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X-RAY CRYSTALLOGRAPHY

Stephen C Wallwork

Stephen Wallwork was educated at Manchester Grammar School and Brasenose College, Oxford, where he studied chemistry. In 1950 he was awarded a DPhil in chemical crystallography, having already started his association with Nottingham University by becoming an assistant lecturer in physical chemistry there in 1949. He was subsequently lecturer, senior lecturer, and reader before taking early retirement from the chemistry department in 1982. In the intervening years he carried out a large number of crystal structure determinations, both inorganic and organic, using a wide variety of techniques. His main scientific interest was in organic molecular complexes, leading more recently to an extensive series of papers on organic semiconductors. He is also the author of a textbook on *Physical Chemistry for Students of Pharmacy and Biology*. In 1982 he played a leading role in the founding of the British Crystallographic Association.

During over thirty years of teaching crystallography by different methods he became convinced that the subject could be most easily understood if students acquired personal experience of each idea as it was taught, before it was built on in subsequent teaching. That is how the present course is organised. He also believes in explaining, rather than in glossing over, details often considered trivial but which, nevertheless, puzzle students.

Since 1982 Dr Wallwork has continued to publish crystal structure determinations. Also, during subsequent part-time teaching in the Department of Chemistry, he studied for an MA in local and regional history in the University of Nottingham, graduating in 1985. This subject had by then become his main spare-time interest and it led to a further part-time post in the Department of History and to publications in that field. His other hobbies include photography and water-colour painting.

CHEMISTRY CASSETTES

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Diagrams by Angela Saunders

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Please read this carefully before you start.

USING THE CHEMISTRY CASSETTE

This Chemistry Cassette learning programme has two components — an audio-cassette and this workbook. The two are designed to be used together so always have the book with you as you work through the cassette.

To help you to locate material in the book you will see that it has been divided into numbered 'frames', each of which contains diagrams, tables, figures, etc. You will be given the appropriate frame number when you need to refer to any of this material.

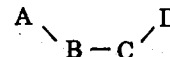
The programme has been designed for individual, self-paced learning and you can work through it at a rate related to your own needs and understanding. Switch off the tape player whenever you want to think, to write some notes or to answer a question. Use the rewind control to revise or repeat material that you might not fully understand on a first hearing. Whenever appropriate make notes to supplement the material in the book; this will enable you to build up a detailed set of personal notes which will serve as your own authoritative guide to the subject.

Running times

Side A: 48 mins

Side B: 47 mins.

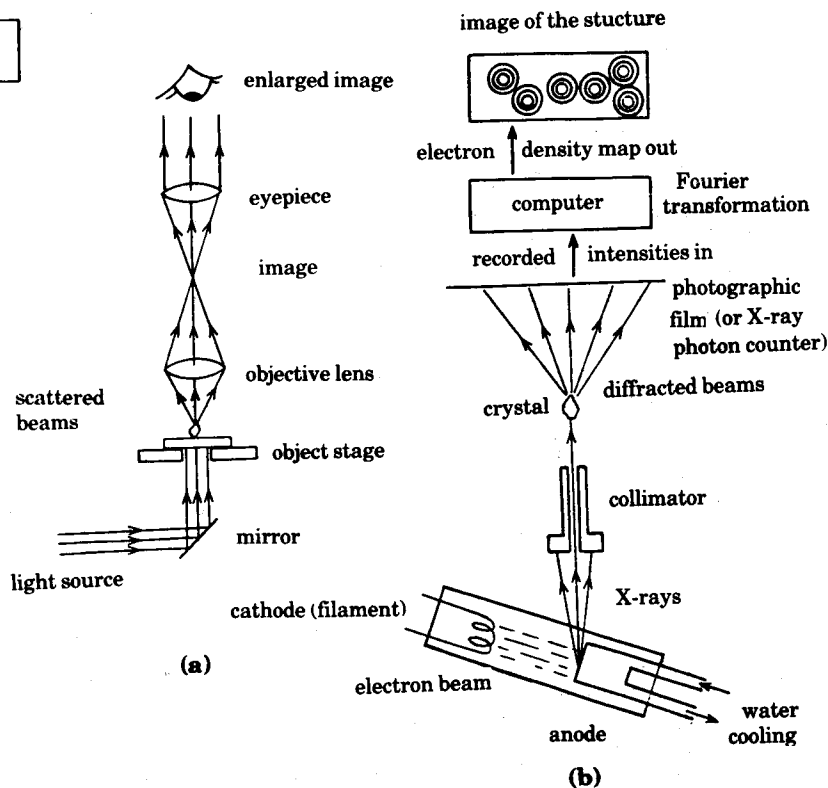
1. Study of simple salts to establish:
 - (a) co-ordination numbers of ions (the number of positive ions surrounding each negative ion and vice versa),
 - (b) characteristic ionic radii,
 - (c) evidence for partial covalency from the directional tendencies of co-ordination patterns and from inter-ionic distances.
2. Study of metals and alloys to establish:
 - (a) co-ordination numbers of atoms,
 - (b) characteristic atomic radii,
 - (c) concentration limits of different crystalline phases in alloys (to assist in plotting phase diagrams) and the structures of these phases,
 - (d) whether 'solid solutions' have atoms of the incorporated substance arranged randomly or in a partially ordered manner (superlattice formation).
3. Study of covalent inorganic, organo-metallic, and organic compounds to establish:
 - (a) molecular geometry – i.e. stereochemistry, bond lengths, bond angles, torsion angles (the projected angle between bonds A–B and C–D in the molecular fragment



as seen along the direction B–C), and dihedral angles between planar parts of molecules (the angles between the plane normals) and deviations of atoms from the planes,

- (b) characteristic bond lengths and angles (to correlate with chemical properties and electronic structure),
- (c) the absolute configuration of an optical enantiomer,
- (d) whether the structure consists of infinitely bonded units or discrete units,
- (e) the arrangement of infinite or discrete units within the crystal, particularly in order to correlate the arrangement with directional properties of the solid,
- (f) the nature of intermolecular interactions (e.g. van der Waals, hydrogen bonding, charge-transfer) and the characteristic geometries (distances, relative orientations) for such interactions,
- (g) evidence for, and effects of, steric hindrances between different atoms or groups within the same molecule,
- (h) the nature of any disorder in the molecular orientations and / or positions,
- (i) the degree and anisotropy of thermal motion of each atom in the structure and its interpretation in terms of vibration and libration (angular oscillation) of whole molecules or groups,
- (j) the space-filling role and nature of trapping or attraction of solvent of crystallization or other guest molecules within the structure.

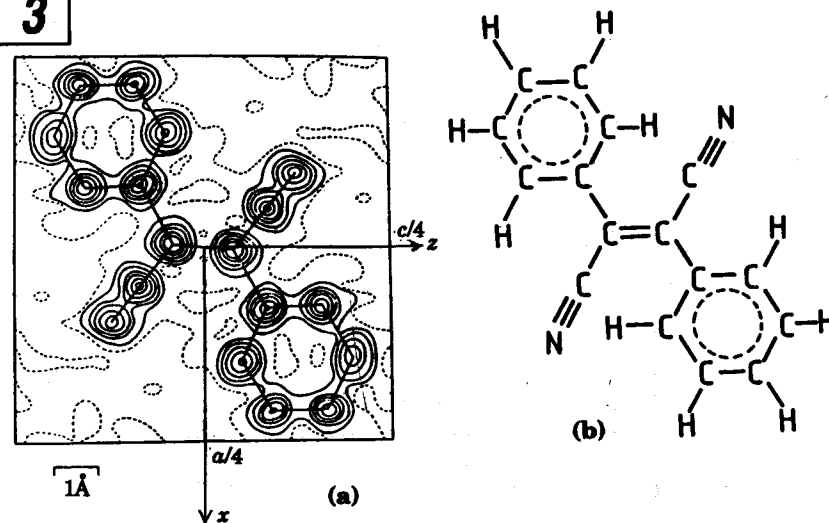
2



(a) Formation of an image of a light-scattering object in an optical microscope.

(b) Formation of an image of the pattern of atoms in an X-ray diffracting crystal by intensity recording and Fourier transformation.

3

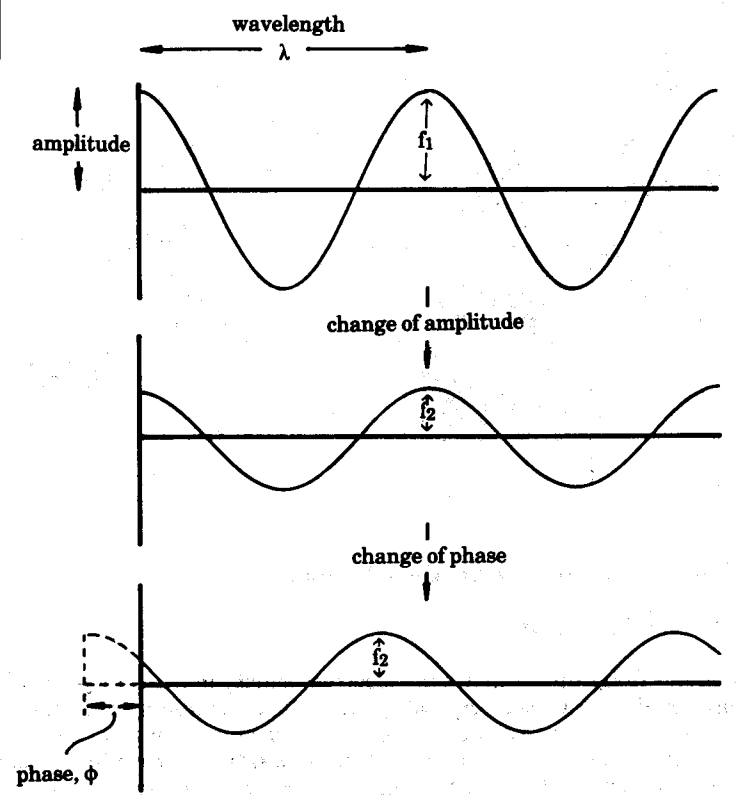


(a) Fourier electron density distribution.

(b) Chemical structure.

The contour diagram (a) shows the electron density in *trans*-dicyanostilbene (b) projected along the crystal y -axis. The contours are drawn at 1, 2, 3, ... 7 electrons per square Ångström unit ($1\text{Å} = 10^{-8}\text{cm} = 10^{-10}\text{m} = 0.1\text{nm}$), and the first contour is dotted. The various parts of this slightly non-planar molecule happen to be oriented not far from perpendicular to the projection axis, so this is almost an undistorted scale diagram. The centres of the peaks show the positions of the centres of the carbon and nitrogen atoms, and these have been joined to show the molecular skeleton. The intensities of the X-ray beams recombined to form this image were not accurate enough to show the low electron-density hydrogen atoms in this example.

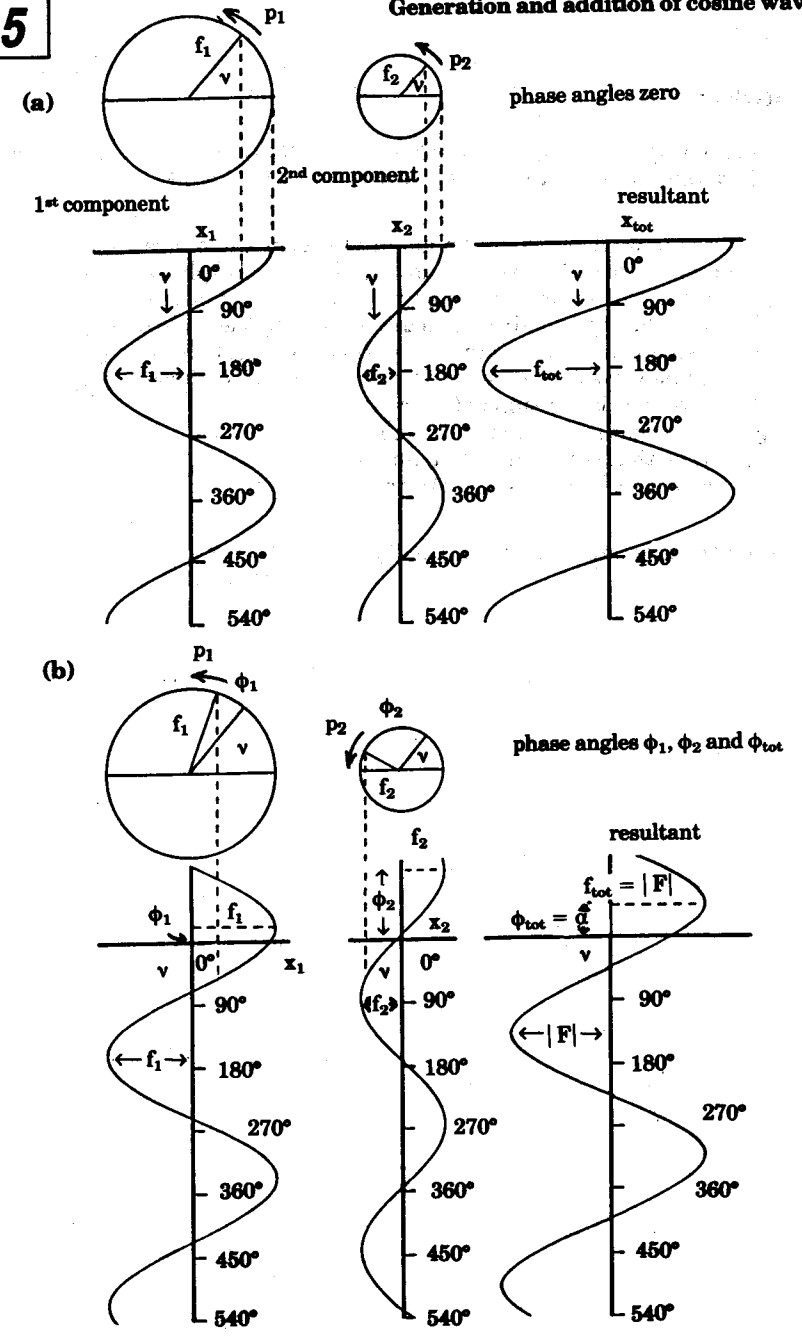
4



Characteristics of waves: wavelength, amplitude, phase

5

Generation and addition of cosine waves



6

PROBLEM 1

By looking up cosine values at 30° intervals and multiplying by the appropriate maximum amplitudes, plot (on any convenient scale) two wavelengths of:

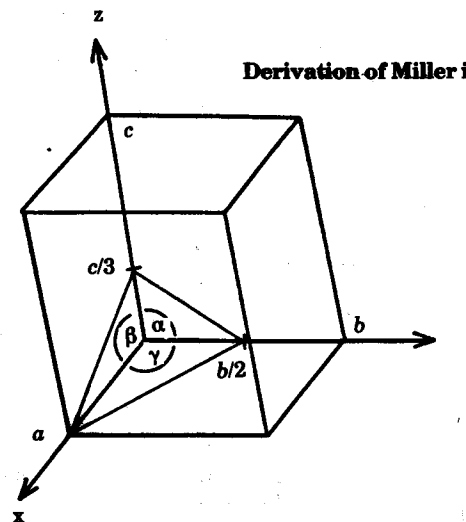
- (a) a cosine wave of maximum amplitude 2 cm and phase angle zero,
- (b) a cosine wave of maximum amplitude 1 cm and phase angle zero,
- (c) a cosine wave of maximum amplitude 1 cm and phase angle -60°,
i.e. such that the maximum occurs at +60° on the scale of angles,
- (d) a cosine wave of maximum amplitude 1 cm and phase angle -120°,
- (e) a cosine wave of maximum amplitude 1 cm and phase angle -180°,
- (f) a wave that is the sum of (a) and (b),
- (g) a wave that is the sum of (a) and (c),
- (h) a wave that is the sum of (a) and (d),
- (i) a wave that is the sum of (a) and (e).

Record the maximum amplitudes and phases of waves (f) to (i).

7

(a)

Derivation of Miller indices for the (123) plane.

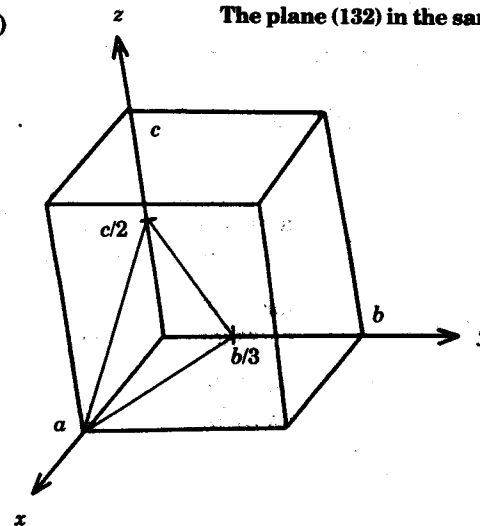


| | | | |
|---|------|------|------|
| | on x | on y | on z |
| (i) intercepts | a | b/2 | c/3 |
| (ii) fractional intercepts | 1 | 1/2 | 1/3 |
| (iii) Miller indices (reciprocal of (ii)) | 1 | 2 | 3 |

These are usually written, one after the other, in round brackets, thus: (123).

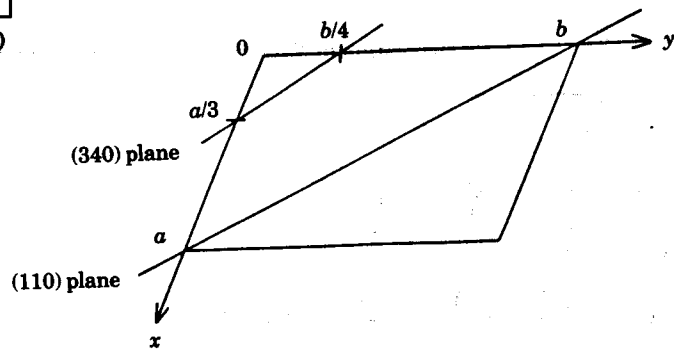
(b)

The plane (132) in the same unit cell as shown in (a).



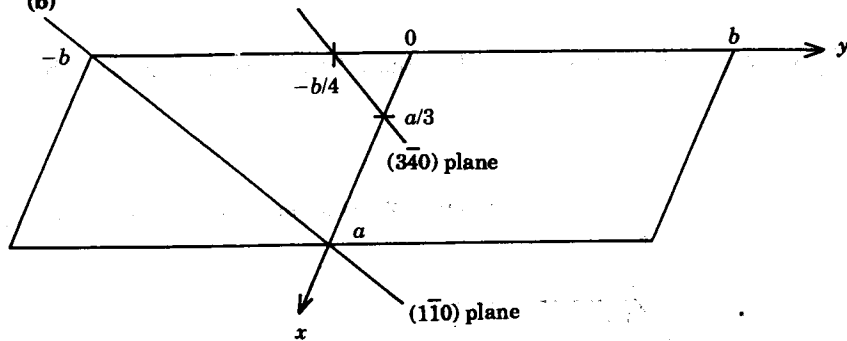
8

(a)



| | | | | |
|----------------------------|-----------|----------|----------|----------|
| (i) intercepts | for (110) | on x | on y | on z |
| | for (340) | a | b | ∞ |
| (ii) fractional intercepts | for (110) | 1 | 1 | ∞ |
| | for (340) | 1/3 | 1/4 | ∞ |
| (iii) reciprocals of (ii) | for (110) | 1 | 1 | 0 |
| | for (340) | 3 | 4 | 0 |
| | | <i>h</i> | <i>k</i> | <i>l</i> |

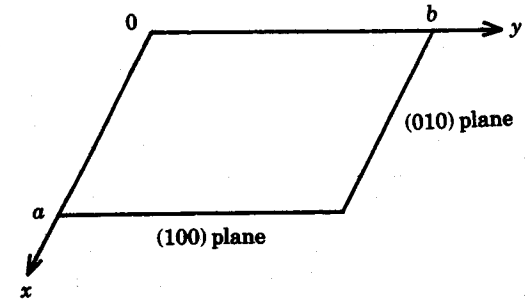
(b)



| | | | | |
|----------------------------|-----------|----------|----------|----------|
| (i) intercepts | for (110) | on x | on y | on z |
| | for (340) | a | -b | ∞ |
| (ii) fractional intercepts | for (110) | 1 | -1 | ∞ |
| | for (340) | 1/3 | -1/4 | ∞ |
| (iii) reciprocals of (ii) | for (110) | 1 | -1 | 0 |
| | for (340) | 3 | -4 | 0 |
| | | <i>h</i> | <i>k</i> | <i>l</i> |

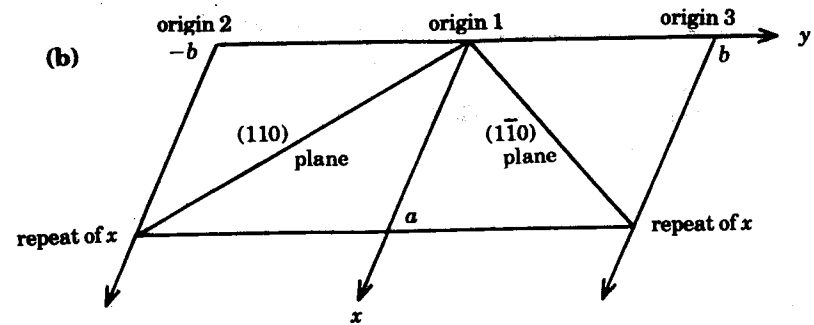
9

(a)



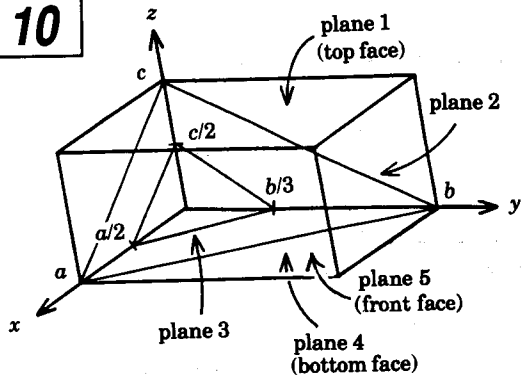
| | | | | |
|----------------------------|-----------|----------|----------|----------|
| (i) intercepts | for (100) | on x | on y | on z |
| | for (010) | a | ∞ | ∞ |
| (ii) fractional intercepts | for (100) | 1 | ∞ | ∞ |
| | for (010) | ∞ | 1 | ∞ |
| (iii) reciprocals of (ii) | for (100) | 1 | 0 | 0 |
| | for (010) | 0 | 1 | 0 |
| | | <i>h</i> | <i>k</i> | <i>l</i> |

(b)



| | | | | | | | | |
|---------------------------|--------------------------------|----------|----------|----------|--------------------------------|----------|----------|----------|
| (i) intercepts | for (110) relative to origin 2 | on x | on y | on z | for (110) relative to origin 3 | on x | on y | on z |
| (ii) fractional intercept | | a | +b | ∞ | | a | -b | ∞ |
| (iii) reciprocals of (ii) | | 1 | 1 | ∞ | | 1 | -1 | ∞ |
| | | 1 | 1 | 0 | | 1 | -1 | 0 |
| | | <i>h</i> | <i>k</i> | <i>l</i> | | <i>h</i> | <i>k</i> | <i>l</i> |

10

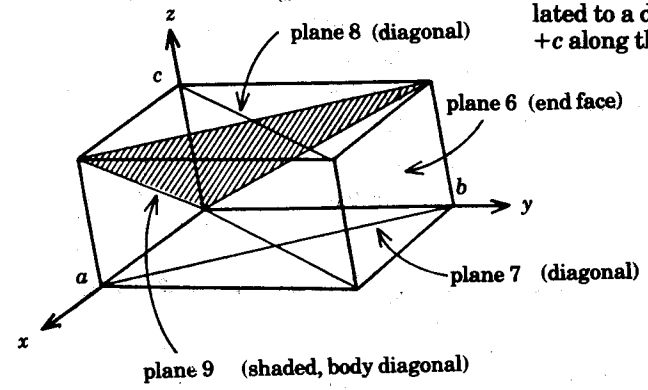


PROBLEM 2

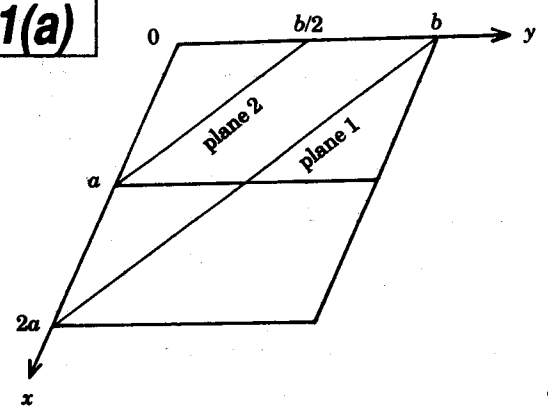
Name the planes 1 to 9 illustrated in this frame.

Hints: Plane 4 will need to be related to a different origin one unit cell away along the z-axis.
Plane 8 will need to be related to a different origin, one unit cell away along the y-axis.

Plane 9 is best related to a different origin at +c along the z-axis.



11(a)



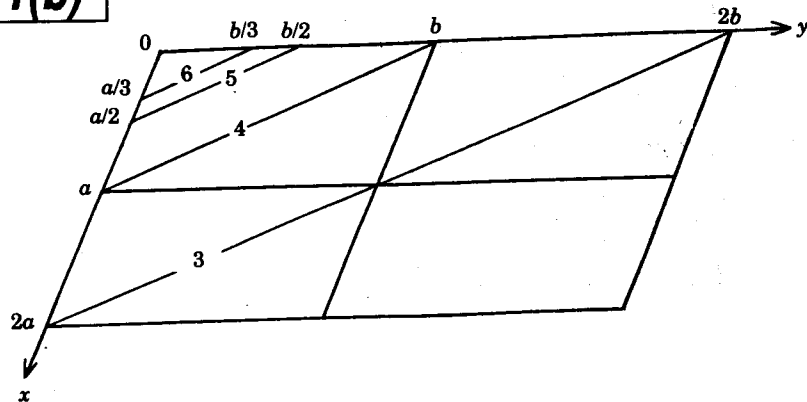
(i) intercept

(ii) fractional intercepts

(iii) reciprocals of (ii)

| | on x | on y | on z |
|---------|------|------|----------|
| plane 1 | 2a | b | ∞ |
| plane 2 | a | b/2 | ∞ |
| plane 1 | 2 | 1 | ∞ |
| plane 2 | 1 | 1/2 | ∞ |
| plane 1 | 1/2 | 1 | 0 |
| plane 2 | 1 | 2 | 0 |

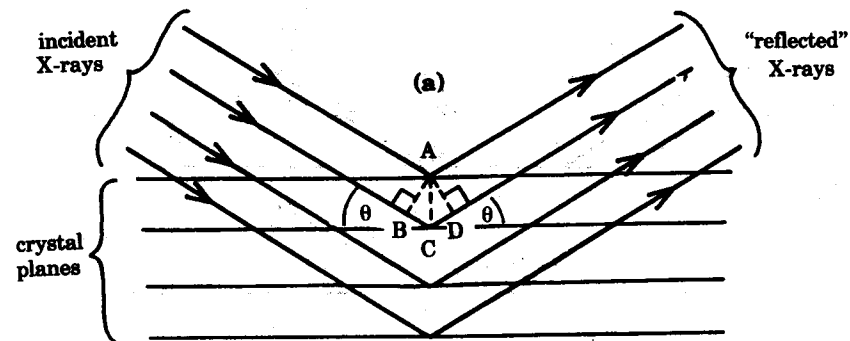
11(b)



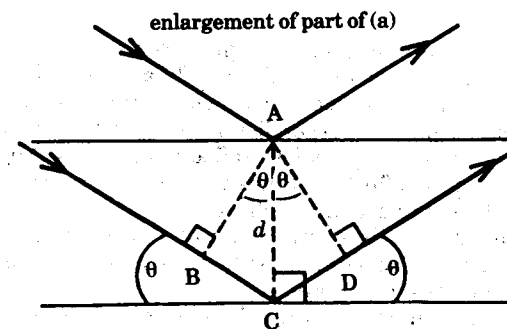
| intercepts | | on x | on y | on z |
|--------------------------------------|---------|------|------|----------|
| | plane 3 | 2a | 2b | ∞ |
| | plane 4 | a | b | ∞ |
| | plane 5 | a/2 | b/2 | ∞ |
| | plane 6 | a/3 | b/3 | ∞ |
| | | "h" | "k" | "l" |
| reciprocals of fractional intercepts | plane 3 | 1/2 | 1/2 | 0 |
| | plane 4 | 1 | 1 | 0 |
| | plane 5 | 2 | 2 | 0 |
| | plane 6 | 3 | 3 | 0 |

Thus, multiplication or division of all three Miller indices by the same factor has no effect on the direction or orientation of the corresponding crystal plane.

12



(b)



The extent to which a second ray (such as that reflected at C) is out of phase with a ray reflected at A on the first plane is determined by:

- (1) the wavelength of the X-rays, and
- (2) the extra distance the second ray has to travel, i.e. BC + CD.

$$\begin{aligned} \text{From the triangle ABC, } BC &= d \sin \theta \\ \text{Similarly, from the triangle ACD, } CD &= d \sin \theta \\ \text{total path difference} &= 2d \sin \theta \end{aligned}$$

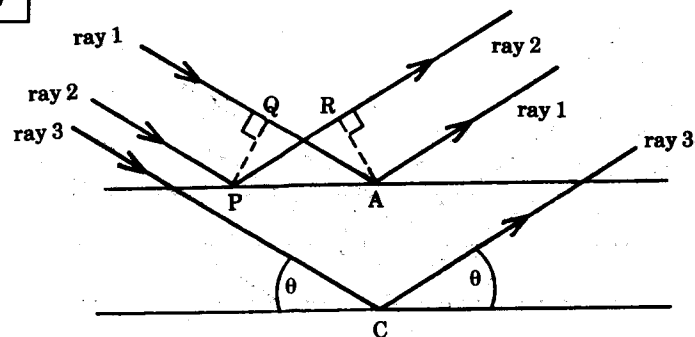
For reinforcement of the two rays, this extra path difference must be a whole number of wavelengths, λ .

So $2d \sin \theta = n\lambda$
This is the Bragg equation or Bragg Law.

A simplified form, for use when regarding each diffracted beam as being of first order from a plane with possibly multiple indices, is

$$2d \sin \theta = \lambda.$$

13



Proof that the path difference between one ray and the next is independent of the points in the planes at which the rays are considered to be reflected.

Since PQA and PRA are similar triangles (identical in shape but mirror images of one another) the distances QA and PR are equal. PQ is a wave front perpendicular to the incident beam at which the rays 1 and 2 are in phase.

To reach the wave front AR perpendicular to the reflected beam, ray 1 has to travel an extra distance QA before reflection and ray 2 has to travel an extra distance PR after reflection. Since these two distances are equal, rays 1 and 2 must still be in phase after reflection.

Rays 1 and 2 must therefore both be out of phase with ray 3 to the same extent after reflection. The same must be true wherever P is relative to A , provided it is still on the same crystal plane.

The phase relationship of the Bragg Law is therefore independent of the positions within the crystal planes at which reflection takes place, and θ depends only on d , the perpendicular spacing between crystal planes.

14

PROBLEM 3

Predict the Bragg angles θ for the first four orders of diffraction from the (100) planes of CsCl ($d_{100} = 0.412 \text{ nm}$) for $\text{Cu K}\alpha$ radiation (wavelength, $\lambda = 0.1542 \text{ nm}$).

PROBLEM 4(a)

Predict the Bragg angle θ for the first order diffraction from the (200) plane of CsCl ($d_{200} = 0.206 \text{ nm}$) for the same X-radiation as in problem 3.

PROBLEM 4(b)

Predict the Bragg angle θ for the first order diffraction from the (300) plane of CsCl ($d_{300} = 0.1373 \text{ nm}$) for the same X-radiation as in problem 3.

15

metal film cassette

film bent into a cylinder, lining the cassette

diffracted beams lying on the surfaces of cones

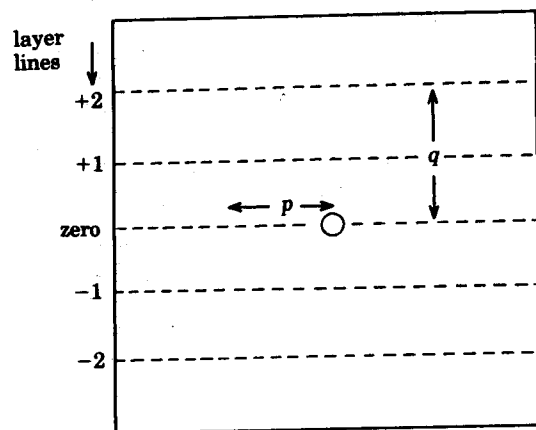
incident X-rays

collimator

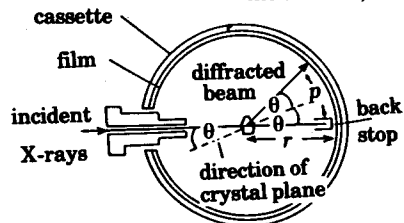
goniometer head for crystal

back stop

(a) arrangement for taking an oscillation or rotation photograph



(b) film after exposure, removal from the cassette, and processing.



(c)

For any spot, caused by a diffracted beam in the zero layer line (equatorial circle),

$$\begin{aligned} p/r &= 2\theta \text{ radians} \\ &= (\pi/180) \times 2\theta^\circ \\ &\text{(where } r \text{ is the camera radius).} \end{aligned}$$

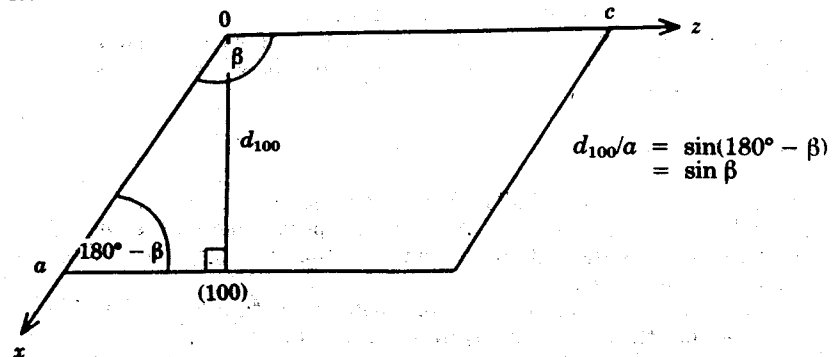
16

PROBLEM 5

The compound 4,4'-dihydroxydiphenyl (DHDP) crystallizes in a monoclinic unit cell in which only the angle β (95.8°) differs from 90° . The unit cell dimensions are

$$a = 1.052, \quad b = 0.534, \quad c = 0.797 \text{ nm.}$$

From the geometry of the parallelogram formed by the unit cell face bounded by a and c , illustrated below, calculate the perpendicular spacing d_{100} .



Draw a scale diagram of the corresponding parallelogram for DHDP and check your calculation by measurement on it. Draw on this diagram the plane (402) and, by measuring the perpendicular distance from the origin to this plane, estimate d_{402} . Then use the Bragg equation in either form to predict the Bragg angle θ and the angle 2θ for reflections from each of the planes (100), (200), (300), (400), (402) for X-rays of wavelength 0.1542 nm.

