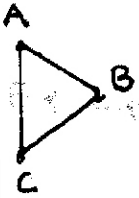


①

# Lecture 1) 230

Symmetry Operations: Interchange objects such that after the interchange the overall appearance is the same as prior to the interchange.



Do not forget the identity operation

The object is said to be in an equivalent position (A, B + C are equiv. positions for  $C_3$  symmetry)

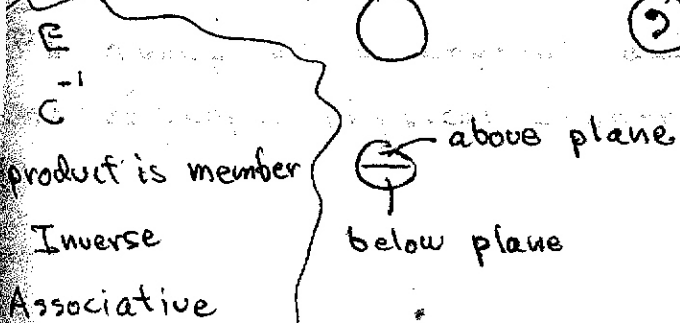
Point Symmetry Operations: Symmetry w.r.t. fixed point.

Group of Symmetry Operations. a) AB in group c) E in group  
b) A<sup>-1</sup> in group d) (ABC) = A(BC)

Principle axis - axis of highest symmetry

The left hand & right hands are enantiomorphous images (mirror) of each other.

Definition of Grp.



Mirror image

+ Any general object above plane  
- Any general object below plane  
of paper.

Symmetry Operations: E, i, C<sub>n</sub>, σ, σ<sub>n</sub>, σ<sub>v</sub>, σ<sub>d</sub>

C<sub>n</sub>  
C<sub>n</sub><sup>-1</sup>  
(C<sub>n</sub>)<sup>2</sup>

Contains principle axis

which bisects the angle between the 2 principle axes

D<sub>n</sub> ⇒ n 2 fold axes ⊥ to n fold axis (C<sub>n</sub>)

S<sub>n</sub> ⇒ improper rotation ( $\frac{2\pi}{n}$  + a reflection in ⊥ plane)

S<sub>n</sub> = σ<sub>n</sub> C<sub>n</sub>

(y, z) → (y, z)

S<sub>2</sub> = i

S<sub>3</sub><sup>3</sup> = σ

S<sub>3</sub><sup>6</sup> = E

Note S<sub>n</sub> ≠ C<sub>n</sub> & σ<sub>n</sub>  
(International)

Example CH<sub>4</sub>

Hermann-Mauguin Notation

I = E

T = i

N = C<sub>n</sub>

N̄ = i C<sub>n</sub>

2

Schoenflies notation

$I = E$ ,  $T = i$ ,  $n = C_n$ ,  $m = \sigma$

$\bar{n} = i C_n$  (inversion)

in Schoenflies this is a reflection for  $S_n$

International Notation

Examples:  $H_2O$ ,  $NH_3$ ,  $PF_3Cl_2$ ,  $4/mmm$

$E, C_2, 2\sigma_v$   
(4 symmetry operations  
stereogram has 4 points)

$E, C_3, C_2, 3\sigma_v$   
(stereogram has 6 points)

$E, C_3, C_2, 3C_2', \sigma_h, 3\sigma_v, S_3, S_3^5$   
(12 pts on stereog  
6 above - 6 below)

$E, C_4, C_2, C_4^3, 2C_2', 2C_2'', i, S_4, S_4^3, \sigma_h, 2\sigma_v, 2\sigma_d$   
8 above & below

Note circle & dot for an object above & below plane - pt group  $\pm$  signs and  $\rho$  used for space groups.

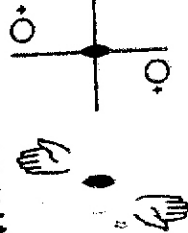
Pt group of a crystal determines the symmetry of the macroscopic physical properties.

Schoenflies

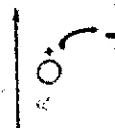
Rotation axes

International

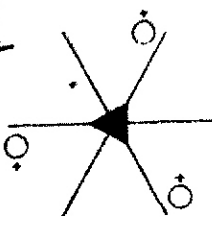
$C_2(2)$



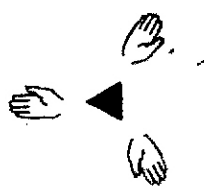
below plane



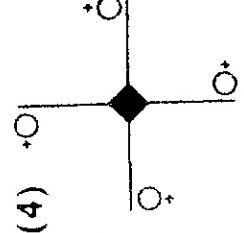
above plane



$C_3(3)$



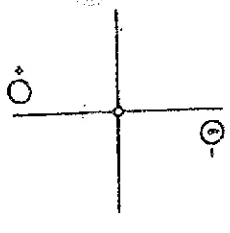
$C_4(4)$



$C_6(6)$

Inversion through a center

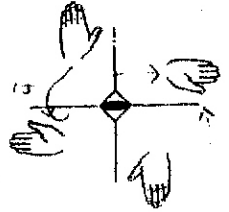
$i(\bar{1})$



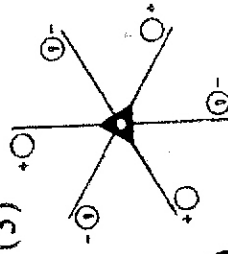
Rotatory inversion axes

$i(\bar{1}) = \text{inversion}$   
 $\sigma(\bar{2}) = \text{mirror plane}$

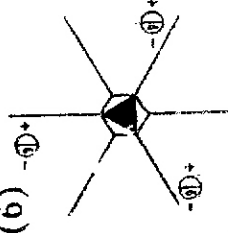
$S_4^3(\bar{4})$



$S_6^5(\bar{3})$

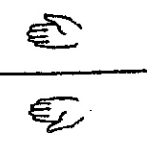


$S_3^5(\bar{6})$

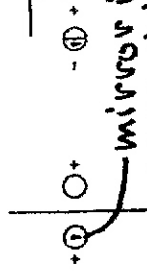


Looking

parallel perpendicular



$\sigma(m)$



mirror image  
 enantiomorphical

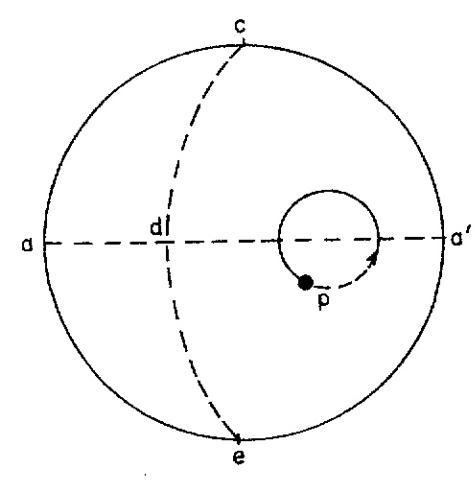
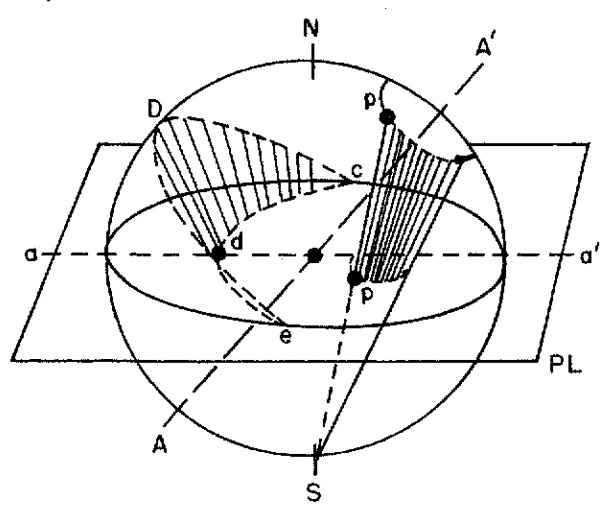
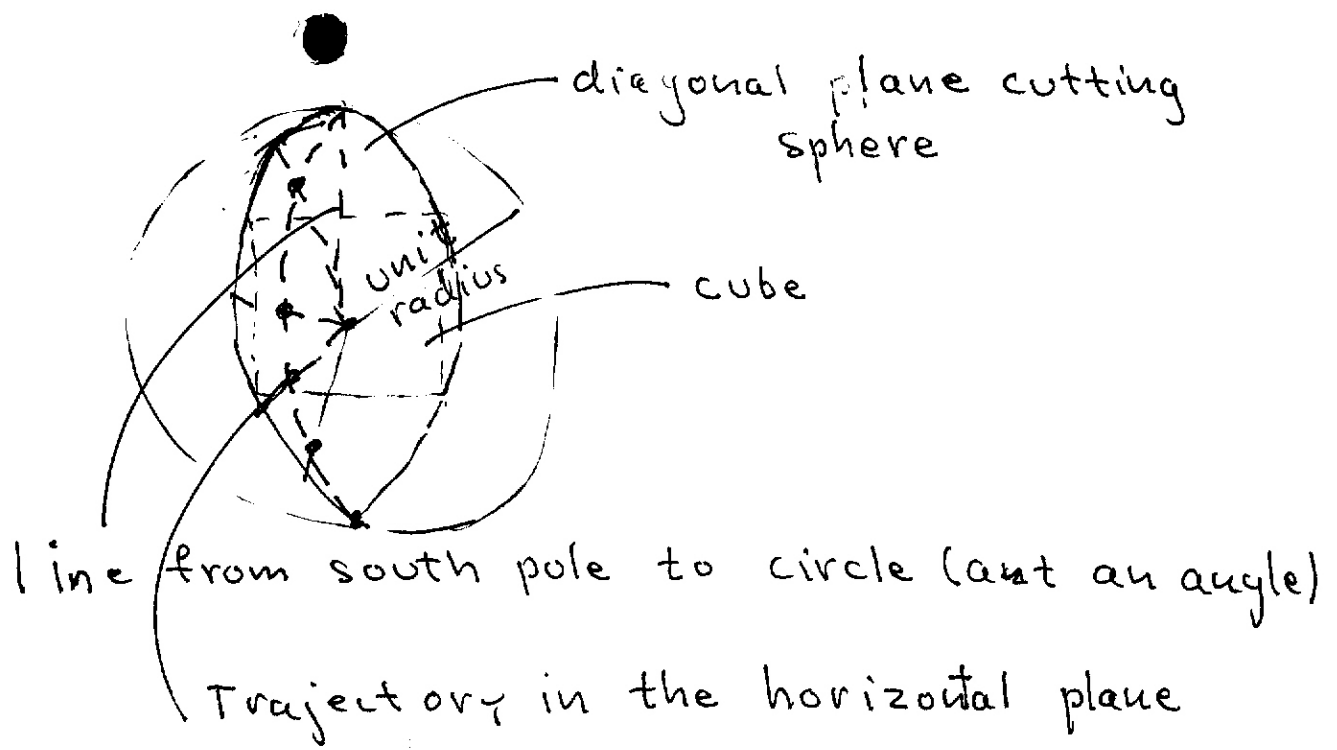
Fig. 1-2 The point symmetry operations and the symbols used to designate them. Hands are used to show the effect for several symmetry operations.

### 3-5 Hermann-Mauguin notation

In the Hermann-Mauguin system the point groups are designated by combinations of the symbols for symmetry elements. Some of the elements of the group are, therefore, immediately apparent from the symbol, and a few conventions make it possible to deduce the entire group structure. This system is preferred by crystallographers because it is easily extended to include translational symmetry elements and because it specifies the directions of the symmetry axes.

The Schoenflies and the Hermann-Mauguin symbols for the thirty-two crystallographic point groups are given in Table 3-1, and many of the features of the Hermann-Mauguin notation will be revealed by comparison with the Schoenflies symbols. The following summary should further clarify the meanings of the symbols:

1. Each component of a symbol refers to a different direction. The terms  $2/m$ ,  $4/m$ , and  $6/m$  are single components and refer to only one direction. In  $4/mmm$ , for example, the  $4/m$  (read "four over  $m$ ") indicates that there is a mirror plane perpendicular to a fourfold rotation axis.
2. The position of an  $m$  in a symbol indicates the direction of the normal to the mirror plane.
3. In the orthorhombic system, the three directions are mutually perpendicular. If we label our axes  $x, y, z$ , the symbol  $mm2$  indicates that mirror planes are perpendicular to  $x$  and  $y$ , and a twofold rotation axis is parallel to  $z$ . The 2 in this case is redundant since we have seen that two perpendicular mirror planes inevitably generate a twofold axis. Note that such symbols as  $m2m$  and  $2mm$  correspond to renaming the axes.
4. If in the tetragonal system the 4 or  $\bar{4}$  axis is in the  $z$  direction, the second component of the symbol refers to mutually perpendicular  $x$  and  $y$  axes, and the third component refers to directions in the  $xy$  plane that bisect the angles between the  $x$  and  $y$  axes.
5. In the trigonal and hexagonal systems, a second component in the symbol refers to equivalent directions ( $120^\circ$  or  $60^\circ$  apart) in the plane normal to the 3,  $\bar{3}$ , 6, or  $\bar{6}$  axis.
6. A third component in the hexagonal system refers to directions that bisect the angles between the directions specified by the second components.
7. A 3 in the second position always denotes the cubic system and refers to the four body diagonals of a cube. The first component of cubic symbol refers to the cube axes, and a third component refers to the face diagonals of the cube.

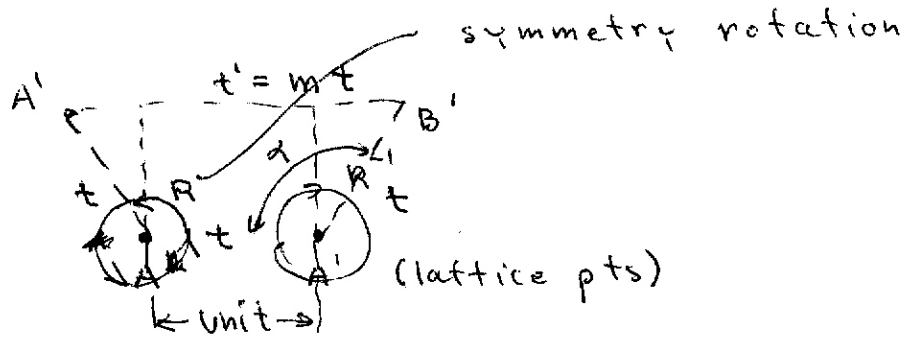


(7)

Development of Pt. Groups.

Molecules - No restriction on  $n$  : For crystals

$$n = 1, 2, 3, 4, 6$$



$$t' = mt$$

$$t' = t + 2t \sin(\alpha - 90)$$

$$= t + 2t(-\cos \alpha)$$

$$\therefore \cos \alpha = -\frac{(m-1)}{2} \leq 1$$

$m = 1$	$2$	$3$	$\neq -1$	$0$
$\cos \alpha$	$0$	$-\frac{1}{2}$	$-1$	$+\frac{1}{2}$
$\alpha$	$90^\circ$	$120^\circ$	$180^\circ$	$60^\circ$
	$270^\circ$			
	$\frac{2\pi}{4}$	$\frac{2\pi}{3}$	$\frac{2\pi}{2}$	$\frac{2\pi}{6}$

So  $n = 1, 2, 3, 4$  or  $6$

→ 32 crystallographic point groups.

① Rotations  $C_1, C_2, C_3, C_4, C_6$   
 (1) (2) (3) (4) (6)










In a similar way, the symbol (*UVW*) means all directions which can be reached from [*UVW*] by repeated operation of the symmetry elements of a given point group.

**Crystal systems.** The 32 crystal classes are conventionally grouped into seven crystal systems, as shown in Table 21. The requirement for membership of a given crystal system is that the symmetry of the class should possess a

TABLE 20

*Symbolism for the symmetry elements of the 32 point groups*

Symmetry element	Symbol on stereogram	International symbol
centre of symmetry . . . . .	no symbol	$\bar{1}$
mirror plane . . . . .	full line (great circle)	$m$
<i>Rotation axes</i>		
1-fold (monad). . . . .	no symbol	$1$
2-fold (diad) . . . . .		$2$
3-fold (triad) . . . . .		$3$
4-fold (tetrad) . . . . .		$4$
6-fold (hexad) . . . . .		$6$
<i>Inversion axes</i>		
1-fold (inverse monad) $\equiv$ centre of symmetry	no symbol	$\bar{1}$
2-fold (inverse diad) $\equiv$ mirror planes normal to the axis	as for mirror planes	$\bar{2} (\equiv m)$
3-fold (inverse triad) $\equiv$ 3-fold rotation axis plus a centre of symmetry		$\bar{3}$
4-fold (inverse tetrad) (includes a rotation diad axis)		$\bar{4}$
6-fold (inverse hexad) $\equiv$ a rotation triad axis plus a plane normal to it		$\bar{6} (\equiv 3/m)$

certain characteristic. The names of the systems, together with the characteristics required for membership, are as follows:

- (i) *triclinic*: no symmetry other than a 1-fold axis (rotation or inverse);
  - (ii) *monoclinic*: a single 2-fold axis (rotation or inverse);
  - (iii) *orthorhombic*: three mutually perpendicular 2-fold axes (rotation or inverse), but no axes of higher order;
  - (iv) *tetragonal*: a single 4-fold axis (rotation or inverse);
  - (v) *cubic*: four 3-fold axes arranged like the body diagonals of a cube;
  - (vi) *trigonal*: a single 3-fold axis (rotation or inverse);
  - (vii) *hexagonal*: a single 6-fold axis (rotation or inverse).
- Choice of axes *Ox*, *Oy*, *Oz*.** The reason for the above grouping into systems is that it is possible to refer all the classes within a single system to a similar set

of axes *Ox*, *Oy*, *Oz*. Moreover, when the axes have been thus chosen, according to certain conventions set out below, a unit cell may be outlined in which the ratio *a*:*b*:*c* has features which are characteristic for the system. This often necessitates the choice of a multiply primitive unit cell, and, indeed, it was precisely to allow for this contingency that we reserved the right to use unit cells that were not primitive. The following list gives the conventions for the choice of *Ox*, *Oy*, *Oz* in relation to the characteristic symmetry elements of each system; it also gives any relations that exist between *a*, *b* and *c*, and between the interaxial angles  $\alpha$ ,  $\beta$  and  $\gamma$ , as defined in Fig. B.1.

- (i) *triclinic*:  $a \neq b \neq c$ ,  $\alpha \neq \beta \neq \gamma$ .
- (ii) *monoclinic*: *Oy* parallel to the 2-fold axis;  
 $a \neq b \neq c$ ,  $\alpha = \gamma = 90^\circ \neq \beta$ .
- (iii) *orthorhombic*: *Ox*, *Oy*, *Oz* parallel to the 2-fold axes;  
 $a \neq b \neq c$ ,  $\alpha = \beta = \gamma = 90^\circ$ .
- (iv) *tetragonal*: *Oz* parallel to the 4-fold axis;  
 $a = b \neq c$ ,  $\alpha = \beta = \gamma = 90^\circ$ .
- (v) *cubic*: *Ox*, *Oy*, *Oz* parallel to the edges of the cube whose body diagonal are the 3-fold axes;  
 $a = b = c$ ,  $\alpha = \beta = \gamma = 90^\circ$ .
- (vi) *trigonal*: *Oz* parallel to the 3-fold axis;  
 $a = b \neq c$ ,  $\alpha = \beta = 90^\circ$ ,  $\gamma = 120^\circ$ .
- (vii) *hexagonal*: *Oz* parallel to the 6-fold axis;  
 $a = b \neq c$ ,  $\alpha = \beta = 90^\circ$ ,  $\gamma = 120^\circ$ .

The trigonal and hexagonal systems, having similar sets of axes, are sometimes regarded as forming a single system. In some systems (for example, the tetragonal) the above rules do not specify all the axial directions, and in the more symmetrical classes of these systems further conventions are introduced. The directions of *Ox*, *Oy*, *Oz* are inserted on the stereograms in Table 21 whenever the conventions fix them completely in relation to the symmetry elements.

**Miller-Bravais and rhombohedral axes.**† The axes we have given in (and (vii) of the above list for the trigonal and hexagonal systems do not displace the 3-fold, and still less the 6-fold, symmetry characteristic of these systems. For this reason a fourth, redundant, axis denoted *Ou* is often added in the *Ox*, *Oy*, *Oz* plane at  $120^\circ$  to *Ox* and *Oy*, with an axial length equal to *a*. The axes are then called *Miller-Bravais axes*. The symbol for a face or set of lattice planes is obtained just as before, except that it now contains four indices, thus: (*hkil*), where the *l* refers to the *Ou* axis. *h*, *k*, *i* are not independent, and it may be shown that  $h+k+i=0$ . The advantage of using the fourth axis is that crystal faces of the same form, say (*hkil*), have sets of indices which are, apart from signs, permutations of one another; this then becomes a common property for all the systems.

The problem of assigning symbols to directions in the trigonal and hexagonal systems does not arise in the text of this book; but since it is usually neglected † The material of this section is not needed for an understanding of the main text but is included here for completeness.



(4)  
Example Symmetries.

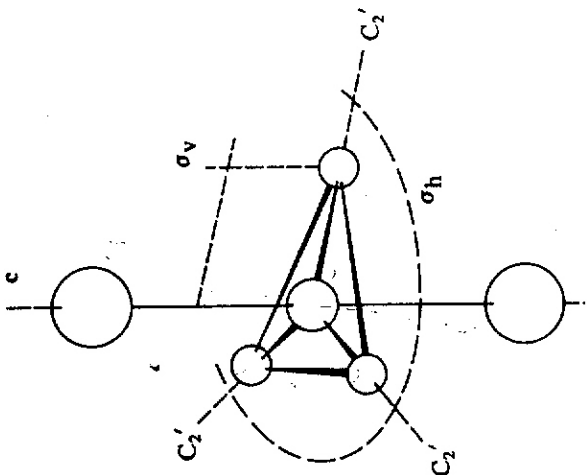
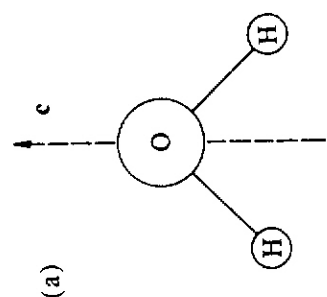
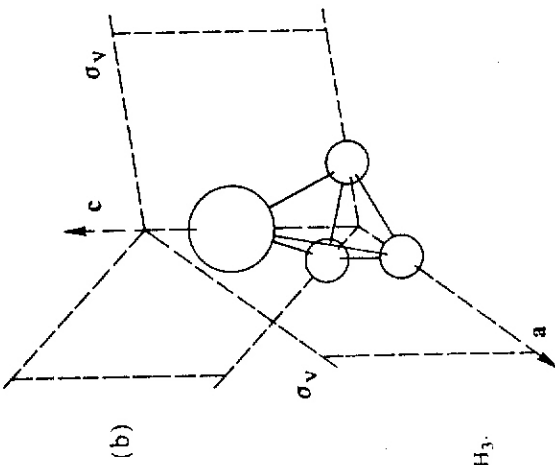
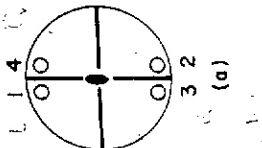
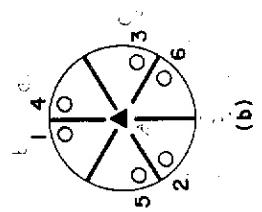
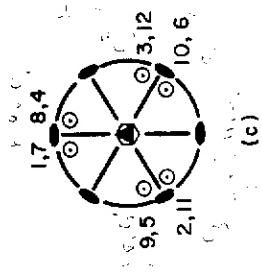


Fig. 1-1 A diagram of a  $\text{PF}_3\text{Cl}_2$  molecule showing some of the symmetry operations. Naturally, an operation that takes a F atom into a Cl atom cannot be a symmetry operation, so it might be helpful to label the atoms.



1-1 A Symmetry Operation

Fig. 1-3 Symmetry of (a)  $\text{H}_2\text{O}$ , (b)  $\text{NH}_3$ .



$D_{4h}$  ( $4/mmm$ )

$D_{3h}$   $\bar{6}m2$

$C_{3v}$

$C_{2v}$   $m\bar{3}m$

Symmetry Operation

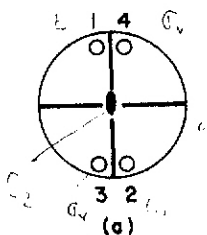
$C_n^m$   
 $S_n^m$   
 $S_n^m$

Inverse

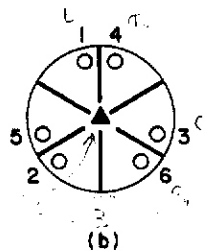
$C_n^{n-m}$   
 $S_n^{n-m}$  m, n even  
 $S_n^{2n-m}$  m, n odd

$S_n^m = C_n^m$  for n odd and m even.

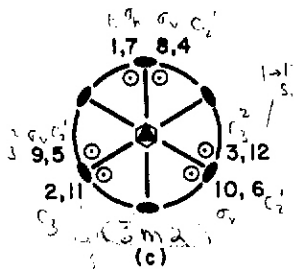
**1-2e Stereographic projection** A stereographic projection is a very useful way to visualize the effects of point symmetry operations. It is usually constructed by assuming that a unit sphere surrounds the object. A point in the +z hemisphere is projected onto the xy-plane by determining the intersection, with that plane, of the line connecting the point to the south pole of the sphere. If the point is in the -z hemisphere the north pole is used. We observe the projections by looking down the +z-axis. The points in the +z or -z hemisphere are respectively labeled by a circle (o) or a dot (•) on the xy-plane.



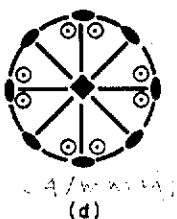
$H_2O$   
 $E, C_2, 2\sigma_v$   
 Orthorhombic  
 $C_{2v} (mm_2)$



$NH_3$   
 $E, C_3, C_3^2, 3\sigma_v$   
 $C_3 (3)$



$PF_3Cl_2$   
 $E, C_3, C_3^2, 3C_2'$   
 $\sigma_h, 3\sigma_v, S_3, S_3^5$   
 $D_{3h} (\bar{3}m)$



$E, C_4, C_2, C_4^3, 2C_2'$   
 $2C_2'', i, S_4, S_4^3$   
 $D_{4h} (4/mmm)$

# Building (Constructing The Point Groups)

Pages 12-13 of Burns

## ① Rotations

$C_1, C_2, C_3, C_4, C_6$  (1, 2, 3, 4, 6 in International Notation)

Gives 5 - Groups

## ② Add $\sigma_h$ - reflection through horizontal plane

Gives  $C_{nh}$

$C_{1h}$	$C_{2h}$	$C_{3h}$	$C_{4h}$	$C_{6h}$
m	(2/m)	$\bar{6}$	(4/m)	(6/m)

Schoenflies

↑ International      ↑ Equivalent to  $S_3$

5 - Groups

## ③ Add mirror planes to $C_1$ to $C_6$ which contain rotation axis ( $\sigma_v$ )

$C_{1v}$	$C_{2v}$	$C_{3v}$	$C_{4v}$	$C_{6v}$
III	(mm2)	(3m)	(4mm)	(6mm)
$C_{1h}$	no slash means mirror plane contains axis			
(m)				

4-fold z axis  
mirror  $\perp$  r z axis  
mirror  $\perp$  r y axis

4 - Groups

## ④ Groups with Improper Rotations

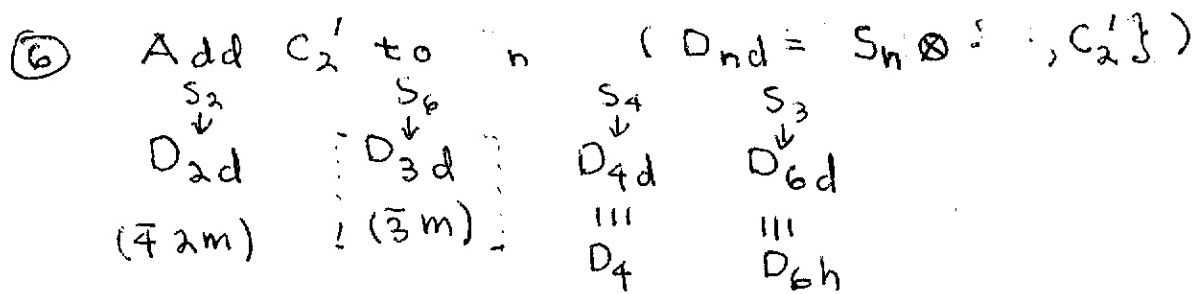
$S_2$	$S_3$	$S_4$	$S_6$
i	III	$\bar{4}$	$\bar{3}$
	$C_{3h}$		

3 New Groups

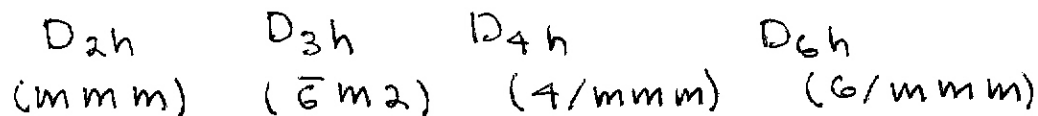
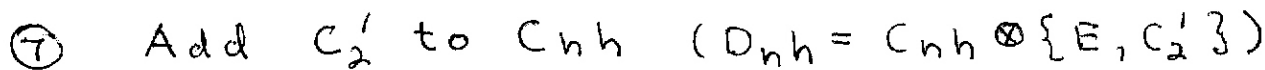
## ⑤ Rotations $\perp$ r to Symmetry Axis ( $C_2'$ ) Group Notation

$D_2$	$D_3$	$D_4$	$D_6$	$(D_1 \equiv C_2)$	$(D_n = C_n \otimes \{E, C_2'\})$
222	32	422	622		

4 New Groups



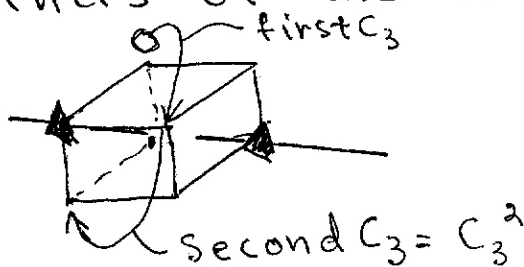
3 New Groups



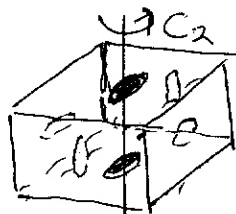
3 New Groups

27 So Far

Finally There Are The Five Cubic Groups.  
 Characterized By Four 3-Fold Axes (Through the corners of the cube)



Note That this Implies a  $C_2$  Axis



By symmetry the two others must be present

Thus There Are at least 4 3-fold and 3 2-fold axis

- This is T or 32 in international notation

- Add  $\sigma_h$  - By symmetry two others as well

This is  $T_h$  ( $m\bar{3}$ )

- Or one can add  $C_4$  to T - gives O ( $432$ )

- Or one can add  $S_4$  to T  $\rightarrow$  gives  $T_d$  ( $\bar{4}3m$ ) (GaAs)

- Finally one can add  $S_2$  to O - gives  $O_h$  ( $m\bar{3}m$ ) (Si)

Silicon is  $O_h$

GeAs is  $T_d (\bar{4} 3 m)$

1) Other symmetry operations.

$$t_m = m_1 \bar{a} + m_2 \bar{b} + m_3 \bar{c}$$

2) Screw Operations.

$$\{C_4 | \frac{1}{2}\}$$

$$\frac{1}{2} = \frac{c}{2} + \frac{a}{2} + \frac{b}{2}$$

← fraction of cell size (unit cell)

entire crystal is in an equivalent position

3) Glide Planes.

Reflection across a plane followed by a translation. Example  $\{\sigma [100] | \frac{1}{2}\}$

$$\frac{1}{2} = \frac{a}{2} + \frac{b}{2}$$

Axial Glide Plane

Reflection followed by translation  $\parallel$  to the mirror

Note that the most symmetric Group is the group of the lattice - holosymmetric point group

Space Group - Spatial Distribution of electron density

230 Space Groups.

Symmorphic  $\Rightarrow$  no displacement required to specify the space group. (displacement of a fraction of a crystal lattice)

there are 73 symmorphic space groups.  
Many glide planes & screw axes but these are generated from products of unit cell translations with the point operations.

To obtain them combine the 32 pt groups with the 14 Bravais Lattices.

Example:

Orthorhombic P lattice <sup>primitive</sup> ( $a \neq b \neq c$ ,  $\alpha = \beta = \gamma = 90^\circ$ )

(1) Take an object (basis  $\Rightarrow$  collection of atoms) that belongs to orthorhombic system.

e.g.  $C_{2v}$  ( $mm2$ ) (page 39)

(2) Put it at each lattice site

Fig. 2-10b shows two examples.

(3) New symmetries are created. -

TABLE 7-3 DIMENSION OF SOME BODY-CENTERED CUBIC STRUCTURES\*

Element	(Å)	Element	(Å)
Ba	5.025	Mo	3.147
Cr	2.884	Na	4.291
Cs	6.067 (78° K)	Nb	3.300
Eu	4.606	Rb	5.605 (78° K)
Fe	2.866	Ta	3.306
K	5.247 (78° K)	V	3.024
Li	3.509	W	3.165

\* Room temperature unless otherwise specified.

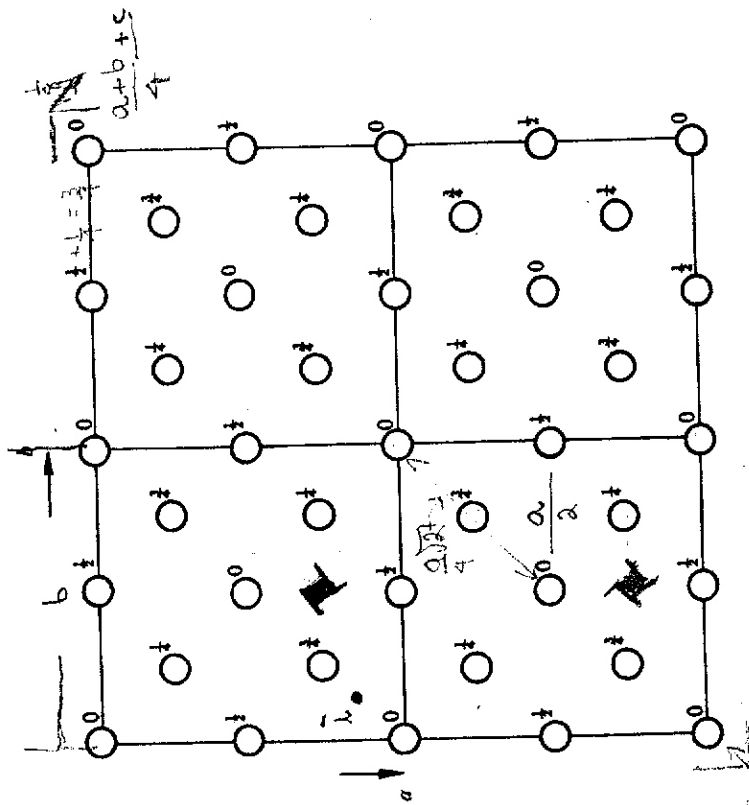


FIG. 7-6 Four unit cells of the diamond structure.

## SOME SIMPLE STRUCTURES

137

a close-packed structure, which would have twelve neighbors equally distributed around each atom, but the combination of eight nearest neighbors and six next-nearest neighbors is favored by several elements (see Table 7-3).

**EXERCISE 7-7** Calculate the efficiency of packing in the body-centered cubic structure.

**EXERCISE 7-8** Use data from Table 7-3 to calculate (a) the density of niobium metal and (b) the radius of a niobium atom.

## 7-5 Diamond structure

Four unit cells of the diamond structure are shown in Fig. 7-6. The space group is  $Fd\bar{3}m$ , and the atoms occupy the positions  $(0,0,0)$ ;  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  + face centering. The unit cell dimension of diamond is 3.567 Å. This structure is also possessed by silicon ( $a = 5.431$  Å), germanium ( $a = 5.657$  Å), and gray tin ( $a = 6.491$  Å).

**EXERCISE 7-9** Calculate the density of diamond.

**EXERCISE 7-10** Calculate the efficiency of packing in the diamond structure.

**EXERCISE 7-11** (a) On a diagram of the diamond structure (Fig. 7-4), draw lines showing which atoms are bonded to which.

(b) Calculate the length of the C—C bond in diamond.

(c) Calculate the C—C—C bond angle.

**EXERCISE 7-12** Calculate the structure factors, in terms of atomic scattering factors  $f$ , for the (111), (200), and (220) planes of diamond.

The great strength of diamond crystals is a consequence of the three-dimensional network of strong covalent bonds that link each carbon atom to four other carbon atoms.

## 7-6 Graphite structure

*Polymorphism* is quite common among the elements; that is, under different conditions of crystallization different structures result. The diamond structure is actually thermodynamically unstable under ordinary conditions of temperature and pressure, although the rate of

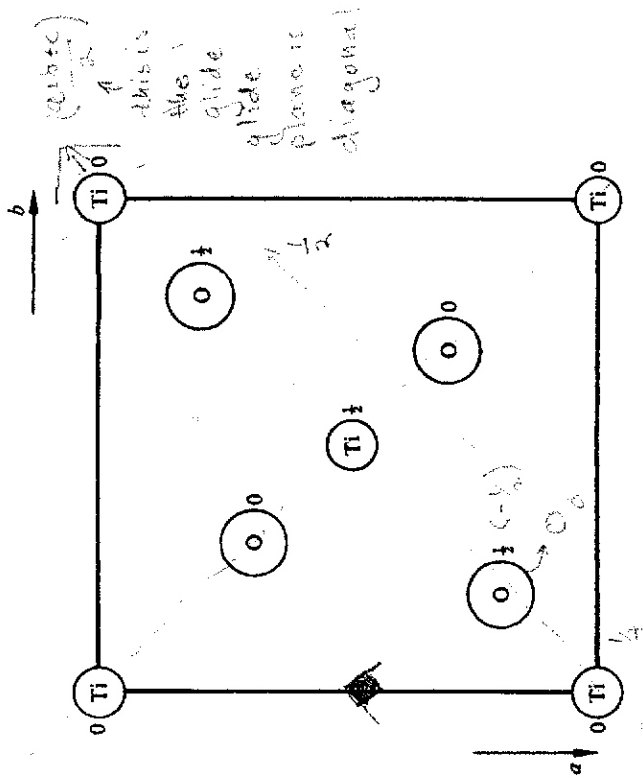


FIG. 7-10 The tetragonal  $\text{TiO}_2$  structure projected onto (001). Titanium ions are at  $0,0,0$ ;  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ . Oxygen ions are at  $0.30, 0.30, 0$ ;  $0.80, 0.20, \frac{1}{2}$ ;  $0.70, 0.70, 0$ ;  $0.20, 0.80, \frac{1}{2}$ .

**7-11 Rutile structure**

The structure possessed by rutile,  $\text{TiO}_2$ , by cassiterite,  $\text{SnO}_2$ , and by a number of other substances with small cations is shown in Fig. 7-10. The structure is tetragonal; for  $\text{TiO}_2$ ,  $a = 4.594 \text{ \AA}$ ,  $c = 2.958 \text{ \AA}$ ; for  $\text{SnO}_2$ ,  $a = 4.737 \text{ \AA}$ ,  $c = 3.186 \text{ \AA}$ . The space group is  $P4_2/mmm$ , the  $\text{Ti}^{4+}$  ions occupy positions  $(2a)$ :  $0,0,0$ ;  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ , and the  $\text{O}^{2-}$  ions occupy positions  $(4f)$ :  $\pm(x, x, 0)$ ;  $\frac{1}{2} + x, \frac{1}{2} - x, \frac{1}{2}$  with  $x$  very nearly 0.30. The titanium ion is surrounded by six oxygen ions which form a slightly distorted octahedron.

EXERCISE 7-16 Calculate the distance from the  $\text{Ti}^{4+}$  ion at  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$  in the rutile structure to each of its six  $\text{O}^{2-}$  neighbors.

EXERCISE 7-17 Describe the nearest neighbor environment of an  $\text{O}^{2-}$  ion in  $\text{TiO}_2$ . Give the distances wherever necessary.

SOME SIMPLE STRUCTURES

**7-12 Zinc sulfide structure**

Zinc blende,  $\text{ZnS}$ , is cubic. The  $\text{Zn}^{2+}$  ions are at  $0, 0, 0$ ,  $0 + \text{face centering}$ , and the  $\text{S}^{2-}$  ions are at  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2} + \text{face centering}$  (see Fig. 7-11). The space group is  $F\bar{4}3m$ , and the lattice dimension for  $\text{ZnS}$  is  $5.409 \text{ \AA}$ . If the zinc and sulfur atoms were identical, this would be the diamond structure. Each atom in  $\text{ZnS}$  is surrounded by a regular tetrahedron of atoms of the opposite type.

EXERCISE 7-18 Calculate the structure factors, in terms of  $f$ , for the  $(111)$ ,  $(200)$ , and  $(220)$  planes of cubic  $\text{ZnS}$ . Compare with the corresponding results for diamond from Exercise 7-12.

**7-13 Zincite structure**

Zincite,  $\text{ZnO}$ , has a hexagonal structure. The space group is  $P6_3mc$ , and both types of atom occupy positions  $(2b)$ :  $\frac{1}{3}, \frac{2}{3}, \frac{1}{2}, \frac{1}{2} + z$ ;  $\frac{2}{3}, \frac{1}{3}, \frac{1}{2}, \frac{1}{2} + z$ ; with  $z$  equal to 0 for zinc and about  $\frac{1}{8}$  for oxygen. The unit cell dimensions for  $\text{ZnO}$  are  $a = 3.250 \text{ \AA}$ ,  $c = 5.207 \text{ \AA}$ .

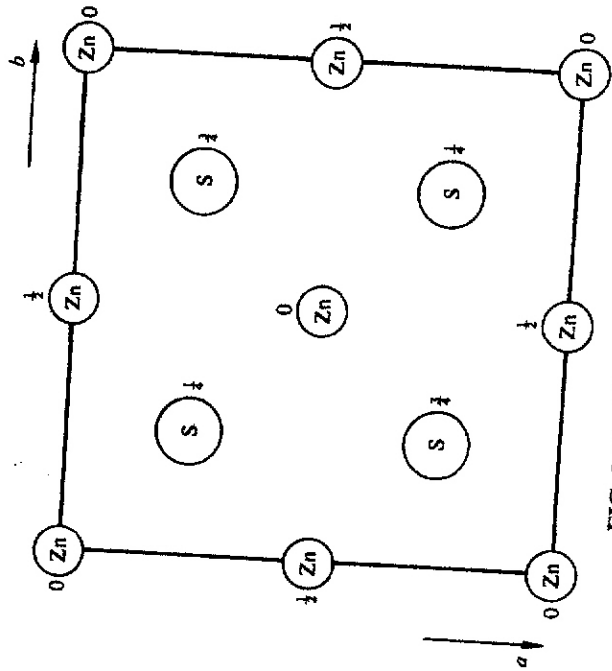
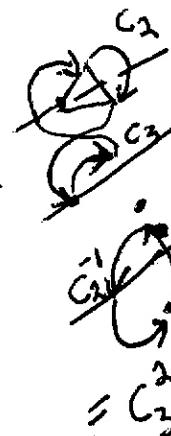
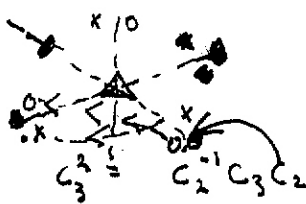


FIG. 7-11 The cubic  $\text{ZnS}$  structure.

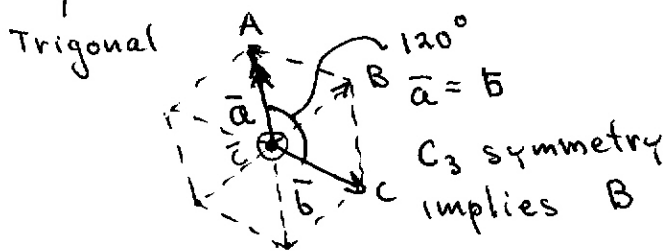


# Points To Be made

1) Explain in T  $4C_3$   $4C_3^2$   $3C_2$   
 $8C_3$  - same class



2) Distinction between hexagonal & trigonal  
 The application of  $C_6$  or  $S_6^5$  as well as  $C_3$  or  $S_6^5$  gives the same conditions on angles and axes.  
 Hexagonal



Trigonal can be centered to give Rhombohedral Lattice  
 Hexagonal cannot!

3) Lattice point - point for which environment is the same as for other lattice points.

4) Symmetry Operations of a crystal in addition to point symmetries

a)  $\vec{r} = m_1\vec{a} + m_2\vec{b} + m_3\vec{c}$  (translation)

Note b) Screw Operations:

$\{C_4|S^2\}$  is  $TiO_2$  symmetry operations ( $E, C_2, 2C_2'', i, \sigma_h, 2\sigma_d, 2\sigma_v$ ) & more

a symmetry operation of the crystal

$\{C_4|S^2\}$   $S^2 = a/2 + b/2 + c/2$  (fraction of a unit cell)

$\{C_4|I\}$  is not

But it is c) Glide planes! - Reflection followed by a translation parallel to the mirror plane

pt group of the crystal  
 Pt group is  $D_{4h}$

$\{\sigma[100]|S^2\}$   $S^2 = b/2$

- b-glide
- n-glide
- d-glide

space group is  $Fd\bar{3}m$ , and the atoms occupy the positions  $(0,0,0)$ ;  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  + face centering. The unit cell dimension of diamond is 3.567 Å.

7-5 Diamond structure

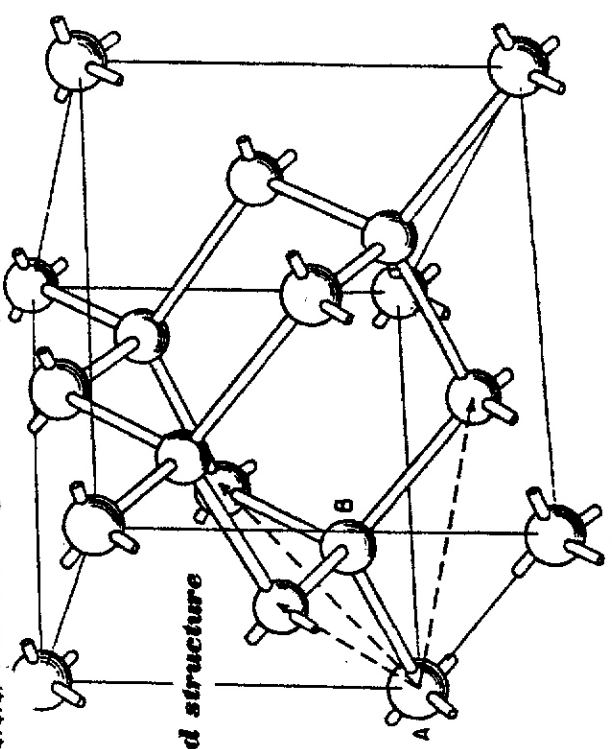


Fig. 2.1. Diamond crystal lattice, showing the tetrahedral bonding, the cubic symmetry, and the primitive translation vectors (as the dashed lines). The balls represent the atoms and the bars the covalent bonds between them.

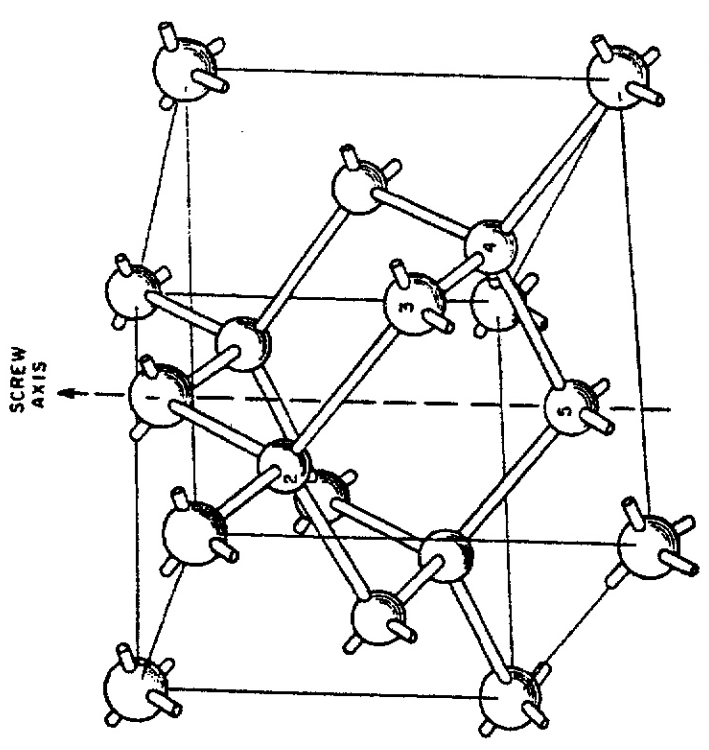


Fig. 2.4. The screw axis in diamond.

This structure is also possessed by silicon ( $a = 5.431$  Å), germanium ( $a = 5.657$  Å), and gray tin ( $a = 6.491$  Å).

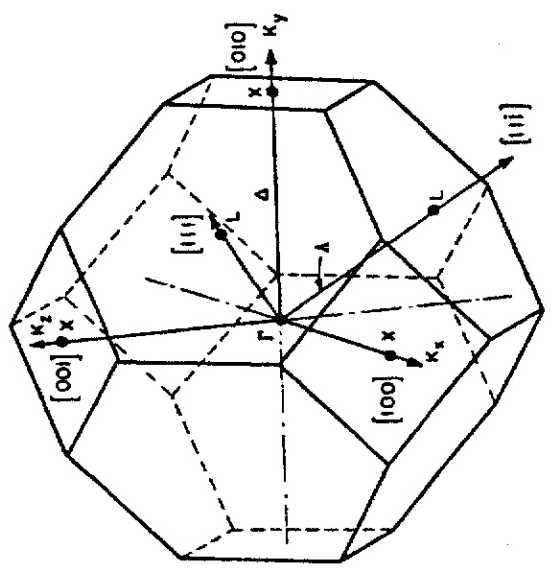


Fig. 2.2. First Brillouin zone of the diamond and zinc blende lattices. The most important symmetry points and lines are indicated. Note that there are six equivalent  $X$  points, eight  $L$  points, etc.

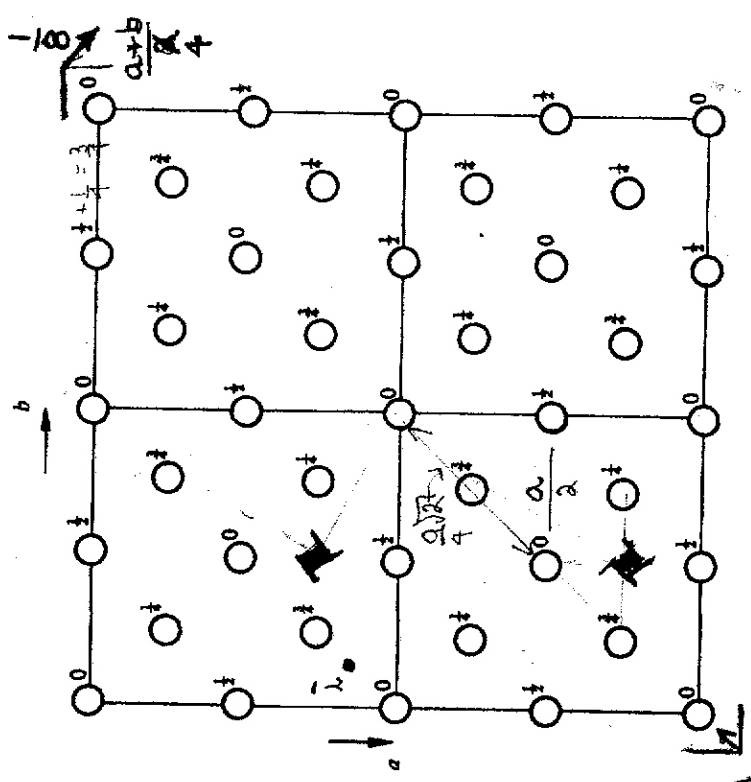


FIG. 7-6 Four unit cells of the diamond structure.