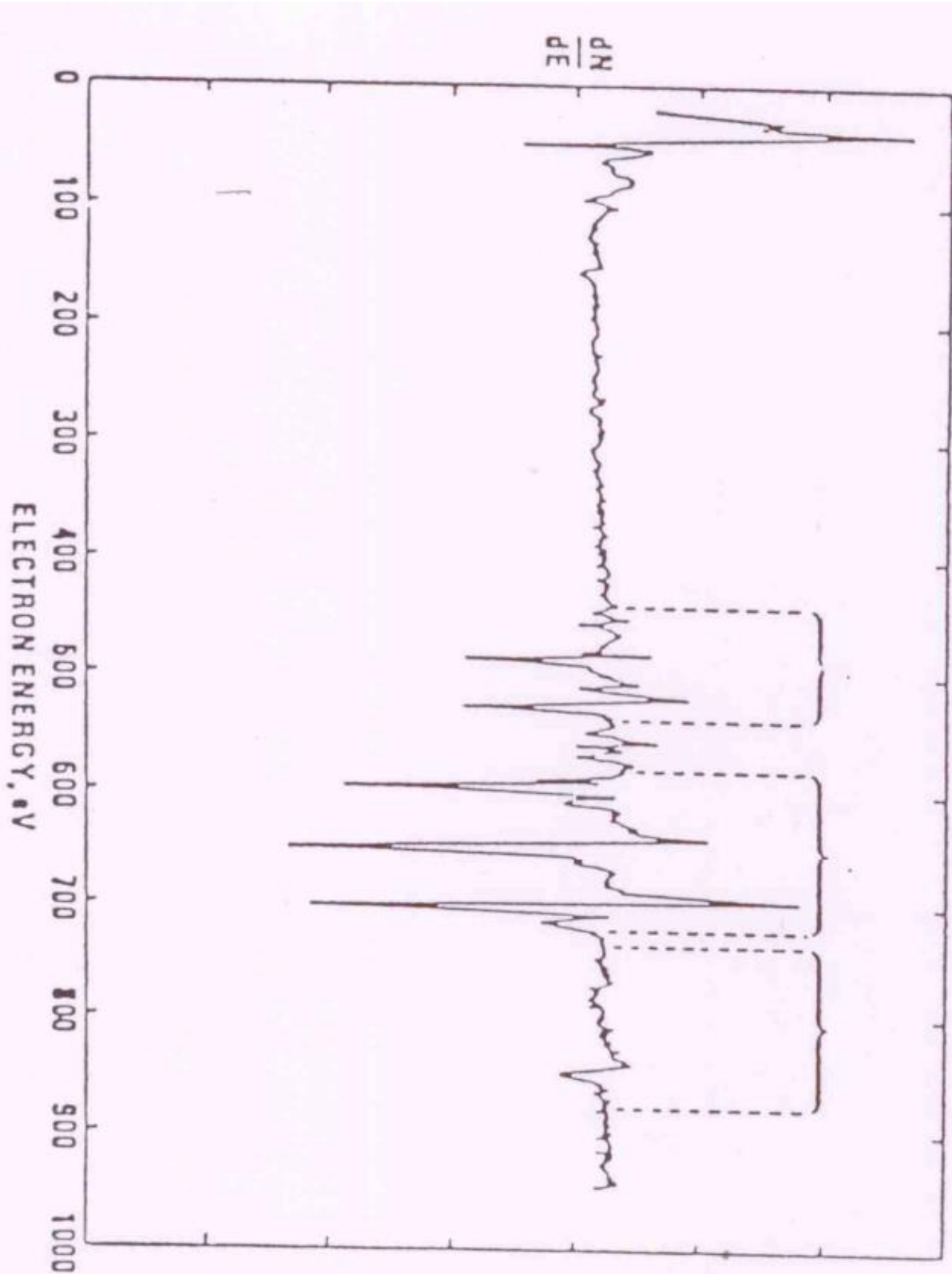


Figure 2: AES of 304 Stainless Steel

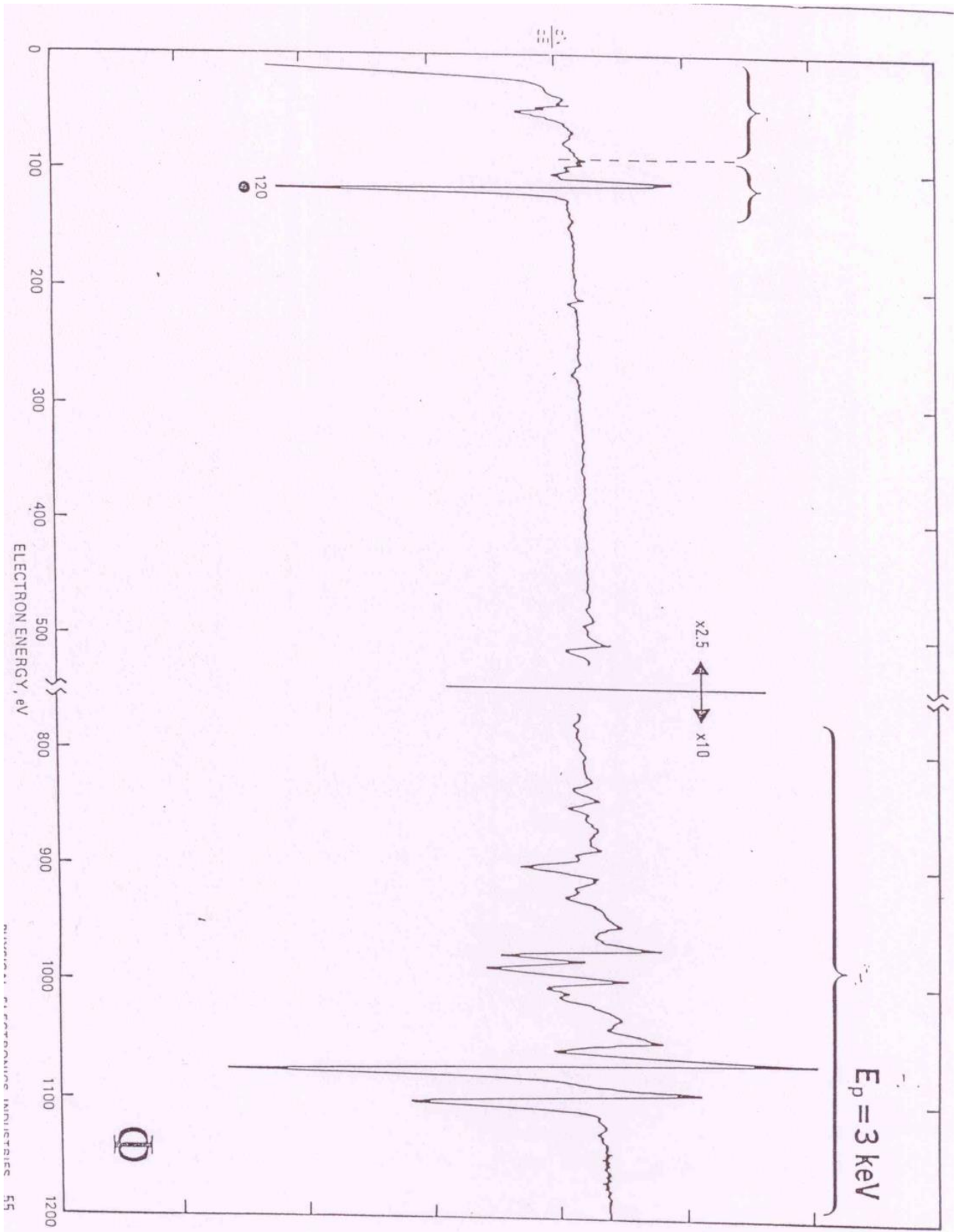
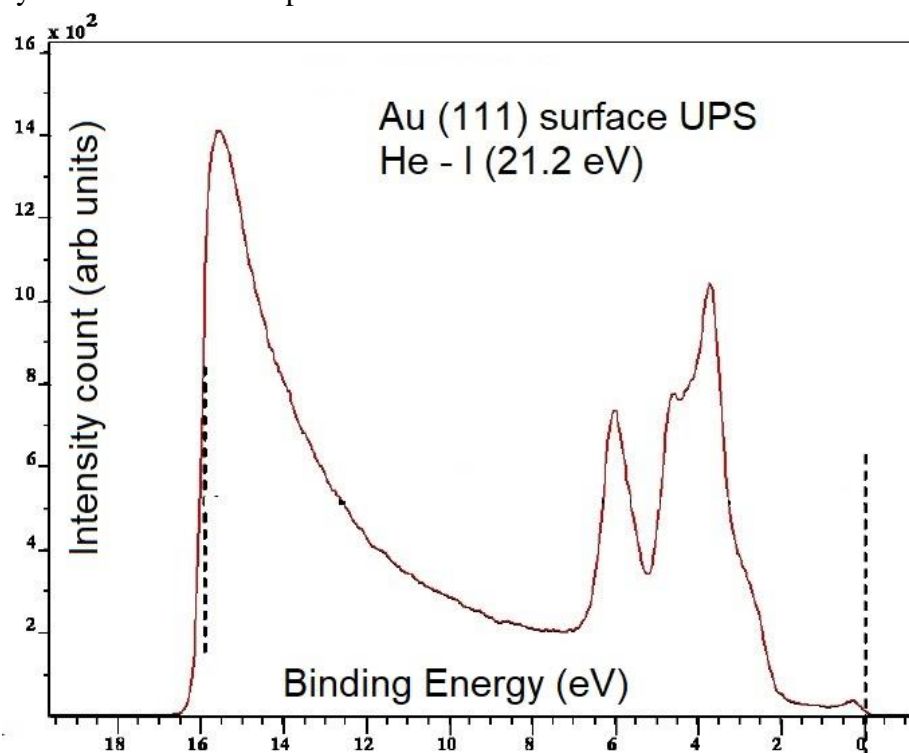
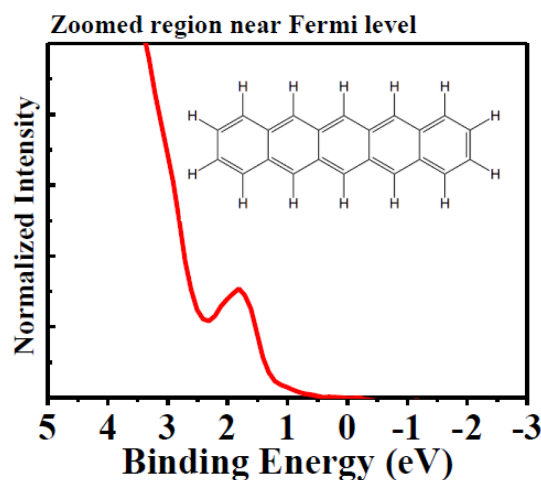
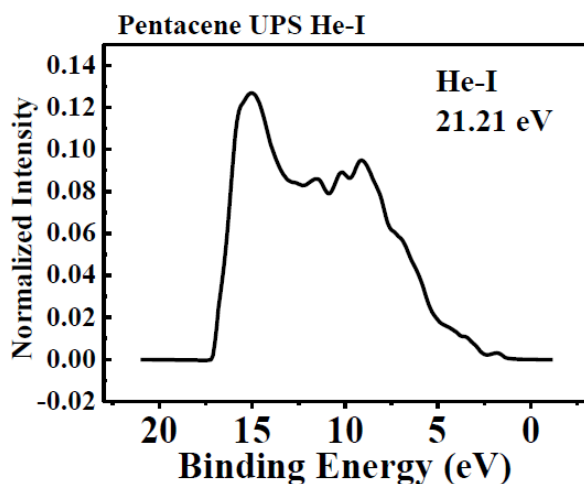


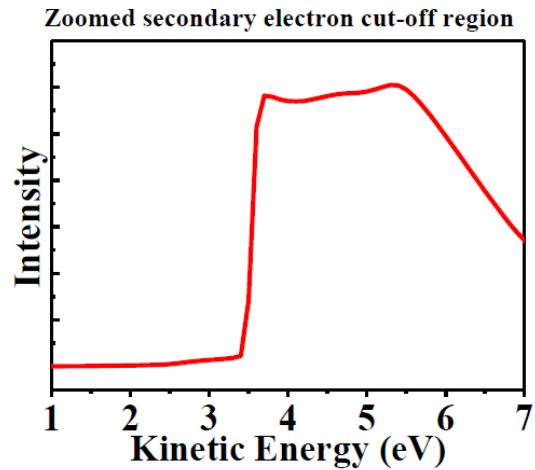
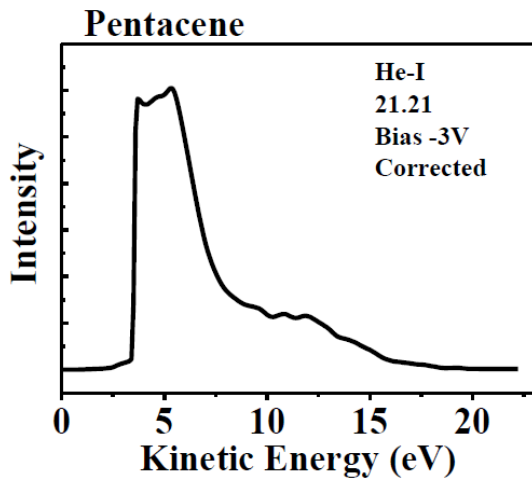
Figure 3 : Auger Spectra of Gallium Phosphide

3. The data shows the UPS spectrum obtained from a single crystal Au (111) surface using a He-I source (21.2 eV photon energy). Determine the work function of this crystal face of Au. Can you comment on the peak structure seen here?



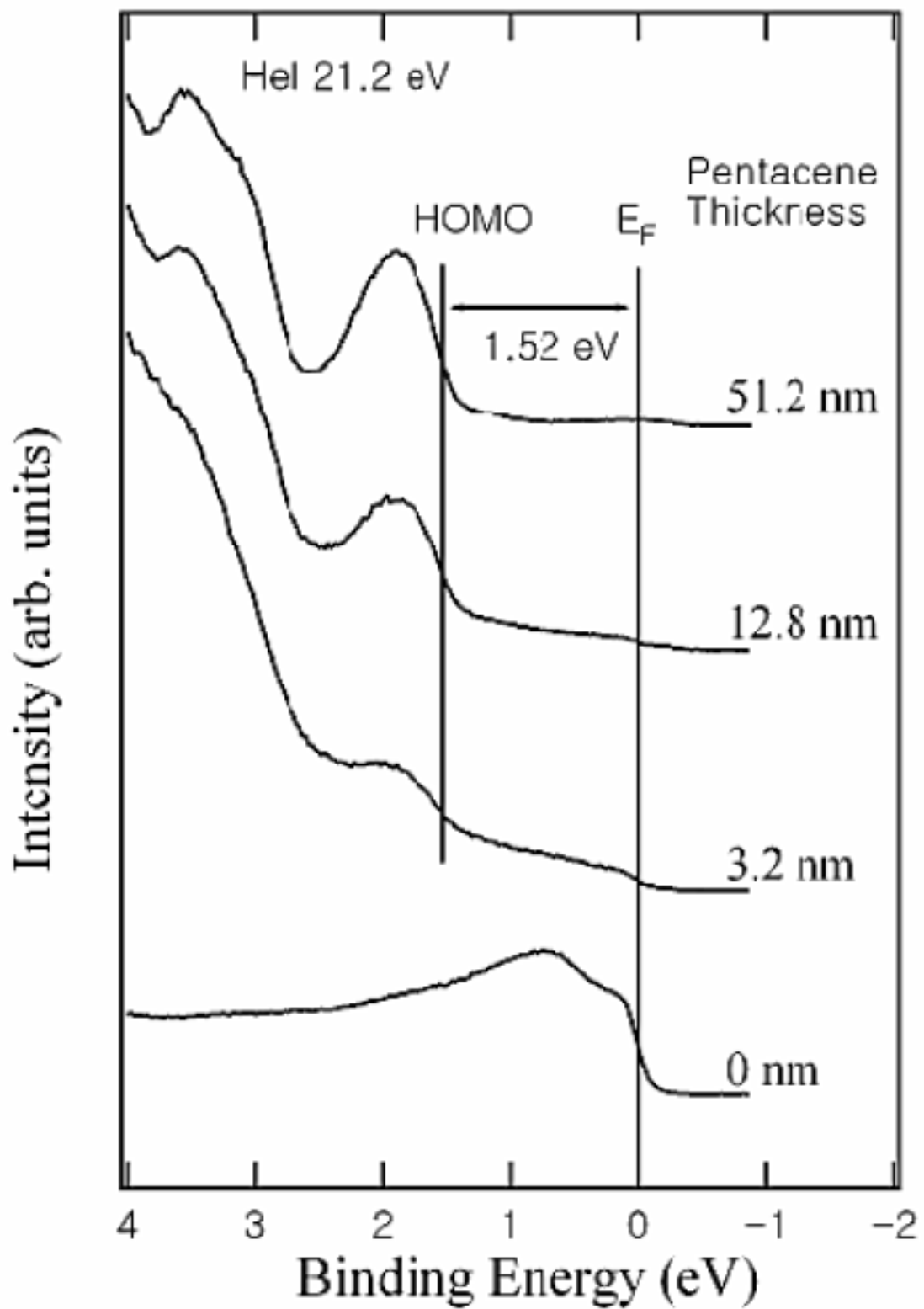
4. The next two figures give He-I UPS data for Pentacene. The second set has a -3V bias applied to the sample. Using the energy of the photon, match the consistency of the two data. The band gap of Penatacene is known to be 2.2 eV. Draw the schematic energy level diagram of Penatcene, showing clearly vacuum level, Fermi level, work function, valence band maximum, conduction band minimum, ionization potential and electron affinity.





5. A thin layer of a molecule on a metal surface is common in many devices today. As a layer of molecule (Pentacene) gets adsorbed on the surface some charge transfer between the metal and the molecular layer often takes place. This is almost similar to what happens in a metal semiconductor contact. As a result a small interface dipole develops. Consider a layer of Pentacene on a metal whose work function is measured to be 3.75 eV. The full spectrum width is not shown here.

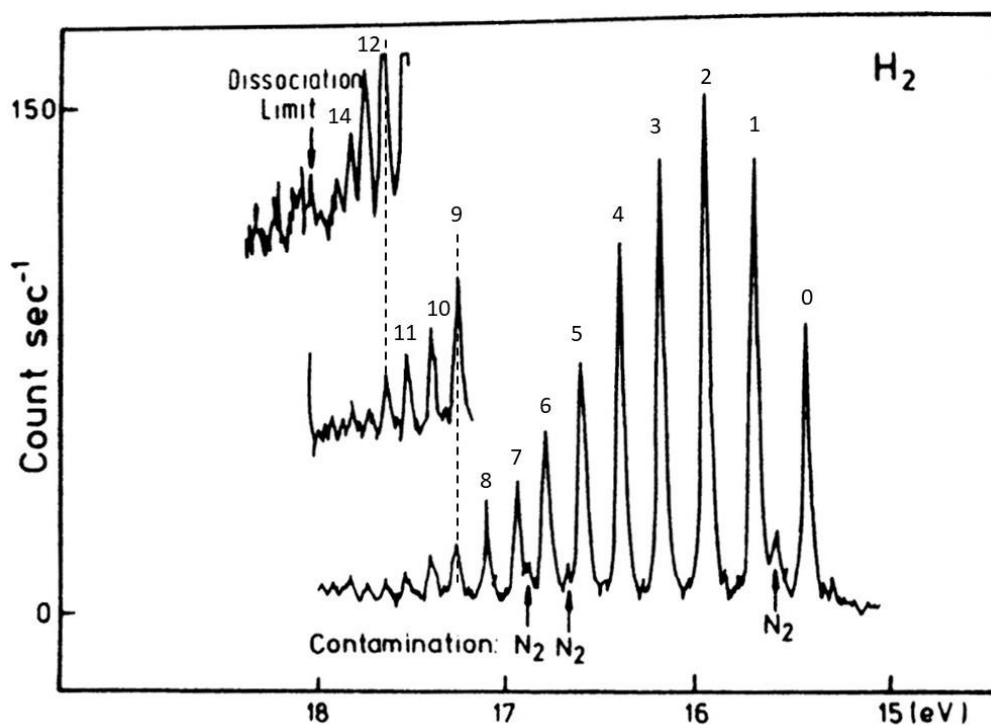
Successively higher amounts of pentacene was deposited and the UPS spectra recorded after each step. The ionisation potential of Pentacene is 4.9V. Using the data shown, construct the band alignment diagram of Pentacene on this metal. In particular, how large is the interfacial dipole?



6. The figure shows the Ultraviolet Photoelectron Spectrum (UPS) of molecular Hydrogen obtained by using UV radiation of 21.2 eV. The peaks are labelled and their positions are given in the table. There are no peaks between 0 eV and the part of the spectrum shown.

From this data answer/analyse the following:

- Which peak corresponds to the ionisation energy of the molecule ($H_2 \rightarrow H_2^+$) ?
- What is the origin of the closely spaced set of peaks?
- Estimate the approximate force constant of the “spring” holding the two H atoms together, using the region around the highest peak. Given that the mass of a proton is $m_p = 1.67 \times 10^{-27}$ kg.
- If you make a plot of the ΔE values (*not the peak energy values*) vs the index of the peaks, you will get a straight line (almost) . Does this imply that the potential is harmonic? If you extrapolate the straight line, it will hit $\Delta E = 0$ at some point. What would be the physical significance of that point?



index	Binding Energy (eV)	index	Binding Energy (eV)
0	15.45	9	17.27
1	15.72	10	17.42
2	15.98	11	17.55
3	16.21	12	17.65
4	16.42	13	17.75
5	16.63	14	17.84
6	16.81		
7	16.96		
8	17.12		

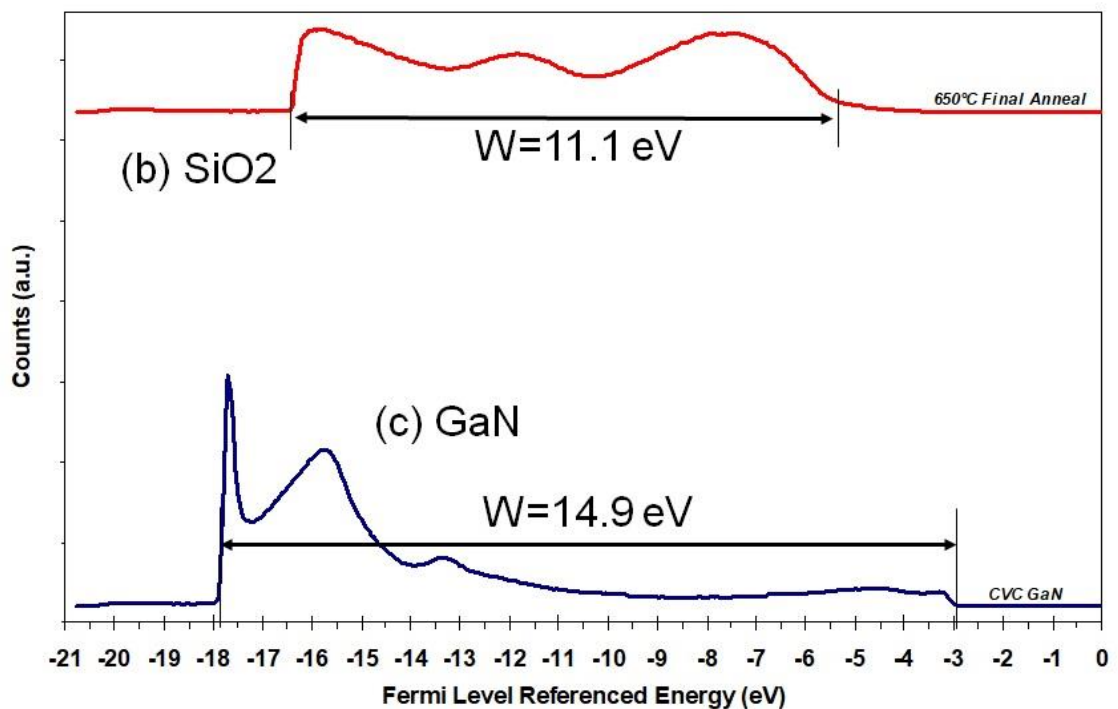
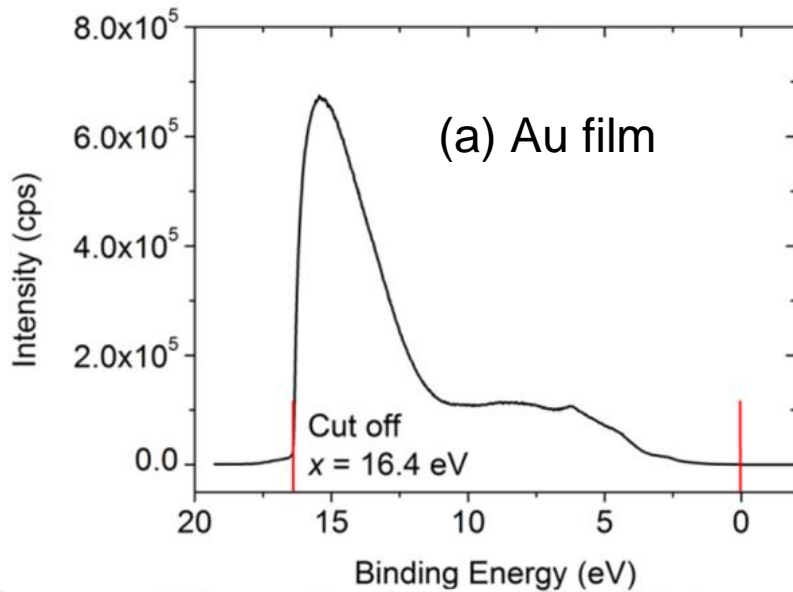
7. The figure gives UPS spectra for three materials, using UV photon of energy 21.2 eV
- Polycrystalline Au film
 - SiO₂ : an insulator with a bandgap of 9.0 eV
 - Undoped GaN : a semiconductor with a bandgap of 3.4 eV

Explain very briefly why the width of the spectrum is smallest for SiO₂?

What is the work function of the Au film?

If the GaN is now heavily n-doped, what would happen to the UPS spectra?

Where is the conduction band of SiO₂ relative to the vacuum level?

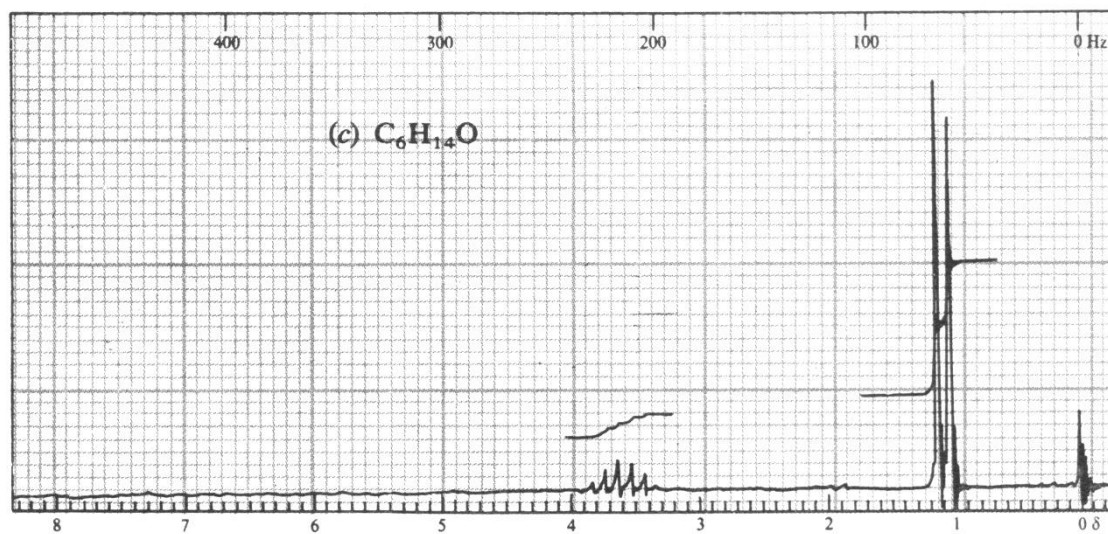
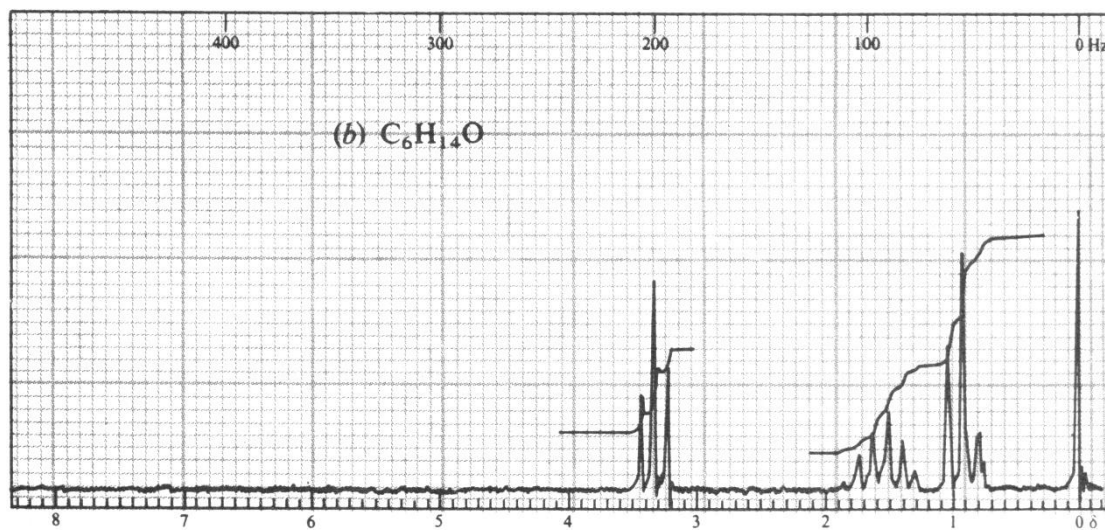
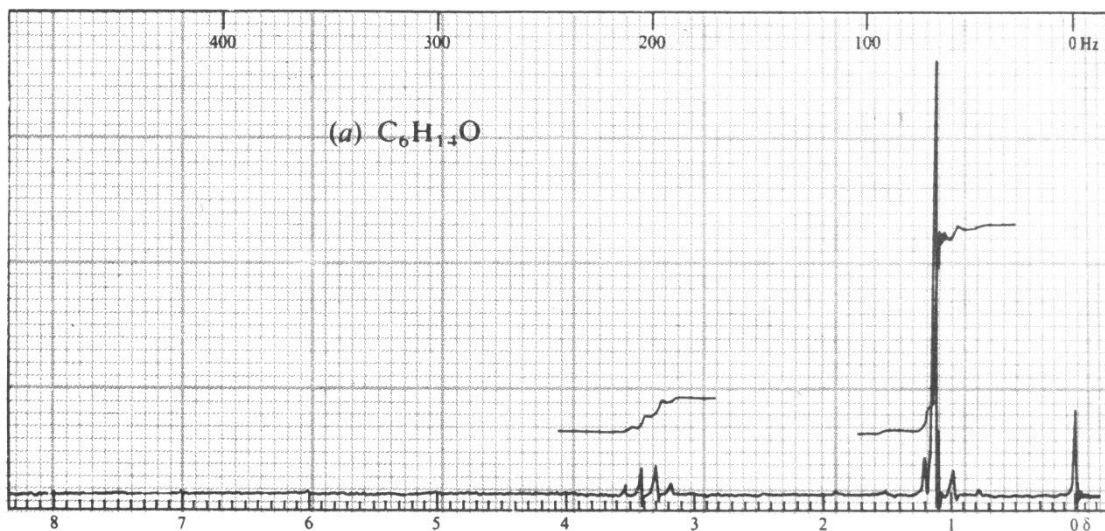


- Consider a solid sample set up for a Nuclear Magnetic Resonance experiment. A resonance is found to be approximately 1 kHz wide, which may be attributed to the dipole-dipole interaction between the nuclei. The main magnetic field (~few Tesla) is applied along the z-axis.
 - If the sample is now set spinning about the z-axis sufficiently fast (for the inter-particle vectors to be averaged) how would you expect the width of the resonance to change?
 - If the sample was set spinning, with the rotation axis pointing along x-axis, by approximately what factor would you expect the resonance line to shrink?
- Consider the three hydrogen-NMR spectra given in the figure (next page). All of them are from compounds with the empirical formula $C_6H_{14}O$. The peak at zero ppm is a marker and not part of the signal from the sample under study.
 - First try to answer: What is the maximum number of carbon-carbon double bonds possible in the structure?
 - In which of the three (a,b,c) can the oxygen have a double bond with carbon?
 - How many chemically different types of hydrogen atoms are there in (a), (b) & (c)?
 - Finally construct the structural formulas consistent with the spectra for (a),(b) & (c). The final drawing must be clear with no ambiguities.

Type of proton	Chemical shift δ , ppm
Cyclopropane	0.2
Primary	0.9
Secondary	1.3
Tertiary	1.5
Vinylic	4.6-5.9
Acetylenic	2-3
Aromatic	6-8.5
Benzylic	2.2-3
Allylic	1.7
Fluorides	4-4.5
Chlorides	3-4
Bromides	2.5-4
Iodides	2-4
Alcohols	3.4-4
Ethers	3.3-4
Esters	3.7-4.1
Esters	2-2.2
Acids	2-2.6
Carbonyl compounds	2-2.7
Aldehydic	9-10
Hydroxylic	1-5.5
Phenolic	4-12
Enolic	15-17
Carboxylic	10.5-12
Amino	1-5

A reference list of chemical shifts of commonly encountered groups is given here – but it is possible to solve the entire problem without this – do not get too occupied with this list!

But the problem *cannot* be solved by a “table lookup”, you need to think in terms of *equivalent hydrogens*, their *proximity* to each other and *signal splittings*.



PH517 : Analytical Techniques (July 2021): Quiz 1

20 marks (to be scaled later) : Time 1 hours (including uploading to Moodle etc) September 6, 2021

1. A certain element X and a binary compound YZ both crystallise in a structure that can be described by the cubic system.

- The location of the basis atoms of X (w.r.t the cubic axes) are

$$\begin{array}{cccc} (0, 0, 0) & (1/2, 1/2, 0) & (1/2, 0, 1/2) & (0, 1/2, 1/2) \\ (1/4, 1/4, 1/4) & (3/4, 3/4, 1/4) & (3/4, 1/4, 3/4) & (1/4, 3/4, 3/4) \end{array}$$

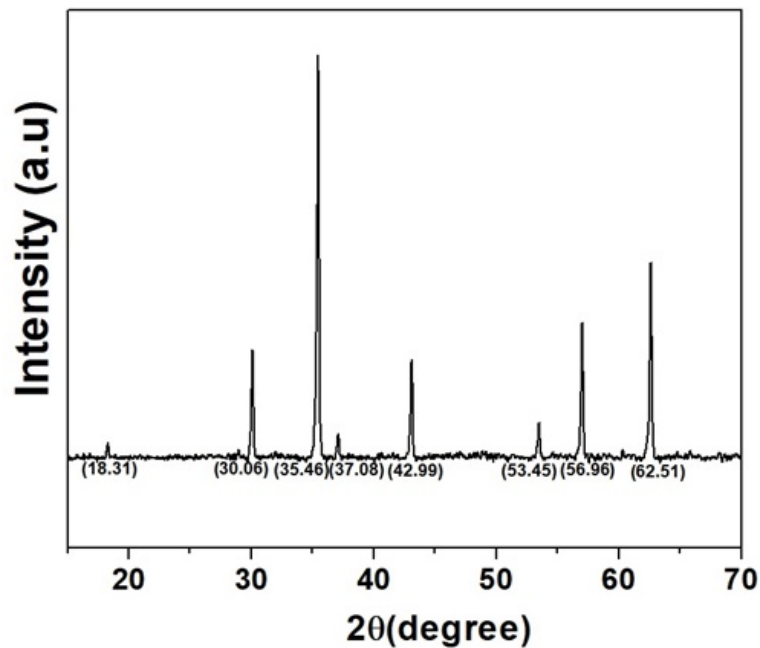
- The location of the basis atoms of YZ (w.r.t the cubic axes) are

$$\begin{array}{cccc} Y_{\text{atoms}} : & (0, 0, 0) & (1/2, 1/2, 0) & (1/2, 0, 1/2) & (0, 1/2, 1/2) \\ Z_{\text{atoms}} : & (1/4, 1/4, 1/4) & (3/4, 3/4, 1/4) & (3/4, 1/4, 3/4) & (1/4, 3/4, 3/4) \end{array}$$

A powder diffraction pattern for both X and YZ are available to you and the atomic/ionic form factors of Y and Z are sufficiently different.

- What would be the indices of the first *six* Bragg peaks for X and YZ ?
- If the lattice constant is 5\AA for both, and the wavelength of the x-ray used is 1.54\AA , at what angle (2θ) would the first reflection appear in each case?

2. From the powder XRD data given in the figure, obtained by using x-rays with $\lambda = 1.54\text{\AA}$

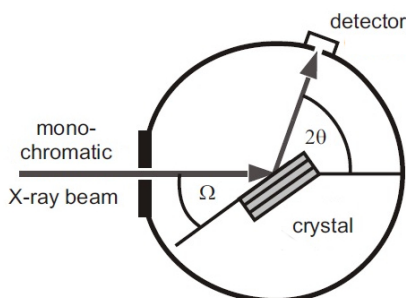


- index all the peaks.
- calculate the (cubic) lattice constant and the lattice type

PH517 : Analytical Techniques (July 2021): Mid semester

30 marks (to be scaled later) : Time 2:30 hours (including uploading to Moodle etc) September 12, 2021
 You should show your calculation with diagrams and upload the pdf copy of the page. Credit is for correct reasoning and calculation, no credit for random guesses even if correct!

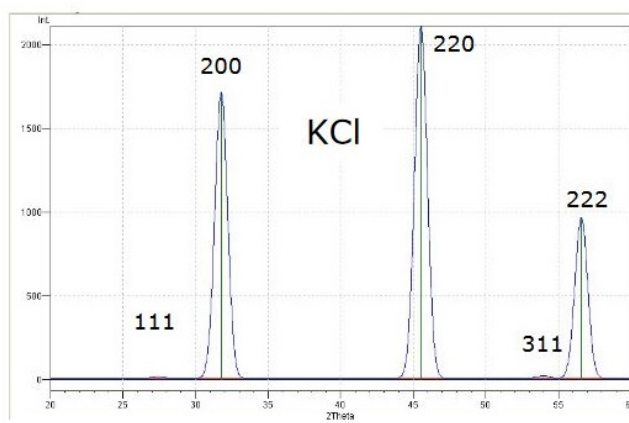
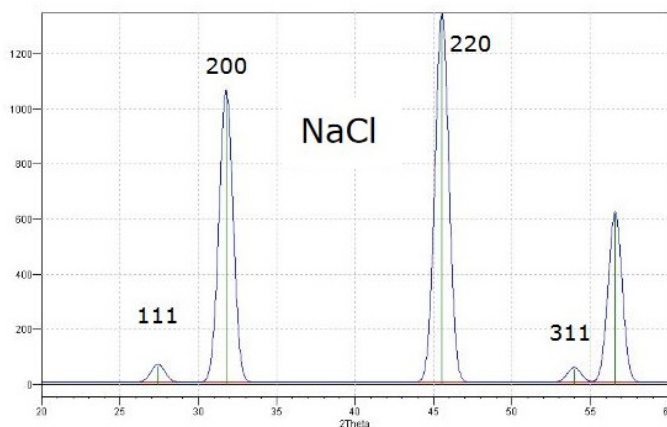
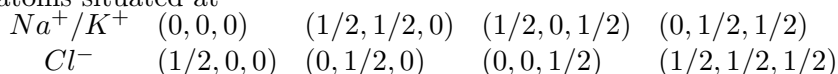
- The figure shows the standard definition of the angles Ω and 2θ , as used in X-ray diffraction. Remember that Ω is the angle the beam makes with the surface of the crystal and 2θ is the angle between the incident and diffracted beam. Suppose you have a crystal of silicon whose top face (on which the beam is incident) is parallel to the 001 face. Remember the beam cannot come from the bottom side of the crystal, neither can the detector go below the sample. Silicon has a cubic lattice constant of $a = 5.43\text{\AA}$ and you are using X-ray with $\lambda = 1.54\text{\AA}$.



- At what $(\Omega, 2\theta)$ value would you get the (004) reflection?
- At what $(\Omega, 2\theta)$ value would you get the (113) and (311) reflections ?

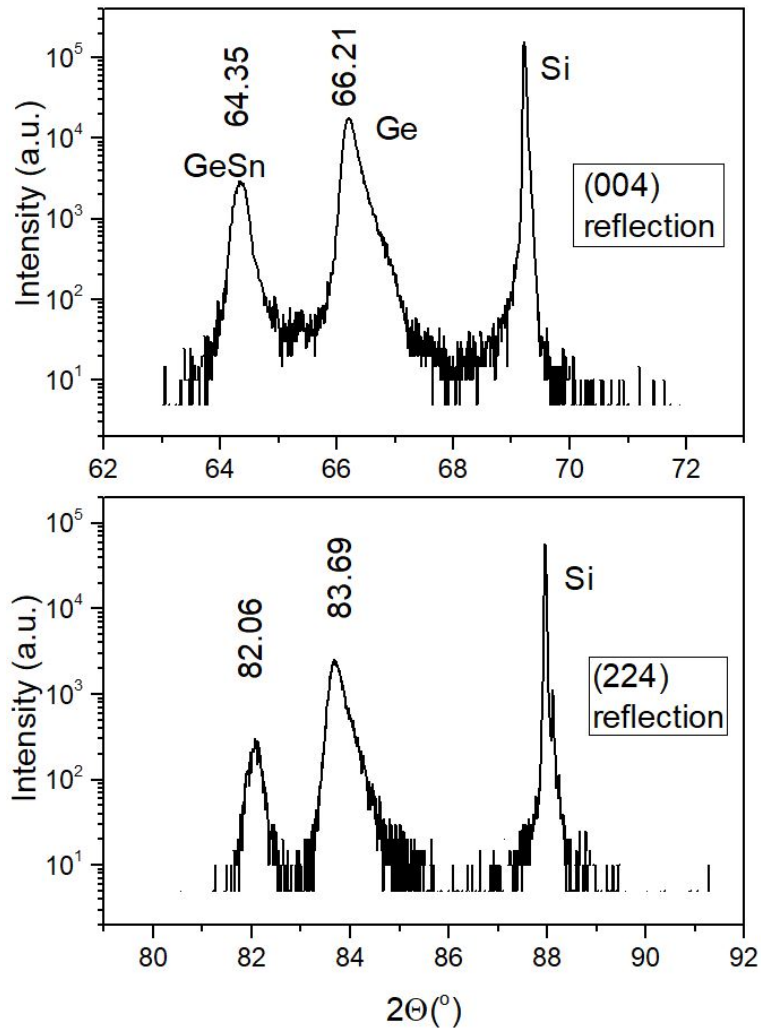
5+5=10 marks

- The unit cell of two common salts NaCl and KCl can be taken to be a simple cubic cell with the atoms situated at



The figure shows diffraction pattern from both. The atomic number of Na , Cl and K are 11, 17 and 19 respectively. Calculate explicitly the structure factor for the (111) reflection in the simplest possible form and explain why the (111) reflection is (almost) absent in KCl . 3+2=5 marks

3. A film of $GeSn$ alloy has been grown on Ge which is on a Silicon substrate. The figure shows the diffraction obtained from the sample. You are given the (004) and the (224) reflection data. The lattice constant of the $GeSn$ alloy is slightly different from Ge . It is also a little different in the in-plane (a_{\parallel}) and the perpendicular direction (a_{\perp}) due to the effect of these substrate. Calculate this difference from the data, the lattice of Si , Ge and $GeSn$ are all FCC. You need to compute the lattice constants correctly to 3 decimal places.



- (a) Assume that the unit cell of $GeSn$ distorts in such a way that the volume of the cell (when compared to the bulk value) remains same. If that is the case what is the value of the bulk lattice constant of $GeSn$? The bulk values are denoted by the superscript b .
- (b) Calculate a number for the degree of relaxation of the alloy film on the substrate, where

relaxation is defined as

$$R = \frac{a_{GeSn}^{\parallel} - a_{Ge}^{\parallel}}{a_{GeSn}^b - a_{Ge}^b}$$

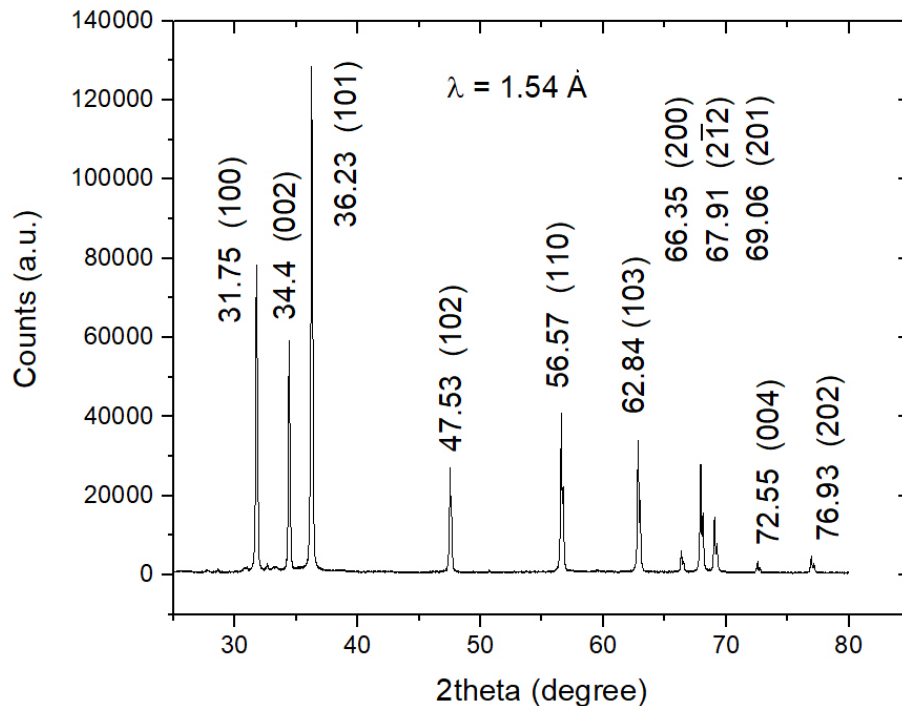
3+2=5 marks

4. Consider a simple cubic monoatomic material (X) with lattice constant $a = 5\text{\AA}$. A thin slice of X of thickness $t = 50\text{nm}$ is cut so that the faces of the cube are parallel to its surface. This is set up for transmission electron diffraction with an electron beam of wavelength $\lambda = 0.005\text{\AA}$. The beam is incident along the $[001]$ direction. Estimate the number of spots in the zero order Laue zone (ZOLZ) you may get, in the following way:

- (a) State your logic clearly with a diagram. (Hint: Every reciprocal lattice point has a finite extent.)
- (b) Derive an algebraic expression. Then calculate a numerical value

2+3=5 marks

5. The following powder XRD pattern is given to you with the peaks (position and index) labelled. Justify with reason (reasonably educated guesses are acceptable too :-) the lengths of the three axes of the unit cell and the angles between them. The x-ray wavelength used is $\lambda = 1.54\text{\AA}$



5 marks

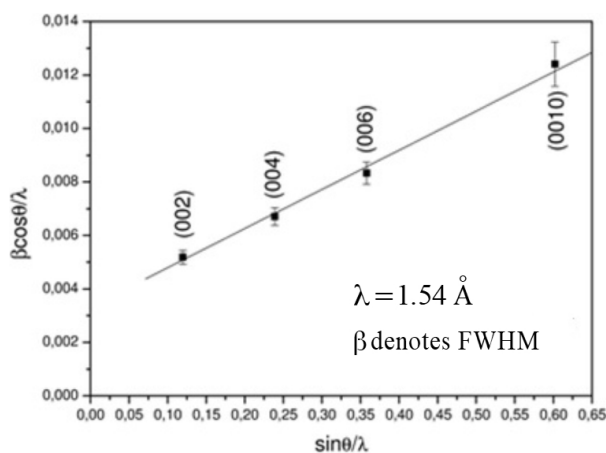
PH517 : Analytical Techniques (July 2021): End semester

50 marks (to be scaled later) : Time 3:30 hours (including uploading to Moodle etc) November 9, 2021

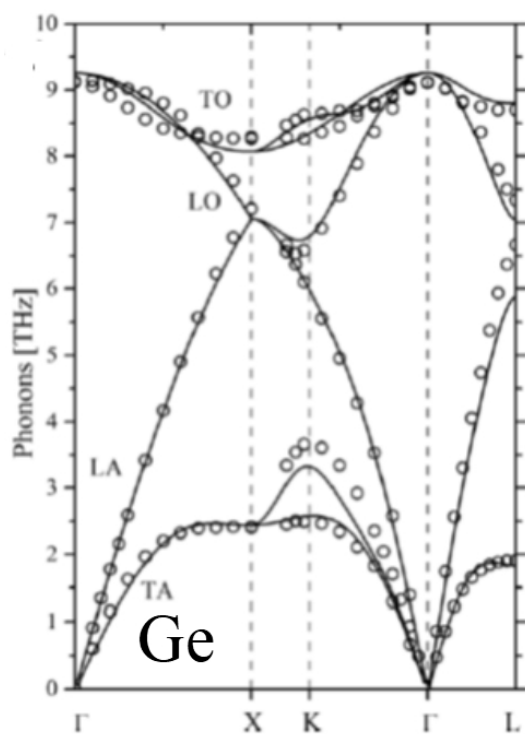
- Section A has 10 questions of **Numerical Answer Type, 2 marks each**. You will need to enter the calculated value in the box provided (in Moodle). In some cases the answer will have to be exact, in some cases the fraction of marks you get will depend on the extent of error upto a limit depending on the question. You do not need to upload your calculations, but you should keep them with you. If required I will ask for that later on.
- Section B has 3 questions of conventional **Pen and Paper Type, 10 marks each**. You will have to upload scanned copies of your work in Moodle. You should show your calculation with diagrams and upload the pdf copy of the page. Credit is for correct reasoning and calculation, no credit for random guesses even if correct!

Section A

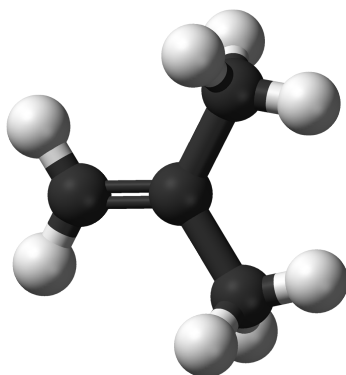
1. A certain material was analysed by X ray ($\lambda = 1.54\text{\AA}$) diffraction after growth and the quantity $\beta \cos \theta / \lambda$ was plotted against $\sin \theta / \lambda$ for a family of peaks. Here β is the FWHM. From the given plot estimate the grain size of the material.



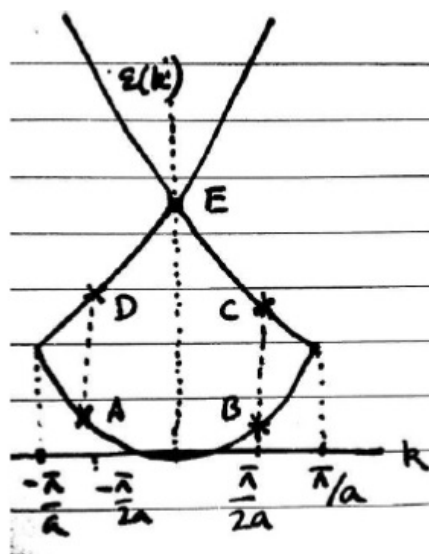
2. The phonon spectra of *Ge* is shown in the figure. From the figure calculate the wavenumber (in cm^{-1}) expected Raman line from a solid sample of *Ge*



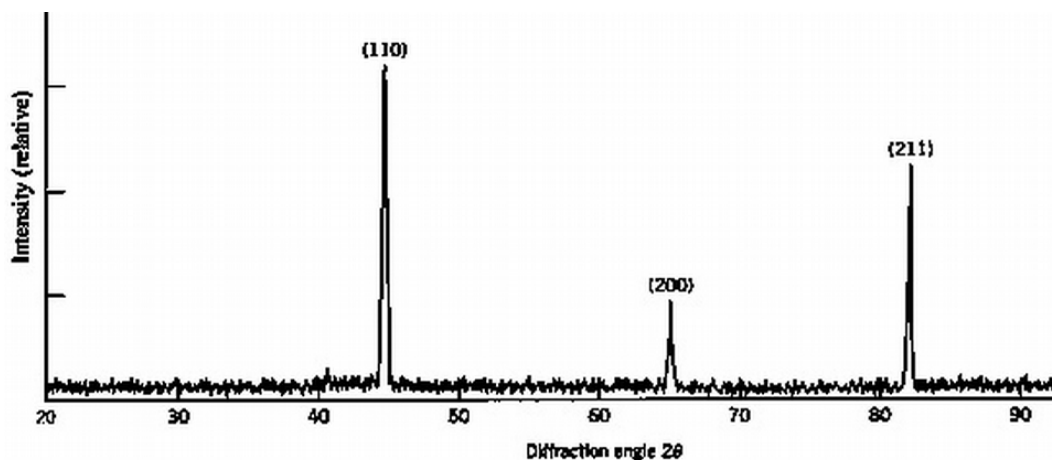
3. How many Hydrogen NMR (Nuclear Magnetic Resonance) peaks would you expect from the following compound? The white balls represent Hydrogen and the black balls represent Carbon.



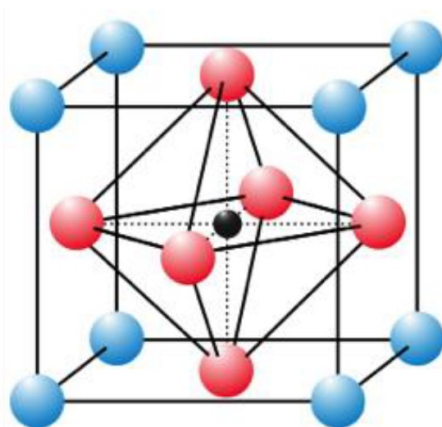
4. The figure shows the energy dispersion $E(k)$ of an electron in a one-dimensional lattice. What is the *physical momentum* of an electron at the point marked C. Express your answer in units of $\hbar\pi/a$.



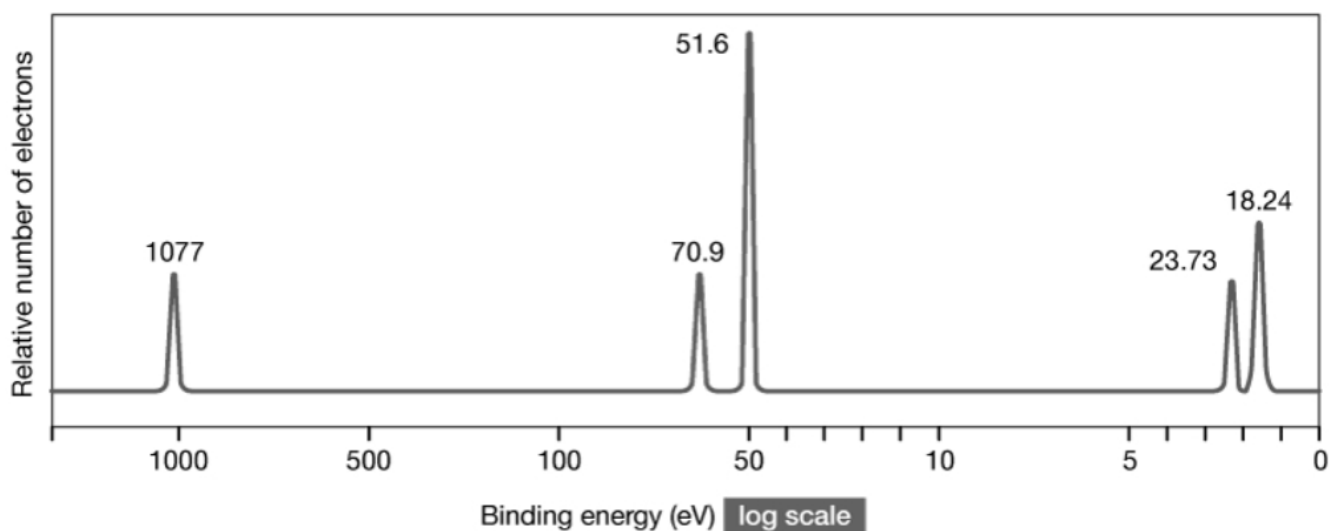
5. The figure below shows the X-ray diffraction data from $\alpha\text{-Fe}$, which is the stable phase of Iron at room temperature. The indices are marked. The X-ray used has $\lambda = 1.54\text{\AA}$. Calculate the cubic lattice constant of Iron using the data. Read off reasonable approximate values from the plot for calculation.



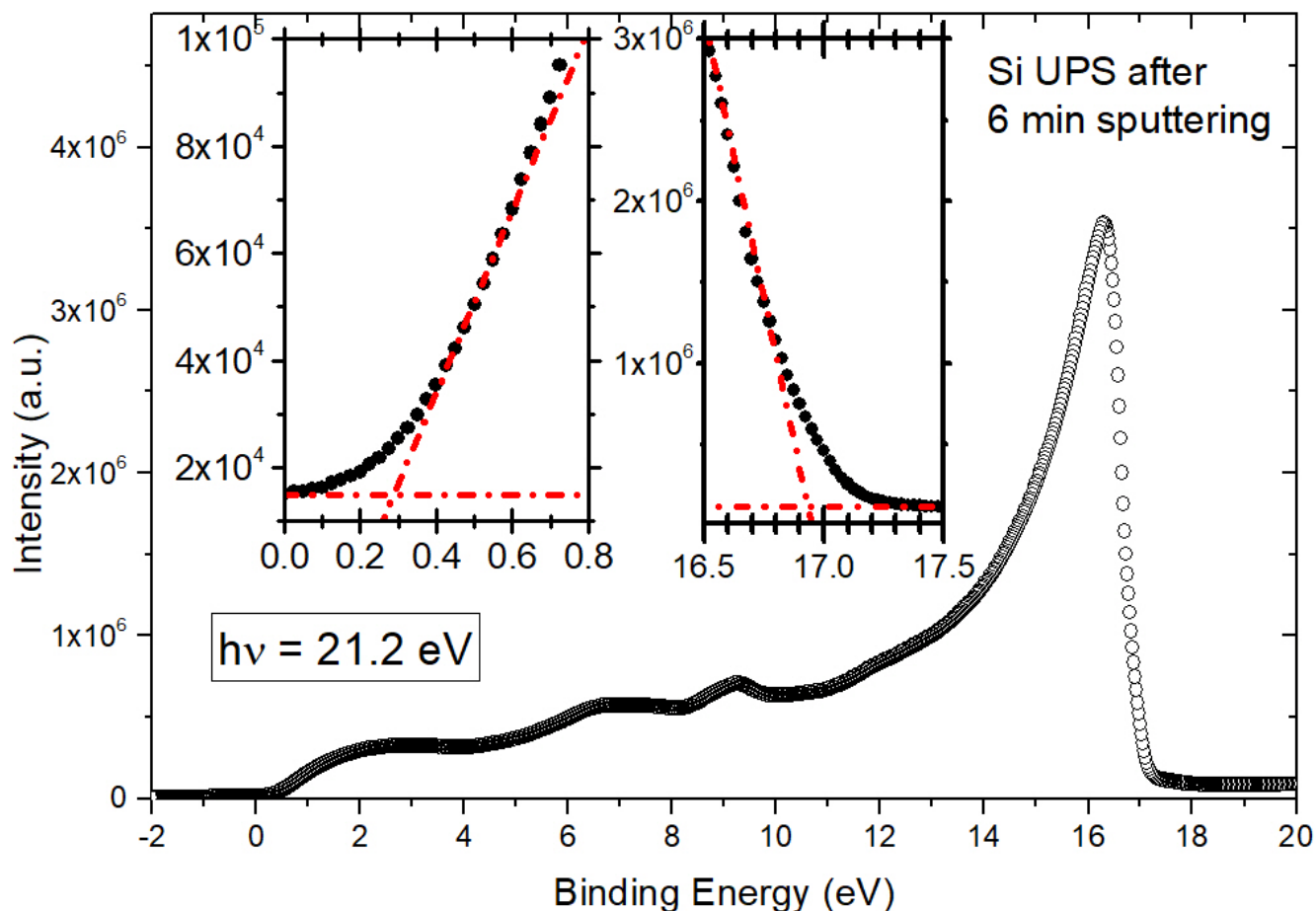
6. A molecule has (say) two hydrogens whose nuclei resonates at frequencies 42.0000 MHz and 42.0001 MHz respectively in a magnetic field of $B = 1$ Tesla. They split each other's signal by 15 Hz. If the magnetic field is increased to $B = 2$ Tesla, what will be the new value of the splitting ?
7. The figure shows a conventional unit cell of a certain compound. The atoms are either at the corner, or center or face-center of the the cube. How many atoms are there in *one formula unit* of the compound ?



8. The figure below shows the complete Photo emission spectrum (XPS) of an element. What is the *atomic number* of this element? Do not go trying to look up a list blindly...look for obvious clues before matching values.



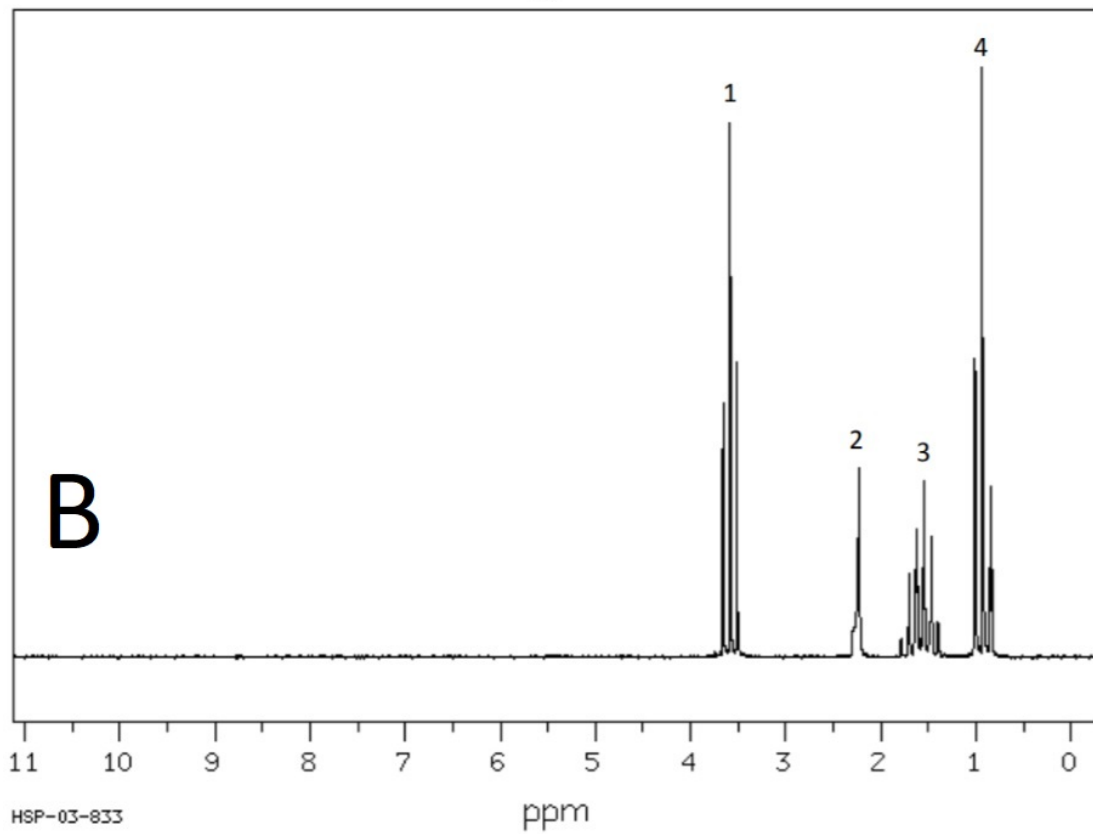
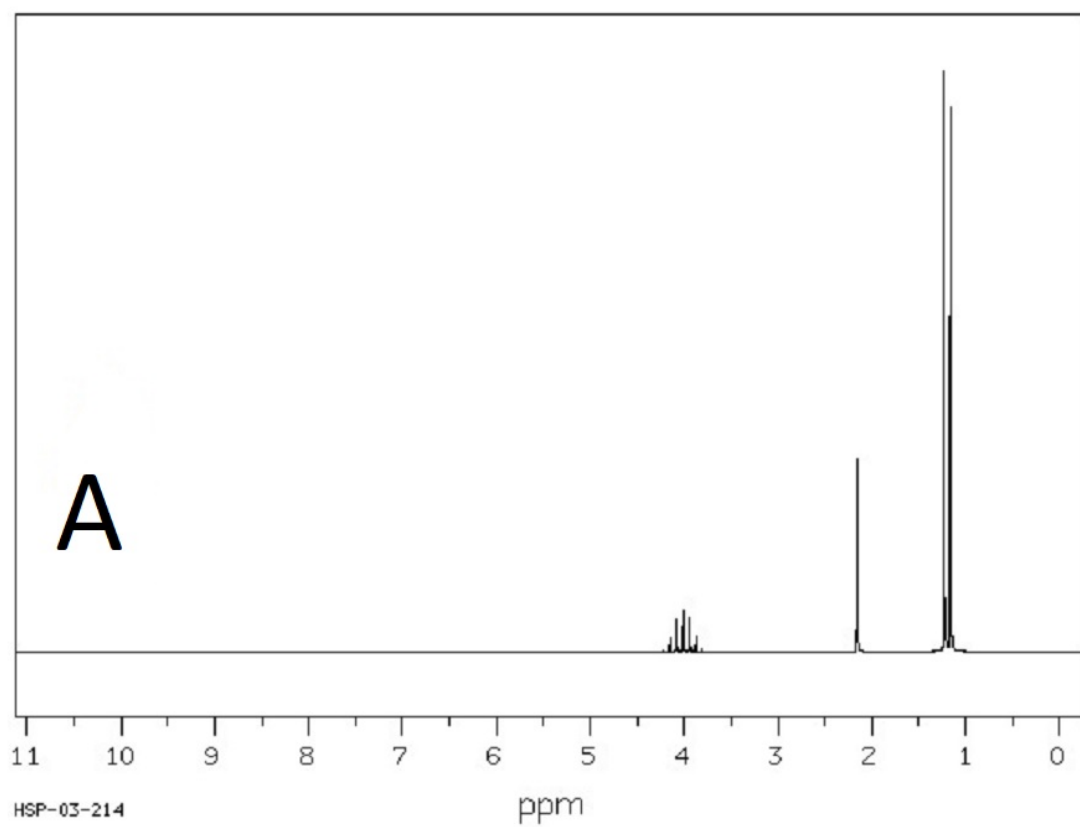
9. A neutron has a de-Broglie wavelength of 2\AA . What is its kinetic energy in milli-electron Volts (meV)?
10. A sample of p-type Silicon has its acceptor level at 0.16eV above valence band and the bandgap is 1.1eV . Ultraviolet photoemission (UPS) data from this sample was taken using a photon energy of 21.2eV . From the given data determine the *electron affinity* of the sample. The two insets show the two cut-off regions. You will need to read-off the values, no curve fitting etc are needed.



Section B

11. Alcohols are formed from parent hydrocarbons by replacing one hydrogen atom with a $-OH$ group. The structural formula will be different depending on which hydrogen is being replaced. If the carbon chain contains three or more carbons there would be different possible isomers depending on the number of carbons present in the backbone. The figure shows proton NMR spectrum of two alcohols formed from the parent compound C_3H_8 (Propane).
- In each case draw the structural formula consistent with the spectrum, with clear reasoning. The credit is entirely for the correct reasoning giving the association of the hydrogens with the peaks - not random guesses!!
 - What is the origin of the unsplit peak in each case?
 - What is the ratio of the areas under the peaks marked (1,2,3,4) in figure (B)
 - Suppose somehow the Hydrogen in the $-OH$ group was replaced by its isotope Deuterium, whose nucleus does not have any spin. What change would you expect in the spectrum?

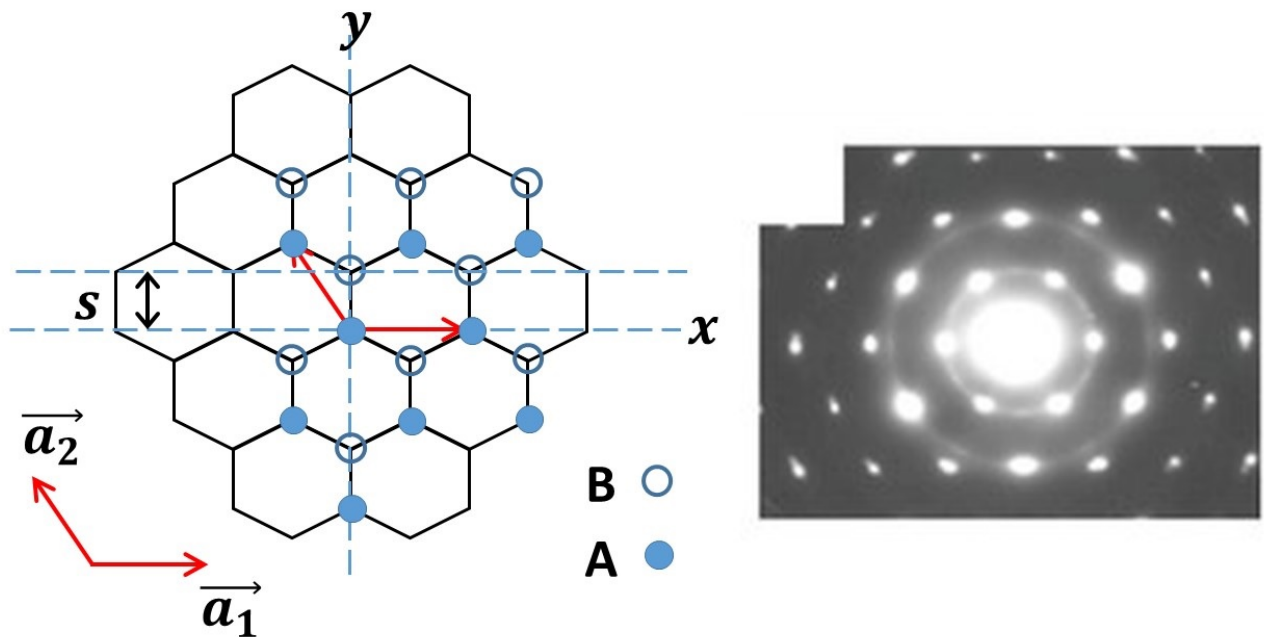
(4+2+2+2=10 marks)



12. The given schematic (left) is that of a single layer of Graphite (Graphene). The two unit vectors of the direct lattice are denoted by the two arrows. The nearest neighbour distance is s and the sides of the hexagons are all equal. Also remember that the A and B sites are not equivalent. An electron beam (wavelength λ) is incident normally on this material. The figure on the right is the transmission electron diffraction pattern obtained. Study the figure carefully and answer the following:

- In terms of s , write down the components of the two unit vectors \vec{a}_1 and \vec{a}_2 , using the xy axes marked in the figure. Calculate the two reciprocal lattice vectors.
- What should be the two hkl families (3 index system) giving the set (ring) of spots nearest to the central spot? Answer with reason, not guesses!
- Index the six nearest spots in correct relative order. Then write the same indices in the four index ($hkil$) system.
- If the camera constant ($L\lambda$, where L is the distance from the sample to the screen) of the electron diffraction set up is $3 \times 10^{-12} \text{ m}^2$ what will be the radial distance of the nearest set of spots, if $s = 0.142 \text{ nm}$?

(2+3+3+2=10 marks)



13. The figure shows a powder XRD pattern from a *tetragonal* material. Tetragonal means $a = b \neq c$, $\alpha = \beta = \gamma = 90^\circ$. The material in question has a complicated basis, so some reflections may be missing. However you can ignore that aspect.

- Make a list of the relevant distances first. This is important!
- Assign the hkl values to the peaks. This will need some educated guesses and observations.. but at the end they must all fall in place!
- Calculate the lattice constants.

(2+6+2=10 marks)

