

Minerals - the building blocks of rocks

As we have seen, the dominant cations in the  $\oplus$  are

Mg	32%	
Si	33%	
Fe	26%	— about 90% of this in core

see also K&H Fig 5.1  
8 dominant elements in crust

also Cox Fig. 1.3  
x-section of  $\oplus$

Al	2.2%	
Ca	2.2%	
Ni	1.6%	— also mostly in core
Cr	0.4%	— also mostly in core
K	0.25%	

Not surprisingly, the dominant minerals are K-Ca-Fe-Mg-Al silicates

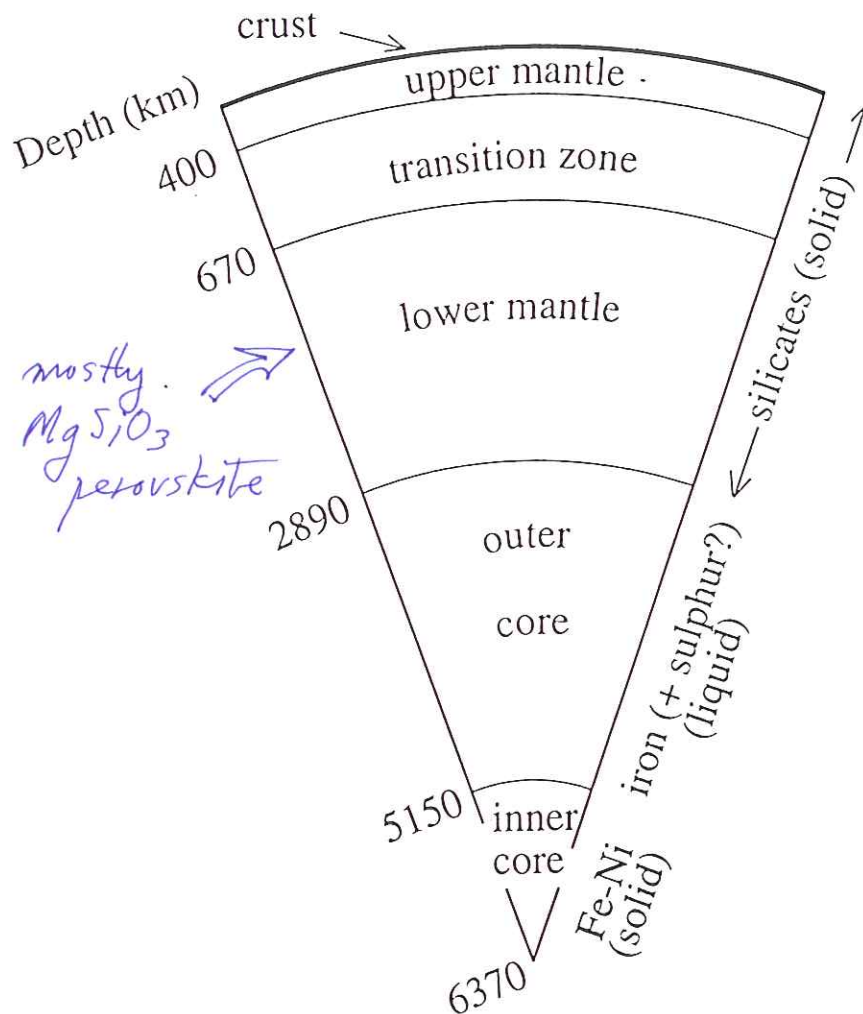
The most common anion, by far, is oxygen  $\ominus$

Planets are not a sea of atoms  
Atoms are condensed into ordered structures - minerals

NB - meaning different than animal, vegetable, mineral - 200 years ago

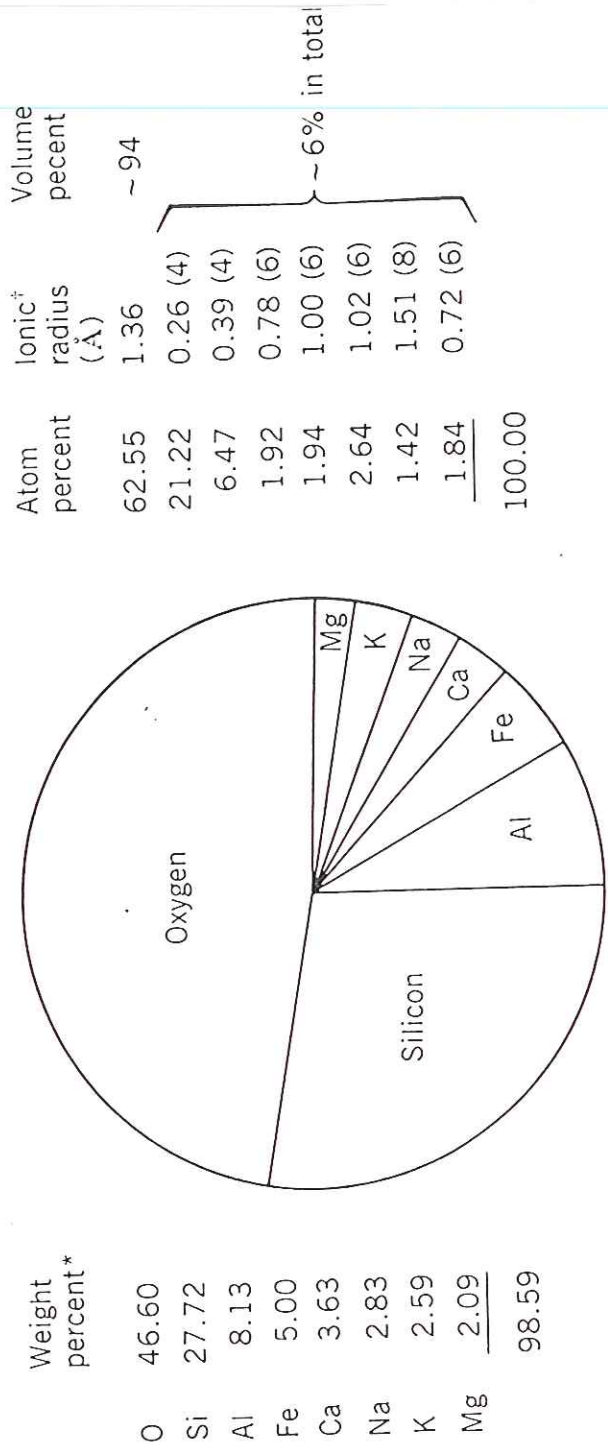
**Table 3-5. Abundances of metallic elements in chondritic meteorites:**

	Percent of total metal atoms
Magnesium (Mg)	32
Silicon (Si)	33
Iron (Fe)	26
Aluminum (Al)	2.2
Calcium (Ca)	2.2
Nickel (Ni)	1.6
Sodium (Na)	1.3
Chromium (Cr)	0.40
Potassium (K)	0.25
Manganese (Mn)	0.20
Phosphorus (P)	0.19
Titanium (Ti)	0.12
Cobalt (Co)	0.10



**Figure 12.9.** A schematic section through the earth. The seismic discontinuity at 400 km occurs at a temperature and pressure consistent with that for the transformation of olivine to spinel. The discontinuity at 670 km may be due to a change in chemical composition at this depth, with the perovskite phase of  $MgSiO_3$  the primary constituent of the lower mantle.

FIG. 5.1 The eight most common elements in the Earth's crust. (\*From Mason, B. and Moore, C. B., 1982, *Principles of Geochemistry*, 4th ed. John Wiley & Sons, Inc., New York. †Ionic radii taken from Table 4.8. Numbers in parentheses refer to coordination number.)



Weight percent





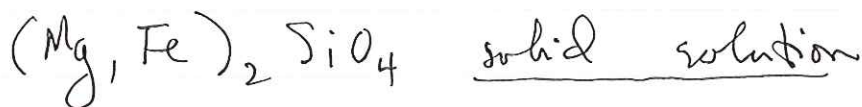
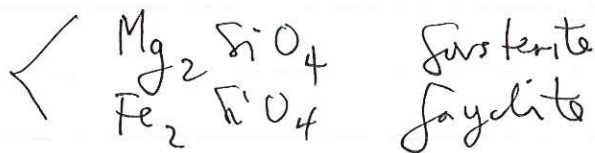
Today's lecture - several topics

- how do we know the structures of minerals - X-ray diffraction
- what are the structures of the most common rock forming minerals?

Dictionary defn of mineral (Klein & Hurlbut page 1)

- homogeneous
- ordered atomic arrangement
- definite chemical composition  
e.g.  $\text{SiO}_2$  quartz
- sometimes one ~~one~~ cation can substitute for another  
e.g.  $(\text{Mg}, \text{Fe})_2 \text{SiO}_4$  olivine

end members



e.g., a common upper-mantle mineral is  $(\text{Mg}_{0.9} \text{Fe}_{0.1})_2 \text{SiO}_4$

90% of cation sites filled by Mg, 10% by Fe

## **DEFINITION OF MINERAL**

Although it is difficult to formulate a succinct definition for the word mineral, the following is generally accepted:

*A mineral is a naturally occurring homogeneous solid with a definite (but generally not fixed) chemical composition and a highly ordered atomic arrangement. It is usually formed by inorganic processes.*

Mineral structure - orderly arrangement of atoms  
begin by talking about non-silicates

Simple example NaCl - halite - table salt

Putnis Fig. 5.2  
K&H Fig 4.30  
4.42

BRING a SALT SHAKER

Perfect cubic symmetry

each  $Na^+$  surrounded by 6  $Cl^-$   
each  $Cl^-$  surrounded by 6  $Na^+$

octahedral coordination (six-fold)

Putnis Fig. 5.3 shows electron density map. Possible to measure ionic radius of  $Na^+$  and  $Cl^-$

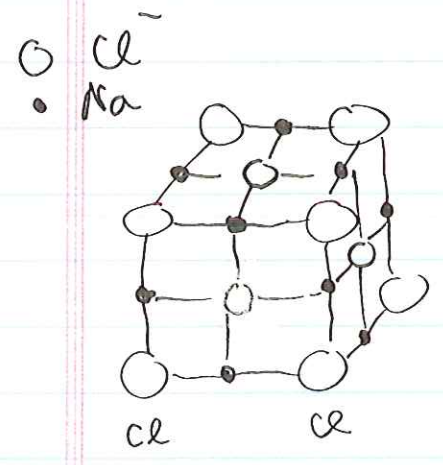
$Na^+$	1 Å
$Cl^-$	1.8 Å

$$1 \text{ Å} = 10^{-10} \text{ m}$$

$$= 0.1 \text{ nm}$$
~~$$= 10^{-4} \text{ μm}$$~~

$$= 10^{-4} \text{ μm}$$

$$= 10^{-7} \text{ mm}$$



Na-Cl bond length 2.8 Å

unit cell dimension 5.6 Å



FIG. 4.30 An idealized ionic structure in two dimensions.

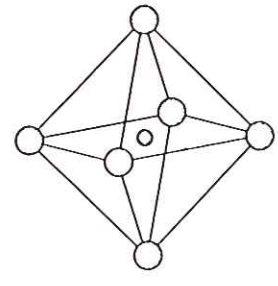
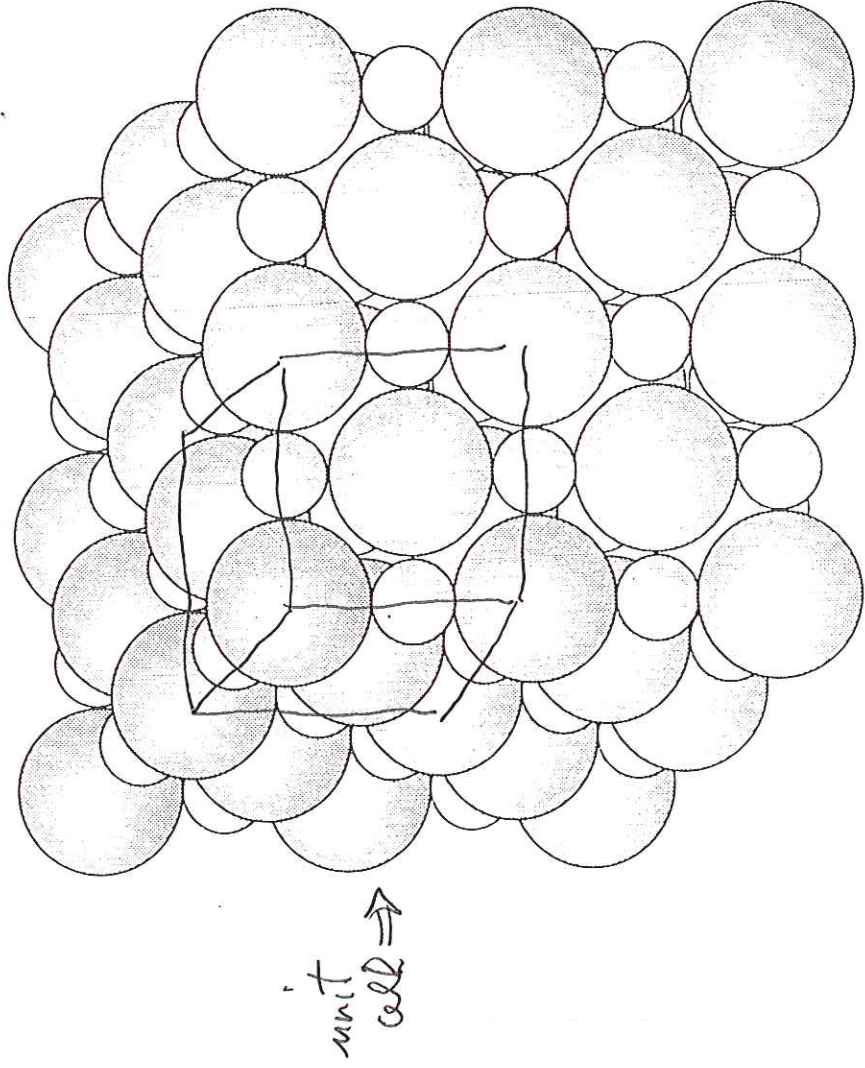
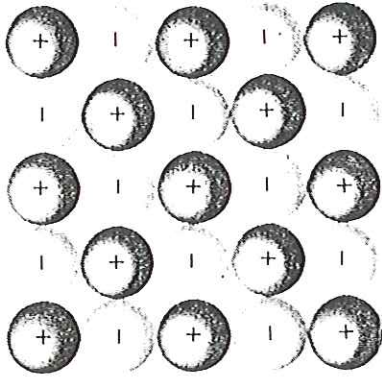


Figure 5.2. The sodium chloride structure, in which  $\text{Na}^+$  is octahedrally coordinated by six  $\text{Cl}^-$  ions. The octahedron, drawn in the same orientation, shows the atoms reduced in size as is usual in 'ball and stick' models.

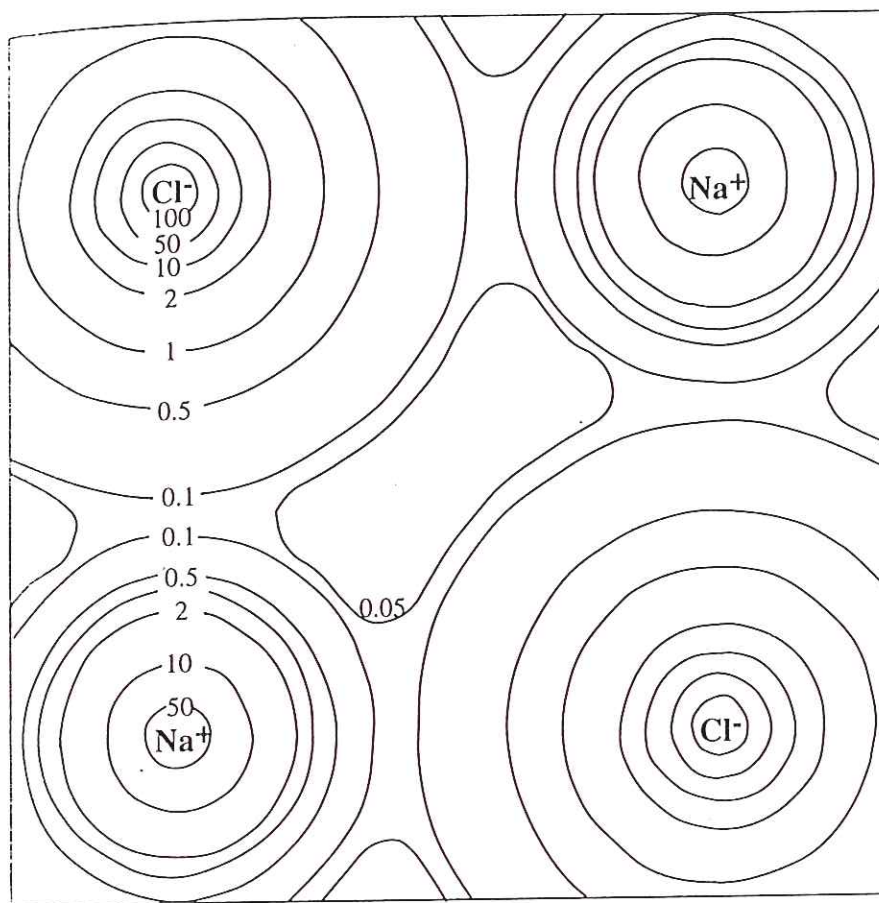


Figure 5.3. An electron density contour map showing that the electrons are concentrated around the ionic centres, with a pronounced minimum in the density between the ions. (After Adams, 1981.)

ionic radii

Na<sup>+</sup> 1 Å

Cl<sup>-</sup> 1.8 Å

bond length 2.8 Å

unit cell 5.6 Å × 5.6 Å × 5.6 Å



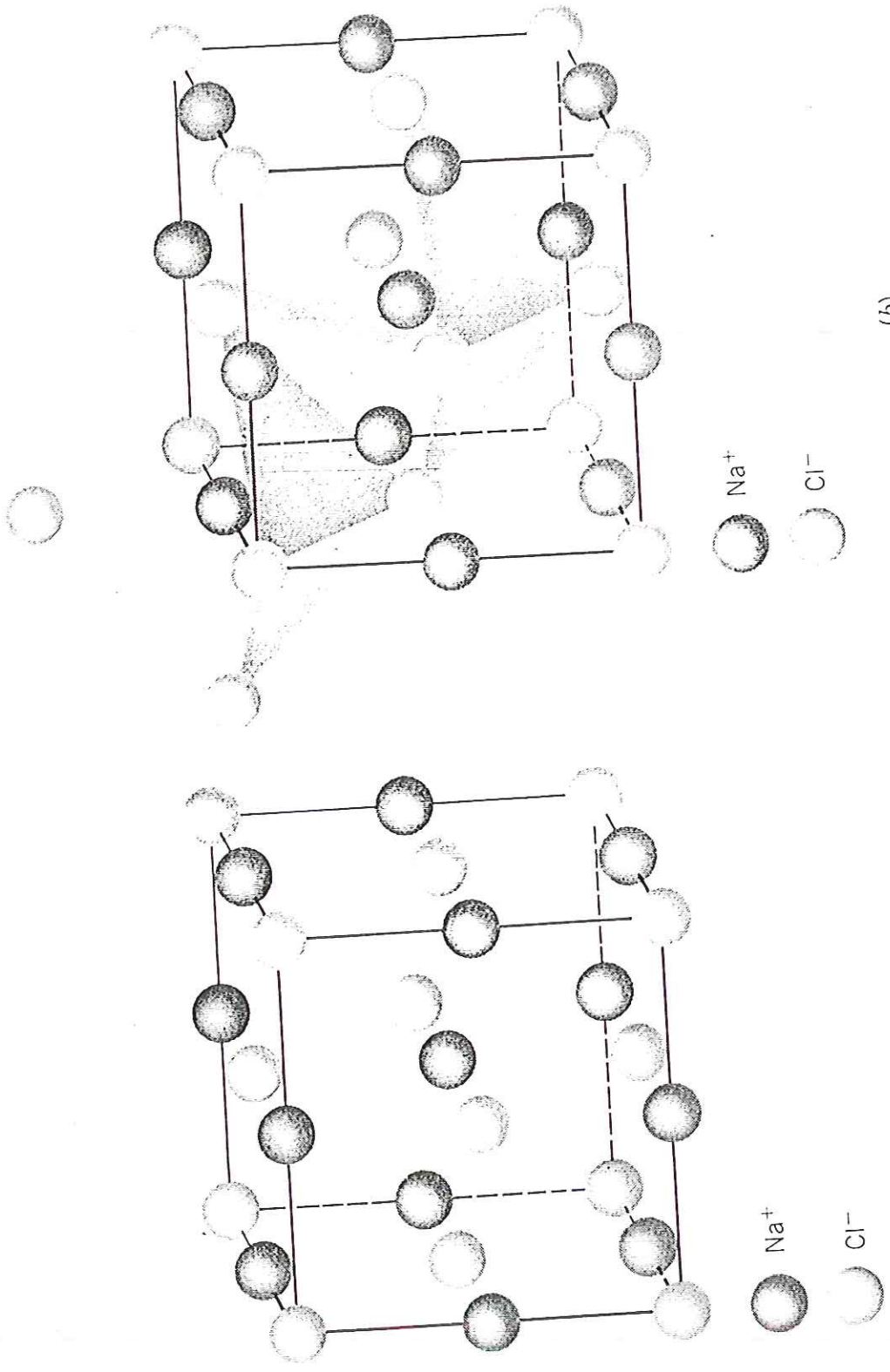


FIG. 4.42 (a) The structure of NaCl, halite ( $F4/m\bar{3}2/m = Fm\bar{3}m$ ). The Na<sup>+</sup> and Cl<sup>-</sup> ions are arranged in a face-centered cubic lattice. (b) The same structure showing the edge-sharing octahedrons about the Na<sup>+</sup>. Similar edge-sharing octahedrons could be drawn about Cl<sup>-</sup>.

FIG. 11.39. Halite, hopper-shaped crystals.

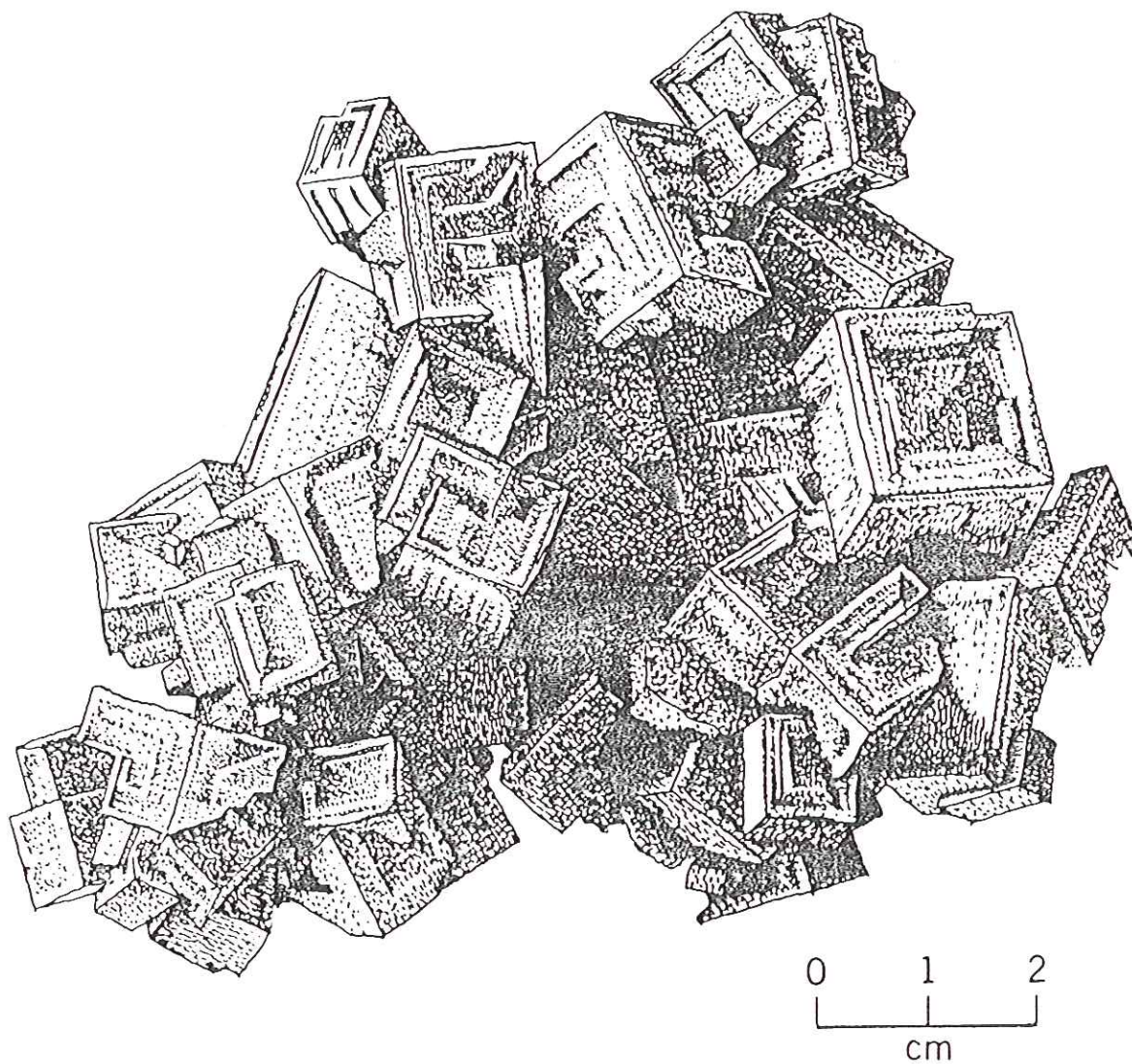
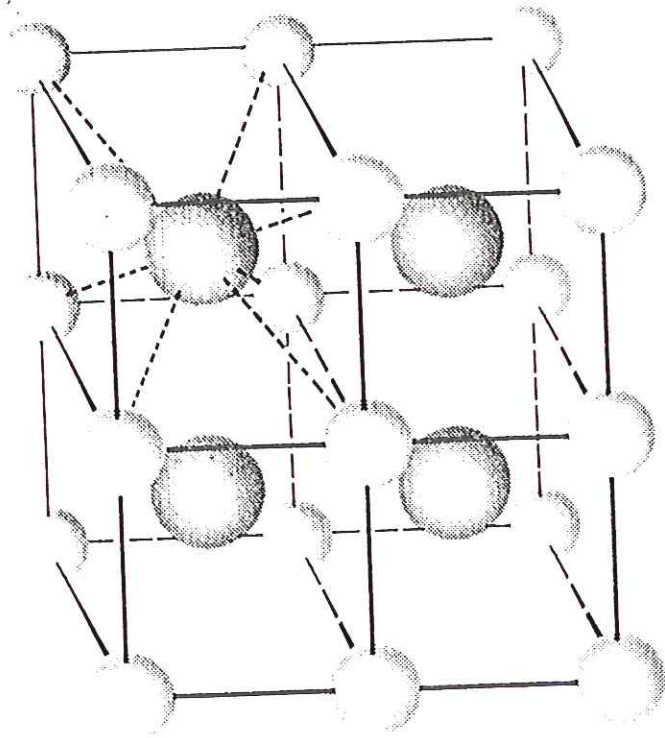


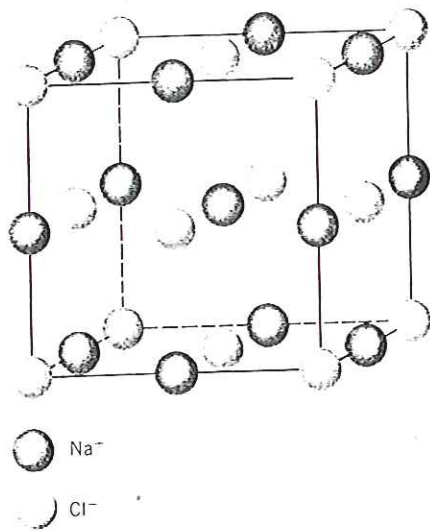




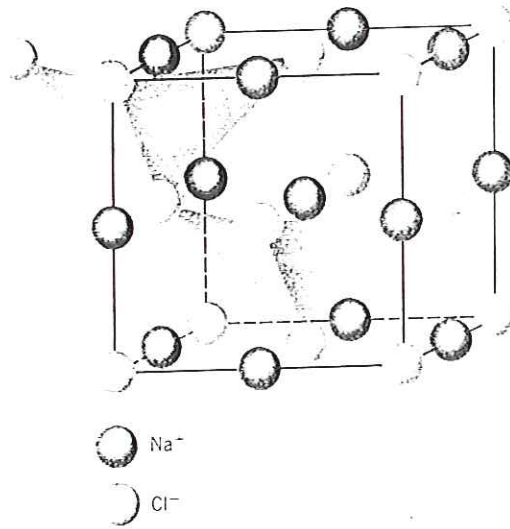


FIG. 4.43 The structure of CsCl ( $P4/m\bar{3}2/m = Pm\bar{3}m$ ). The ions are distributed in a primitive cubic lattice. Each cation is surrounded by eight neighbors, and so is each anion.





(a)



(b)

FIG. 4.42 (a) The structure of NaCl, halite ( $F4/m\bar{3}2/m = Fm\bar{3}m$ ). The  $\text{Na}^+$  and  $\text{Cl}^-$  ions are arranged in a face-centered cubic lattice. (b) The same structure showing the edge-sharing octahedrons about the  $\text{Na}^+$ . Similar edge-sharing octahedrons could be drawn about  $\text{Cl}^-$ .

FIG. 11.37. The structure of halite. Compare this illustration with Fig. 4.42.

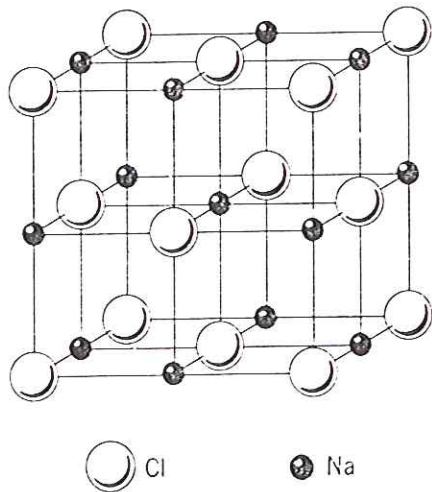
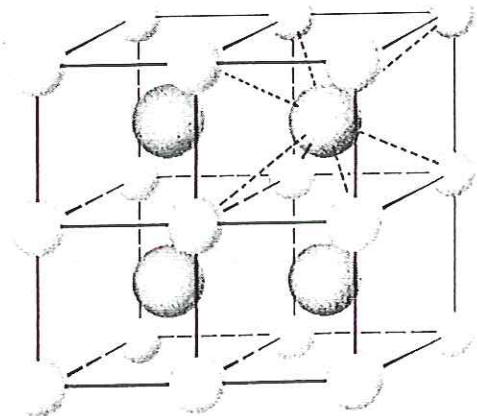


FIG. 4.43 The structure of CsCl ( $P4/m\bar{3}2/m = Pm\bar{3}m$ ). The ions are distributed in a primitive cubic lattice. Each cation is surrounded by eight neighbors, and so is each anion.





See K & H Figs. 4.22 and 4.24

~~AX~~ AX

smaller is not good -  
why? Then anions

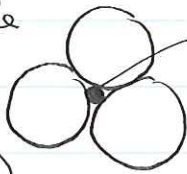
A = cation

X = anion, e.g. Cl

start to feel each other too much or O

3-fold coordination

just push the  
anions apart



what is size of cation  
that can just fit?

answer:  $R_A = 0.155 R_X$

NB - bigger  
ones can fit too



4-fold tetrahedral coordination

~~etc.~~

$R_A = 0.225 R_X$

etc.

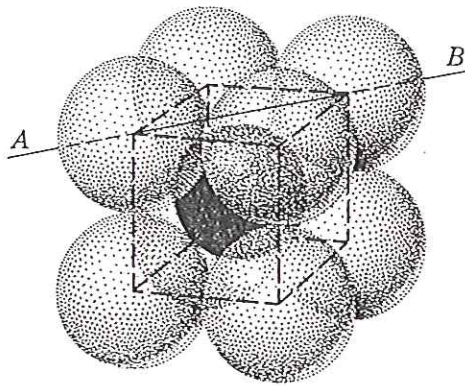
In general, higher coordinated interstitial  
~~sites~~ sites can accommodate larger  
cations

$$\text{NaCl} : R_{\text{Na}} / R_{\text{Cl}} = \frac{1}{1.8} = 0.6$$

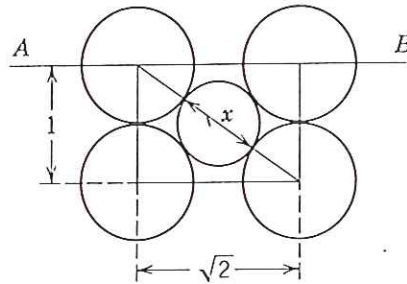
$$\text{CsCl} : R_{\text{Cs}} / R_{\text{Cl}} = \frac{1.7}{1.8} \approx 0.9$$

$\text{Cs}^+$  ion is 70% bigger than  $\text{Na}^+$   
needs more room - hence crystallizes  
in 8-fold coordination

FIG. 4.22 (a) Cubic or 8-coordination of X ions about an A ion.  $R_A : R_X > 0.732$ . (b) Limiting condition for cubic coordination. (c) Octahedral or 6-coordination of X ions about an A ion.  $R_A : R_X = 0.732-0.414$ . (d) Limiting condition for octahedral coordination. (e) Tetrahedral or 4-coordination of X ions about an A ion.  $R_A : R_X = 0.414-0.255$ . (f) Limiting condition for tetrahedral coordination. (g) Trigonal or 3-coordination of X ions about an A ion.  $R_A : R_X = 0.225-0.155$ . (h) Limiting condition for trigonal coordination. (i) Linear or 2-coordination of X ions about an A ion.  $R_A : R_X < 0.155$ .



(a)

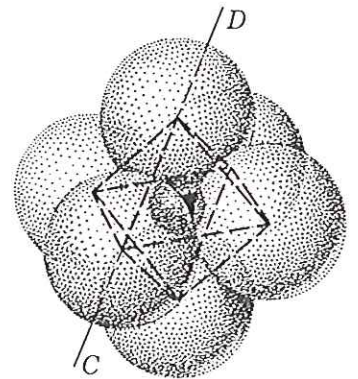


$$(1+x)^2 = (1)^2 + (\sqrt{2})^2$$

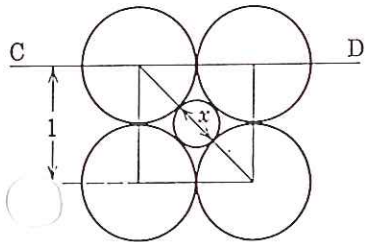
$$1+x = \sqrt{1+2} = 1.732$$

$$x = 0.732$$

(b)



(c)

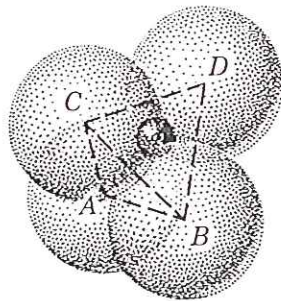


$$(1+x)^2 = (1)^2 + (1)^2$$

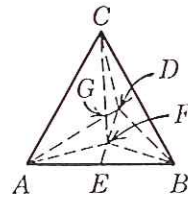
$$1+x = \sqrt{2} = 1.414$$

$$x = 0.414$$

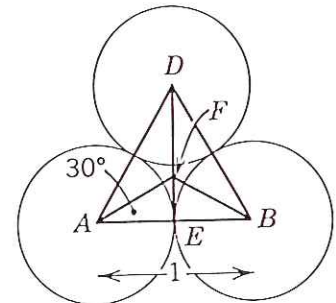
(d)



(e)



G is location of center of small ion, in center of tetrahedron



In base triangle

$$\cos 30^\circ = \frac{AE}{AF}$$

$$\therefore AF = \frac{AE}{\cos 30^\circ} = \frac{1/2}{\cos 30^\circ}$$

$$= \frac{1}{2} \cdot \frac{2}{\sqrt{3}} = \frac{1}{\sqrt{3}}$$

In vertical triangle CAF

$$CF = \sqrt{AC^2 - AF^2} = \sqrt{(1)^2 - \left(\frac{1}{\sqrt{3}}\right)^2} = \sqrt{1 - \frac{1}{3}}$$

$$\frac{\sqrt{2}}{\sqrt{3}} = .81649$$

Also  $CG = \frac{3}{4} CF$ , because center of tetrahedron G is  $\frac{1}{4}$  up from the base.

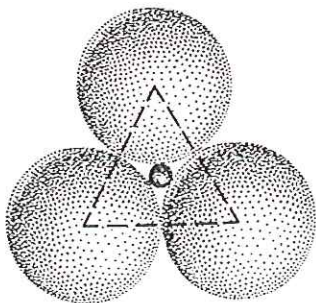
$$\text{Furthermore } CG = \frac{1}{2} + \frac{1}{2}x$$

$$\therefore \frac{1}{2} + \frac{1}{2}x = \frac{3}{4} \cdot .81649 = .6124$$

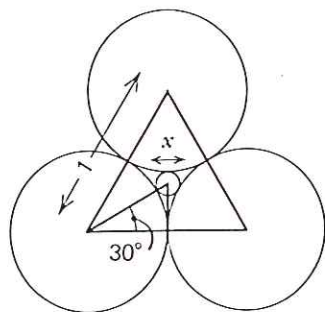
$$\therefore \frac{1}{2}x = .612 - .5 = .1124$$

$$x = 0.225$$

(f)



(g)



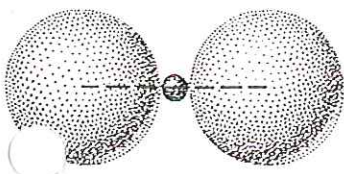
$$\cos 30^\circ = \frac{1/2}{1/2 + 1/2 x}$$

$$1/2 + 1/2 x = \frac{1/2}{\cos 30^\circ} = \frac{1/2}{0.8660} = 0.5774$$

$$1/2 x = 0.5774 - 0.50 = 0.0774$$

$$x = 0.155$$

(h)



(i)

Minimum Radius Ratio $R_A : R_X$	Coordination Number C. N.		Packing Geometry	
< 0.155	2	Linear		
0.155	3	Corners of an equilateral triangle (triangular coordination)		
<del>0.255</del> 0.225	4	Corners of a tetrahedron (tetrahedral coordination)		
0.414	6	Corners of an octahedron (octahedral coordination)		
0.732	8	Corners of a cube (cubic coordination)		
1.0	12	Corners of a cuboctahedron (close packing)		

FIG. 4.24 Atomic packing schemes.



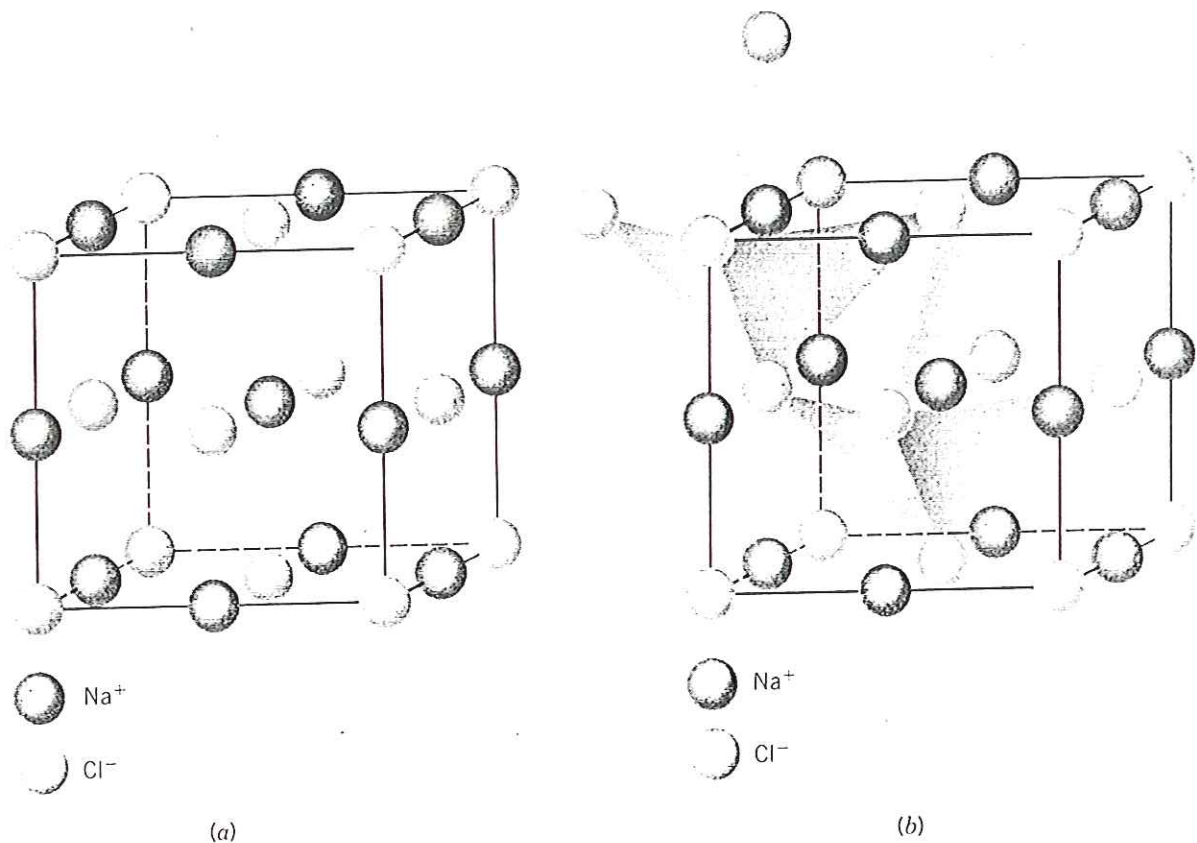
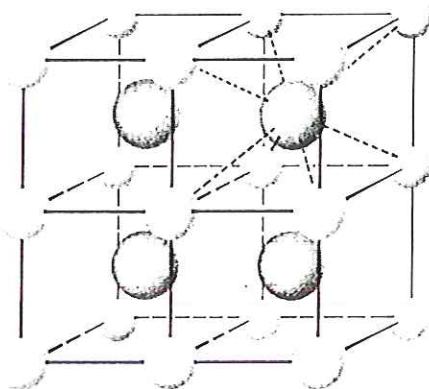


FIG. 4.42 (a) The structure of NaCl, halite ( $F4/m\bar{3}2/m = Fm\bar{3}m$ ). The Na<sup>+</sup> and Cl<sup>-</sup> ions are arranged in a face-centered cubic lattice. (b) The same structure showing the edge-sharing octahedrons about the Na<sup>+</sup>. Similar edge-sharing octahedrons could be drawn about Cl<sup>-</sup>.

FIG. 4.43 The structure of CsCl ( $P4/m\bar{3}2/m = Pm\bar{3}m$ ). The ions are distributed in a primitive cubic lattice. Each cation is surrounded by eight neighbors, and so is each anion.

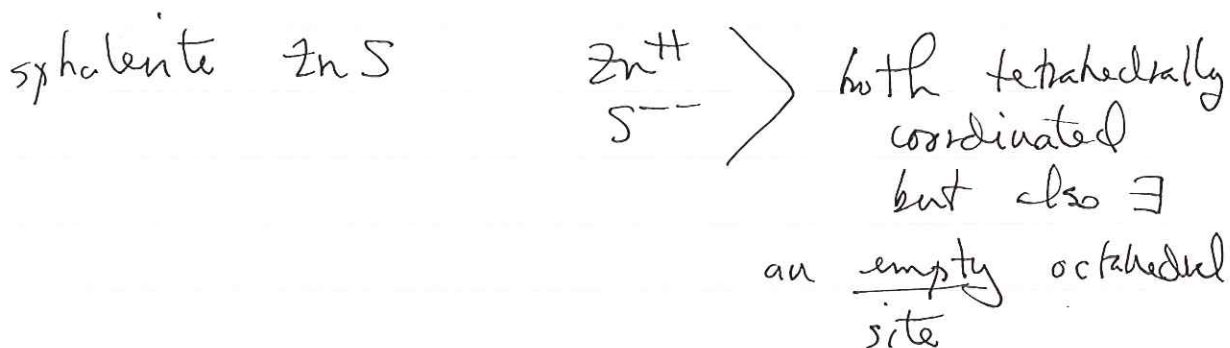
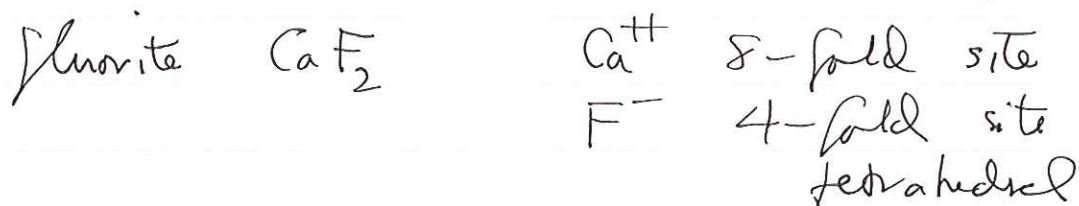


In both NaCl and CsCl the cation and anion have the same coordination

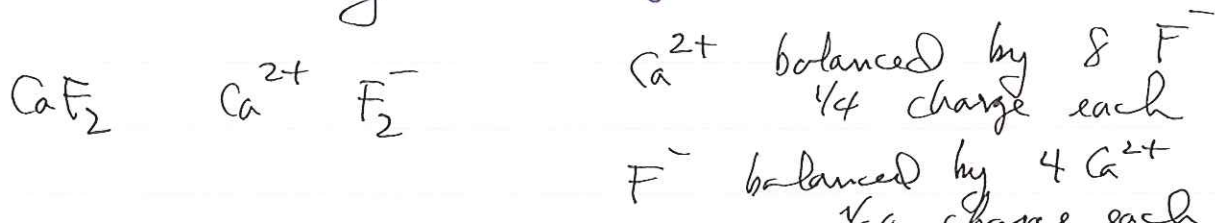
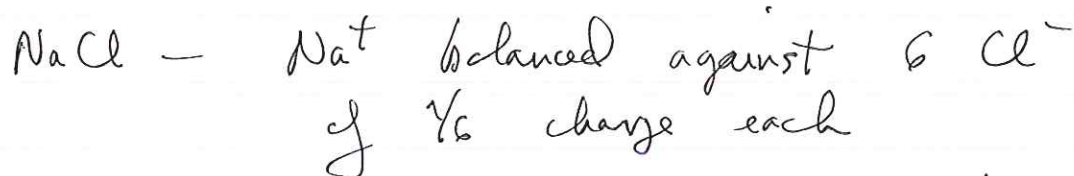


In other minerals, however, the two may be differently coordinated

For ~~example~~ example - K&H Fig. 4.18



K&H Fig. 4.26 illustrates concept of charge-sharing



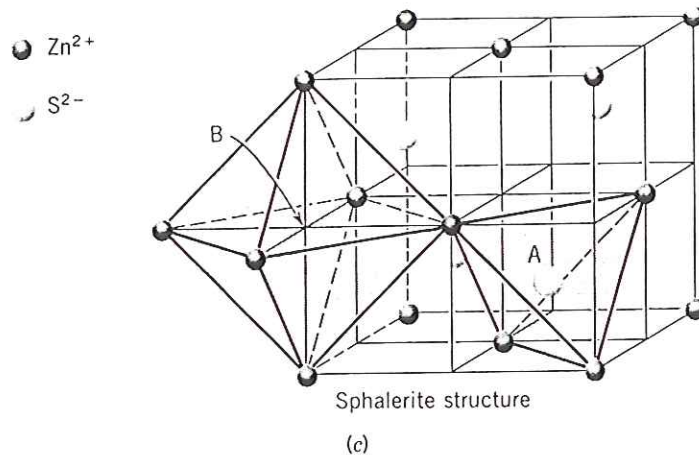
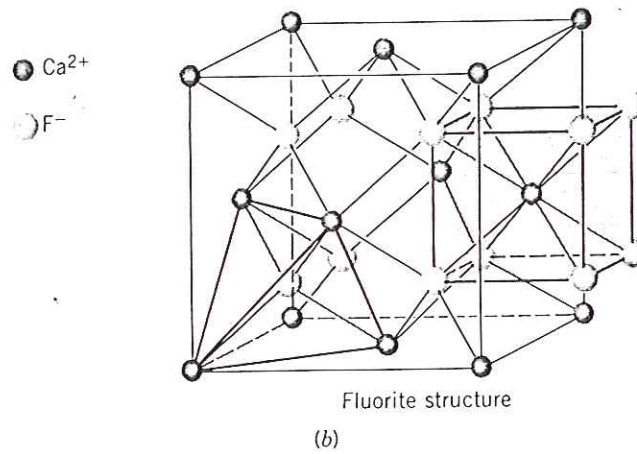
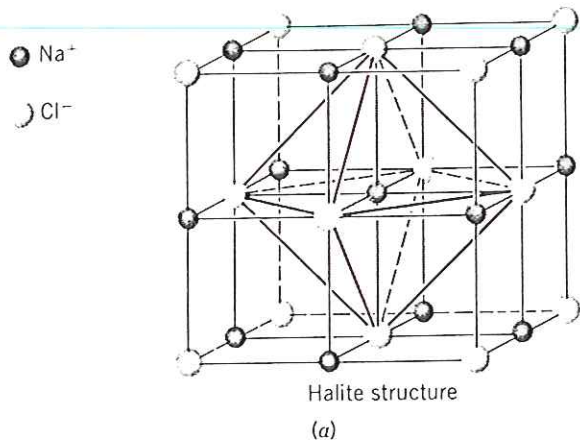
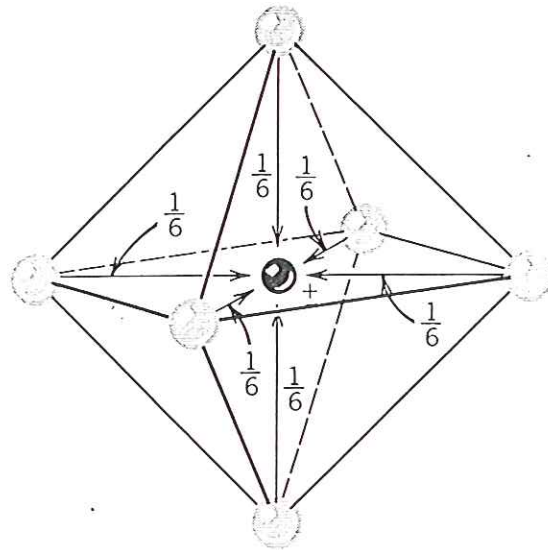


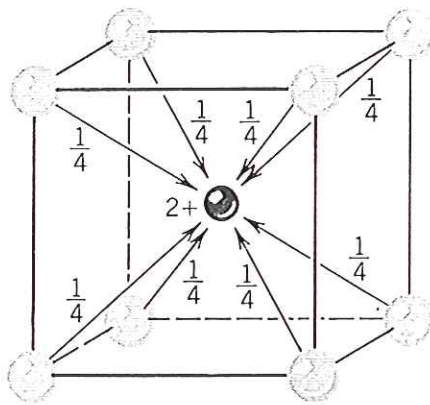
FIG. 4.18 Visualization of coordination polyhedra in various structure types. (a) The halite, NaCl, structure ( $F4/m\bar{3}2/m = Fm\bar{3}m$ ) with the ions arranged on a face-centered cubic lattice. Both Na<sup>+</sup> and Cl<sup>-</sup> are in 6-coordination (C.N. 6) with each other. A coordination polyhedron about Na<sup>+</sup> is shown; it is an octahedron. (b) The fluorite, CaF<sub>2</sub>, structure ( $Fm\bar{3}m$ ) with the Ca<sup>2+</sup> ions arranged on a face-centered cubic lattice. F<sup>-</sup> is coordinated to four Ca<sup>2+</sup> (C.N. 4); this is tetrahedral in shape. Each Ca<sup>2+</sup>, however, is coordinated to eight neighboring F<sup>-</sup> (C.N. 8); this is cubic in shape. (c) The sphalerite, ZnS, structure ( $F\bar{4}3m$ ), with Zn<sup>2+</sup> ions on a face-centered cubic lattice. Each S<sup>2-</sup> (in position marked A) is surrounded by four Zn<sup>2+</sup> ions, in tetrahedral coordination (C.N. 4). The position marked B is empty and has octahedral surroundings.



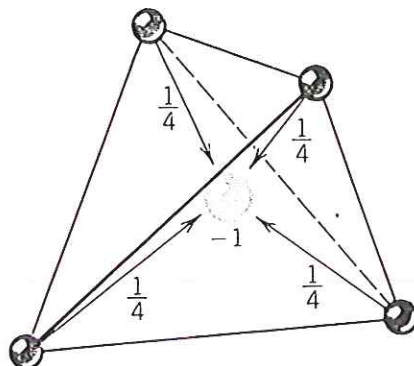
FIG. 4.26 Illustration of the neutralization of a central ion by bonds from the nearest neighbors. Each of these bonds has an electrostatic valency (e.v.). The total of all bonds with specific e.v.'s neutralizes the central ion. (a) Octahedral coordination in the halite structure (see Fig. 4.18a). (b) Cubic coordination of  $F^{-1}$  around  $Ca^{2+}$  in the fluorite structure (see Fig. 4.18b). (c) Tetrahedral coordination of  $Ca^{2+}$  around  $F^{-}$  in the fluorite structure (see Fig. 4.18b).



C. N. = 6; e. v. =  $\frac{1}{6}$   
 $6 \times (\frac{1}{6}) = 1$



C. N. = 8; e. v. =  $\frac{1}{4}$   
 $8 \times (\frac{1}{4}) = 2$



C. N. = 4; e. v. =  $\frac{1}{4}$   
 $4 \times (\frac{1}{4}) = 1$

Table 4.9 lists ionic radii of various cations and gives their preferred coordination with oxygen ~~1.36 Å~~ 1.36 Å

$K^+$  1.51 Å biggest common cation  
8-12

$Na^+$   
 $Ca^{2+}$  } next biggest 8-6

$Fe^{2+}$   
 $Fe^{3+}$   
 } octahedral

$Al^{3+}$  octahedral or tetrahedral

$Si^{4+}$  tetrahedral

The silica tetrahedra is the building block of silicate minerals

These can be strung together into chains, double chains, sheets as shown in Fig. 6.3

Before discussing this, however — how are crystal structures determined?

oxygen ionic radius 1.36 Å

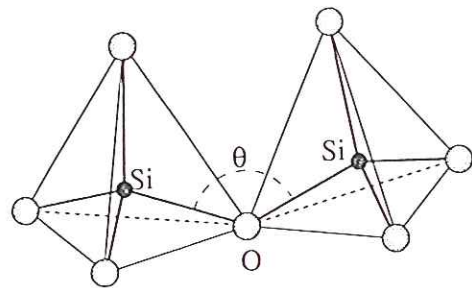
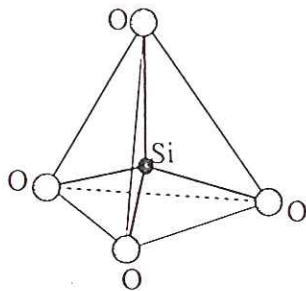
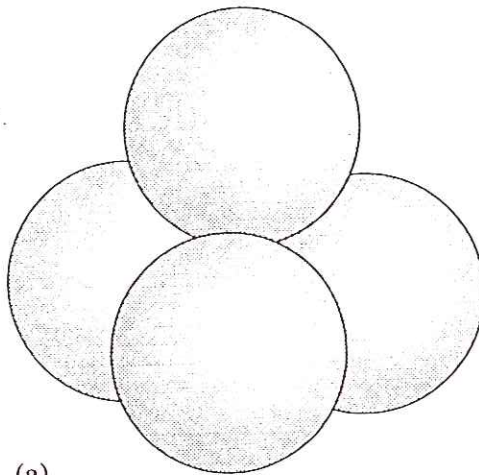
Table 4.9

**SOME COMMON ELEMENTS (EXCLUSIVE OF HYDROGEN) THAT OCCUR IN ROCK-FORMING MINERALS, ARRANGED IN DECREASING IONIC SIZE**

Ion	Coordination Number with Oxygen	Ionic Radius Å
O <sup>2-</sup>		1.36 (3)
K <sup>+</sup>	8-12	1.51 (8)-1.64 (12)
Na <sup>+</sup>	8-6 } cubic to	1.18 (8)-1.02 (6)
Ca <sup>2+</sup>	8-6 } octahedral	1.12 (8)-1.00 (6)
Mn <sup>2+</sup>	6 }	0.83 (6)
Fe <sup>2+</sup>	6 }	0.78 (6)
Mg <sup>2+</sup>	6 } octahedral	0.72 (6)
Fe <sup>3+</sup>	6 }	0.65 (6)
Ti <sup>4+</sup>	6 }	0.61 (6)
Al <sup>3+</sup>	6 }	0.54 (6)
Al <sup>3+</sup>	4 }	0.39 (4)
Si <sup>4+</sup>	4 } tetrahedral	0.26 (4)
P <sup>5+</sup>	4 }	0.17 (4)
S <sup>6+</sup>	4 }	0.12 (4)
C <sup>4+</sup>	3 triangular	-0.08 (3)

\*The first column lists the most common ionic (valency) states of the elements. The second column lists their most common coordination with respect to oxygen, and the third column lists ionic sizes for specific coordinations (the number in parentheses is **C.N.**). A complete listing of elemental abundances is given in Table 5.1.

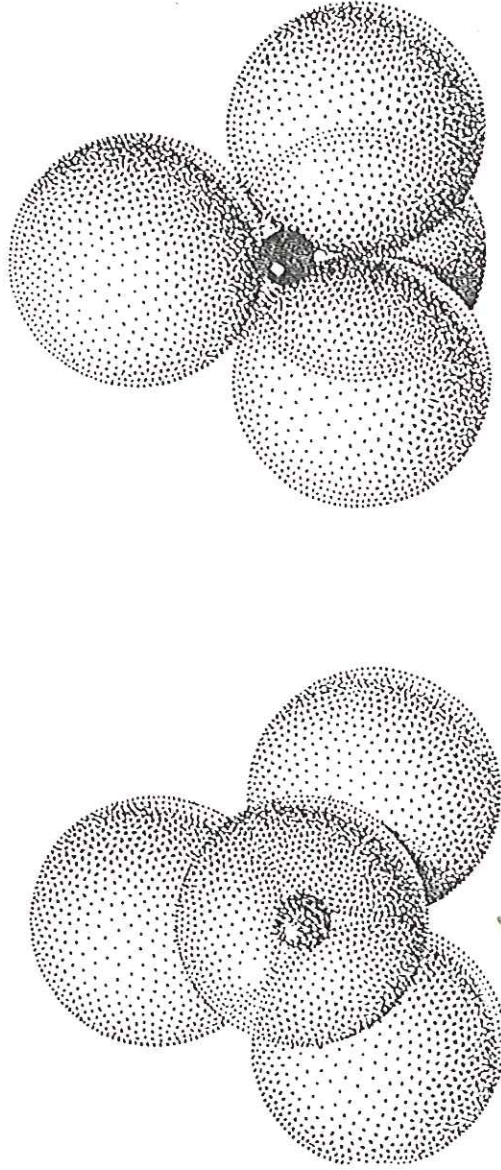
$\text{Si}^{4+}$        $0.26 \text{ \AA}$   
 $\text{O}^{2-}$        $1.36 \text{ \AA}$   
 $\text{Si-O}$  bond length       $1.62 \text{ \AA}$

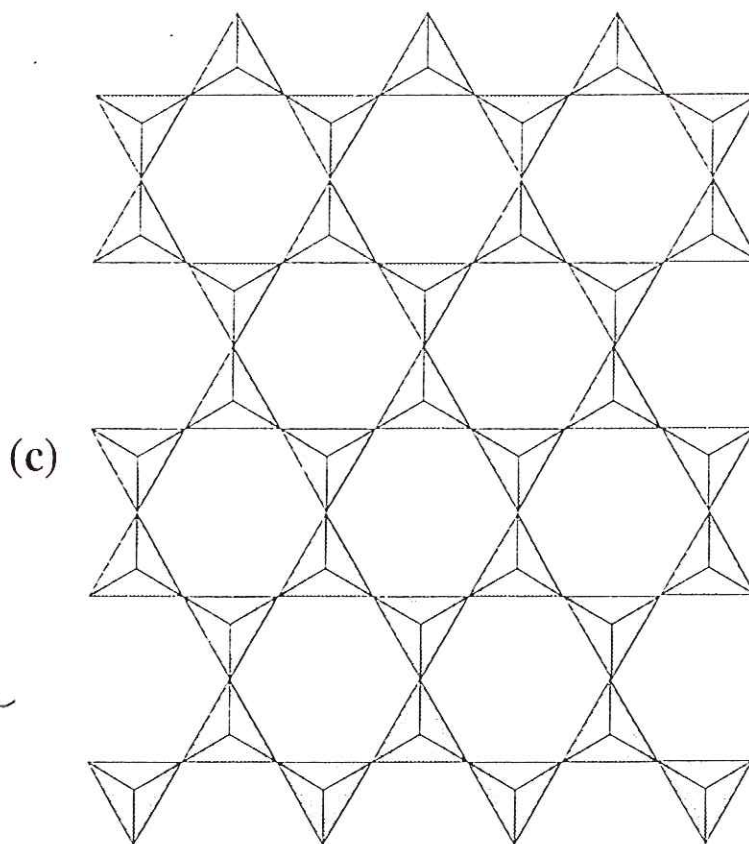
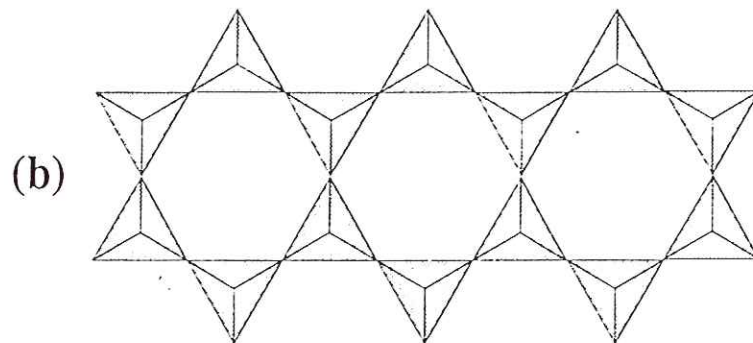
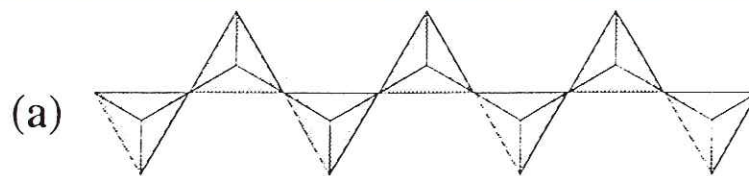


**Figure 6.1.** Silicate structures are built up from  $\text{SiO}_4$  tetrahedra. (a) A space-filling model showing four oxygen atoms at the corners of a tetrahedron, obscuring the Si atom at the centre. (b) A less realistic, but clearer model of an  $\text{SiO}_4$  tetrahedron, showing the Si-O bonds. (c) Two  $\text{SiO}_4$  tetrahedra sharing a corner to form an  $\text{Si}_2\text{O}_7$  pair. The angle  $\theta$  is the Si-O-Si bond angle.



G. 13.2. Close packing representation of  $\text{SiO}_4$  tetrahedron.





*show  
quartz  
structure*

**Figure 6.3.** (a) Part of an infinite single chain of  $\text{SiO}_4$  tetrahedra with each tetrahedron sharing two corners, as in the pyroxene structure. (b) Part of an infinite double chain of  $\text{SiO}_4$  tetrahedra with half the tetrahedra sharing two corners, and the other half sharing three corners, as in the amphibole structure. (c) Part of an infinite sheet of  $\text{SiO}_4$  tetrahedra, each tetrahedron sharing three corners, as in the sheet silicate structures.



## X-ray diffraction

W.H. & W.L. Bragg — father and son  
Nobel Prize in Physics 1915

X rays are electromagnetic waves

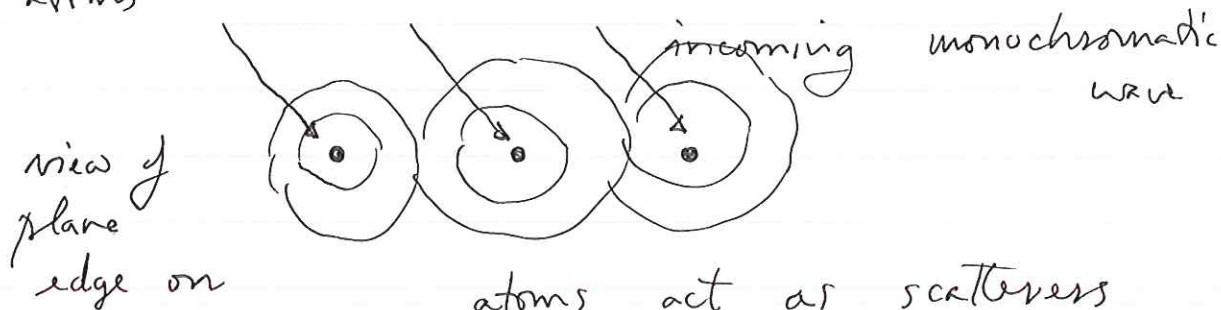
Wavelengths  $\lambda \sim$  ~~0.7 - 2.3 Å~~ 0.7 - 2.3 Å  
depending upon the source  
See Table p. 277 K & H

$\lambda \sim$  size of atoms — i.e., the size of the electron clouds

This prevents direct imaging of atoms in the xtal lattice.

Rather, the waves are diffracted

Consider waves incident upon a ~~the~~ plane of atoms



use Fig 7.3  
K & H to  
explain this

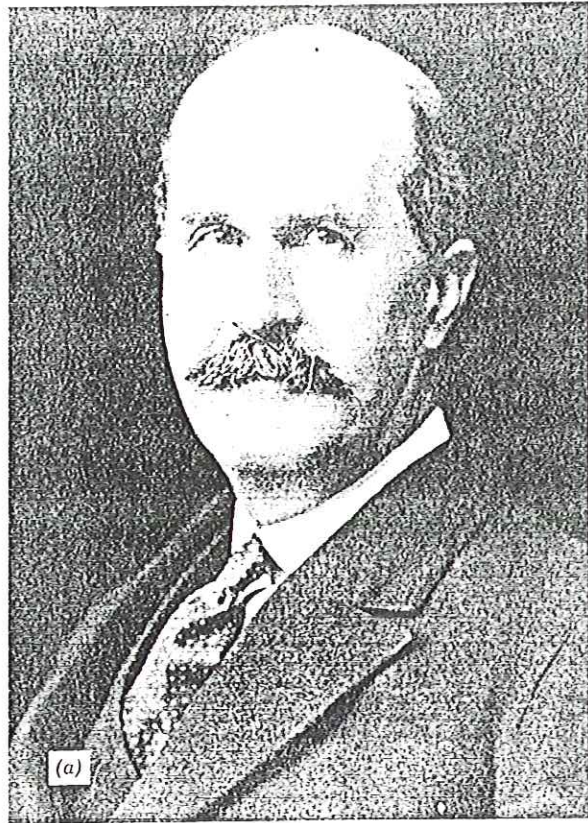
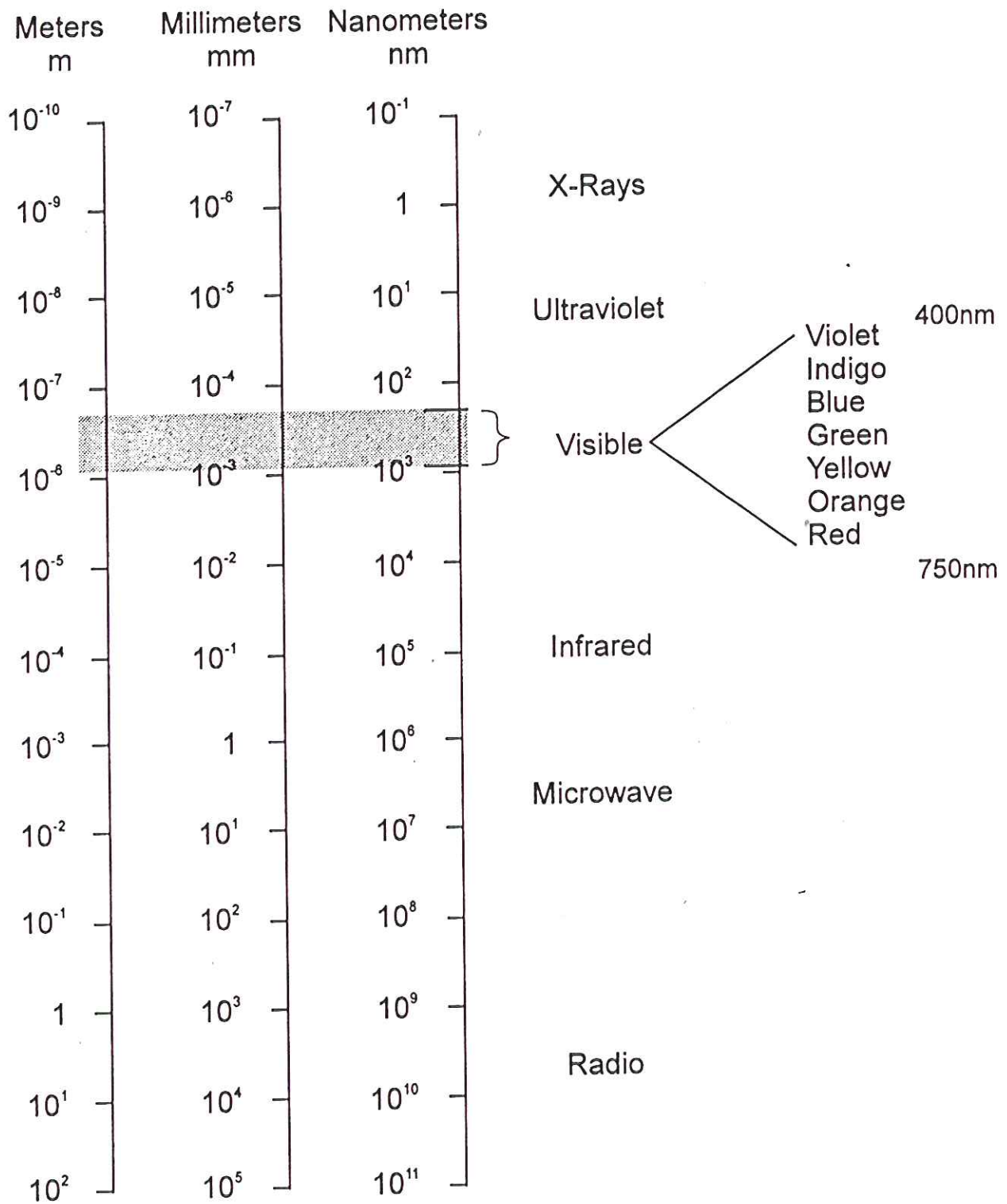


FIG. 1.7. Portraits of (a) Sir William Henry Bragg (1862–1942) and (b) his son Sir William Lawrence Bragg (1890–1971). Father and son received the Nobel Prize for Physics in 1915. Both men are eminently known for their researches in the field of crystal structure by X-ray methods. (a from Godfrey Argent, London, photograph by Walter Stoneman; b from Times Newspapers, Ltd., London.)

# Wavelength

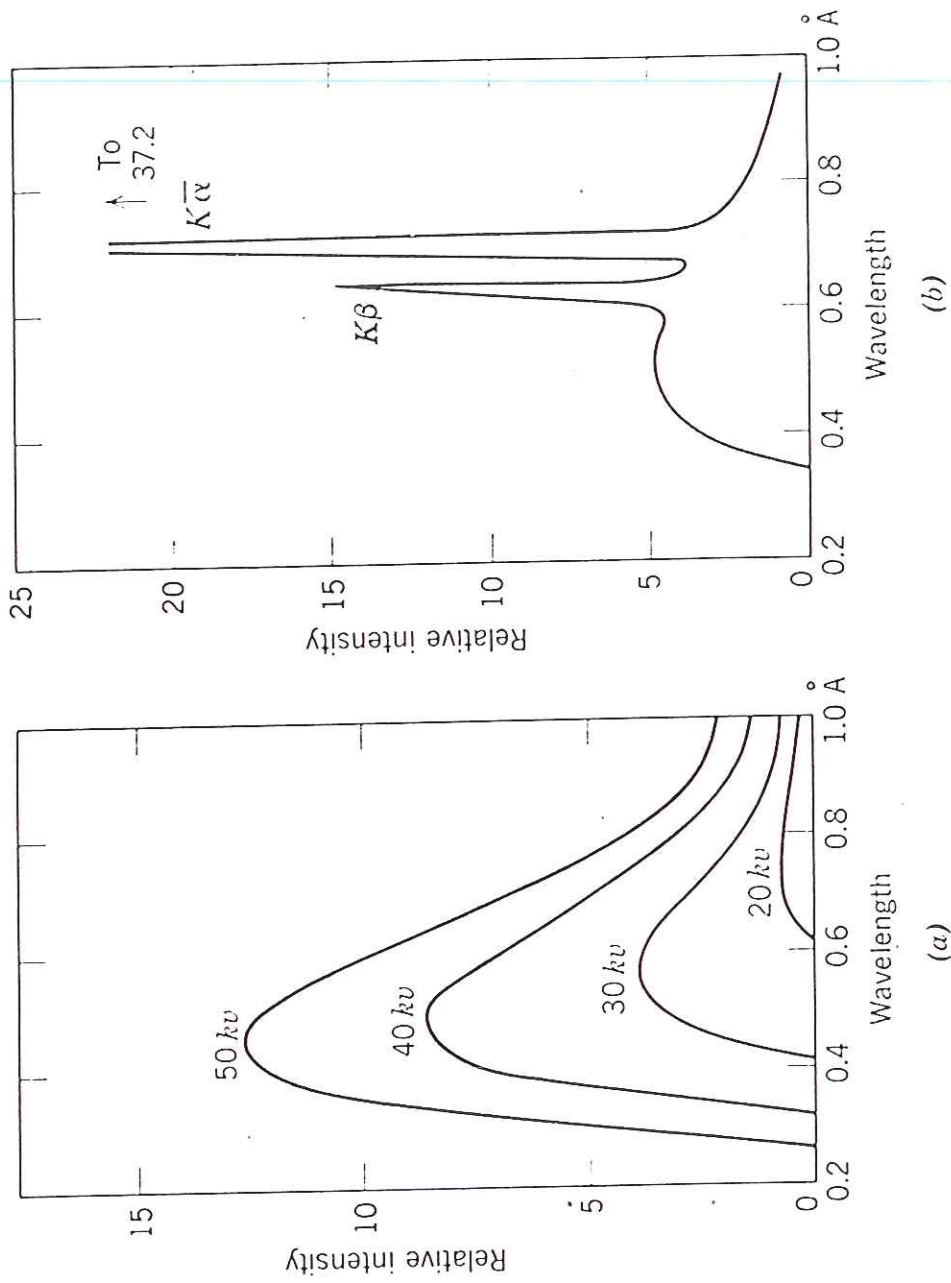




The wavelengths of the characteristic X-radiation emitted by various metals have been accurately determined. The  $K\bar{\alpha}$  wavelengths (weighted averages of  $K\alpha_1$  and  $K\alpha_2$ ) of the most commonly used are:

	$\text{\AA}$	$\text{\AA}$
Molybdenum	0.7107	Cobalt 1.7902
Copper	1.5418	Iron 1.9373
	Chromium	2.2909

FIG. 7.2. X-ray spectra. (a) Distribution of intensity with wavelength in the continuous X-ray spectrum of tungsten at various voltages. (b) Intensity curve showing characteristic wavelengths superimposed on the continuous X-ray spectrum of molybdenum. (After Ulrey, C. T., 1918, An experimental investigation of the energy in the continuous X-ray spectra of certain elements. *Phys. Reviews*, v. 11, pp. 401-410.)





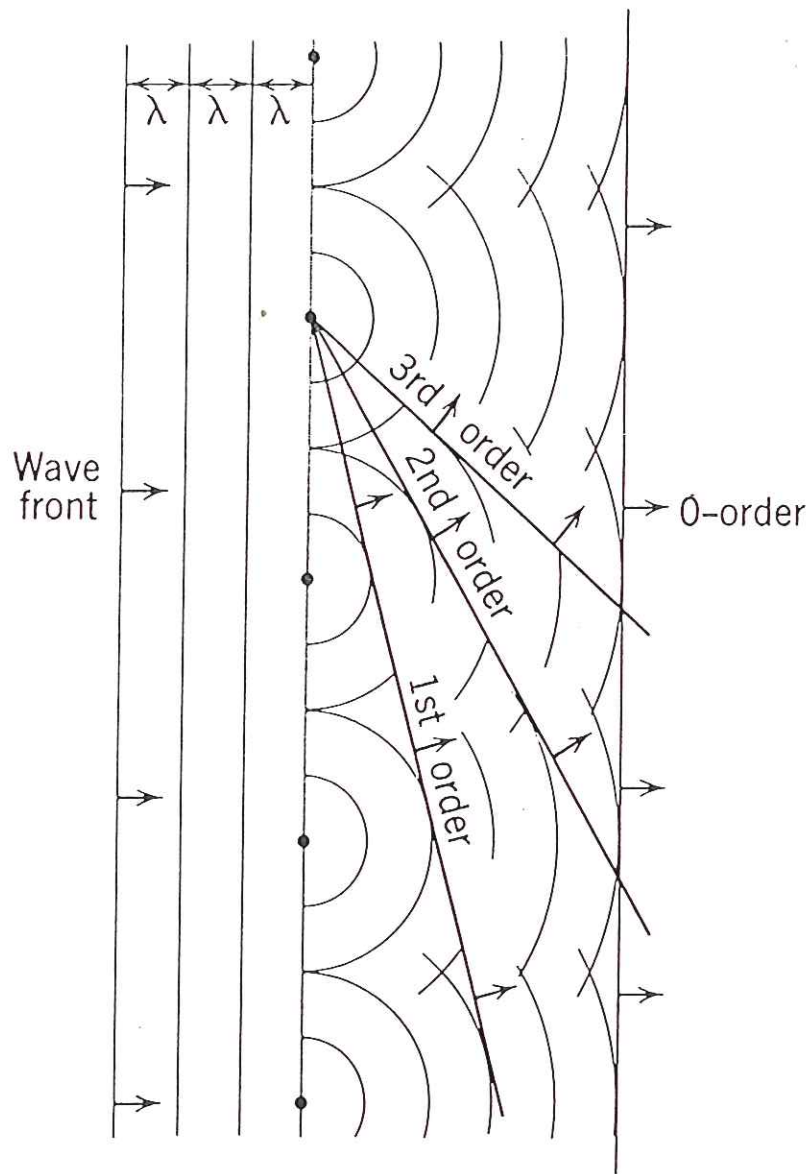


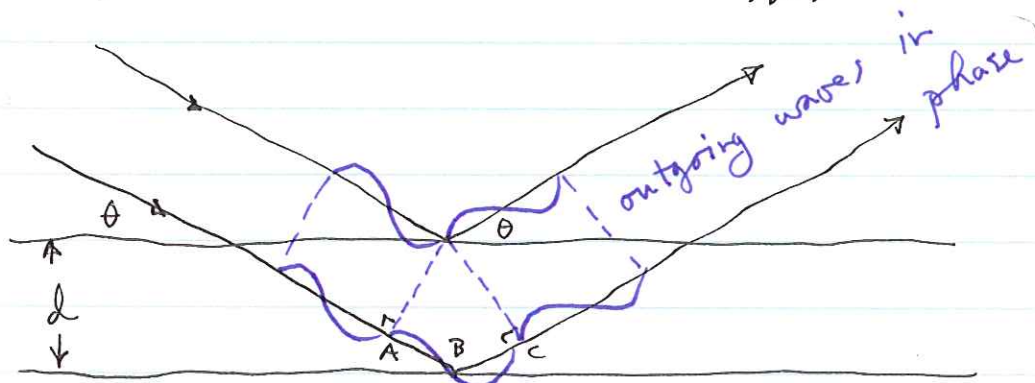
FIG. 7.3. Scattering of X-rays by a row of equally spaced, identical atoms.

In most directions these ~~waves~~  
destructively interfere

But in certain ~~directions~~ directions  
they interfere constructively

See figure 3.11

$$\text{length } AB + BC = 2d \sin \theta$$



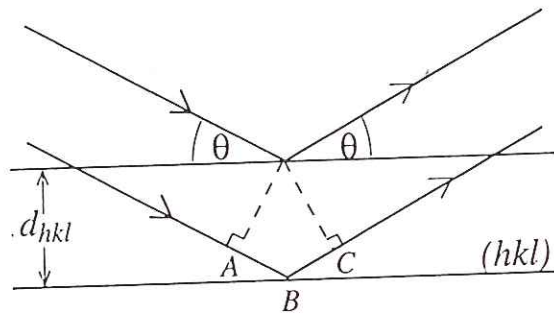
$n=1$ : fit exactly one  
wavelength here

The outgoing waves from all planes will  
be in phase if

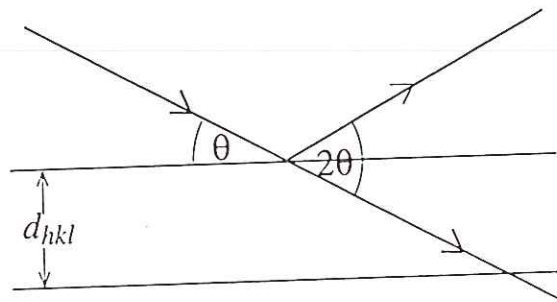
$$AB + BC = 2d \sin \theta = n\lambda$$

← Bragg equation

← can also fit  
 $n=2, 3, \dots$   
wavelengths



(a)



(b)

Figure 3.11. The condition for Bragg reflection from planes  $hkl$  with spacing  $d_{hkl}$ . (a) The path difference between X-rays 'reflected' from successive planes is  $AB+BC$ . (b) X-rays incident on a set of planes at the Bragg angle  $\theta$  are diffracted through an angle  $2\theta$ .

$$2d_{hkl} \sin \theta = n\lambda$$

In practice it is more convenient to treat  $n^{\text{th}}$  order reflection from  $(hkl)$  planes as 1st order reflection from planes  $(nh, nk, nl)$ . Thus the second order reflection from  $(100)$  planes is equivalent to the first order reflection from  $(200)$  planes, i.e.

$$2d_{100} \sin \theta = 2\lambda \text{ is equivalent to } 2d_{200} \sin \theta = \lambda$$

and we write the Bragg Equation as:

$$\lambda = 2d_{hkl} \sin \theta \quad (3.5)$$

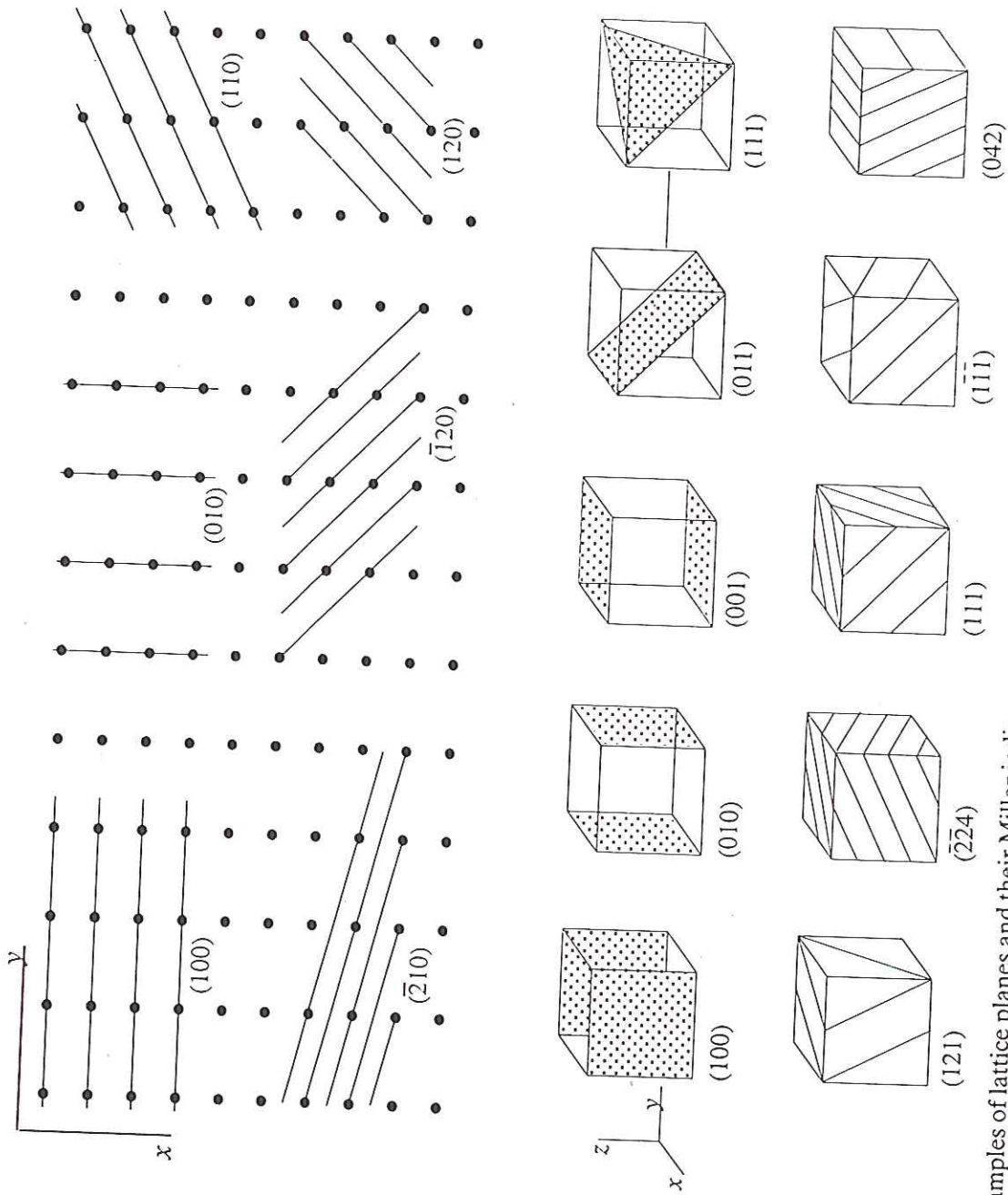
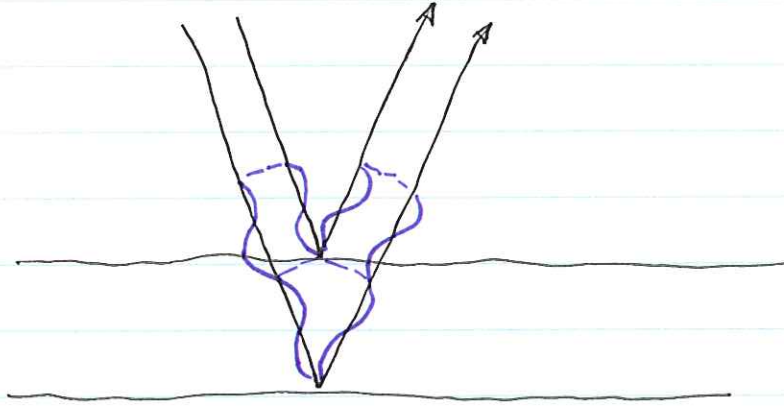


Figure 1.14. Examples of lattice planes and their Miller indices.





$n=2$   
reflection — must fit in  
two wavelengths

Note that the total angle ~~which~~ by which the X-ray is deflected is  $2\theta$ .

See Figure 3.11

Note that 3.11 refers to the spacing as  $d_{hkl}$  in xtallography

This is conventional notation to denote the orientation of a plane

See Fig 1.14 but don't worry about the details

Also conventional to build the integer  $n$  into  $hkl$  rather than keep explicitly:

$$\lambda = 2 d_{hkl} \sin\theta \quad d_{hkl} = \frac{\lambda}{2 \sin\theta}$$

Technique applied in ~~the~~ <sup>several</sup> different ways:

- single crystal diffractometer  
fix  $\lambda$  — monochromatic  
move detector  
record several thousand hkl  
reflections

Fig 3.24

Fig 3.23 — each hkl  
gives rise to a dot  
(outgoing beam)

Fig 7.12 — photo of an  
instrument

- powder method — used  
for quick mineral identification

much better than "scratch &  
sniff" method used in lab

Fig 3.12

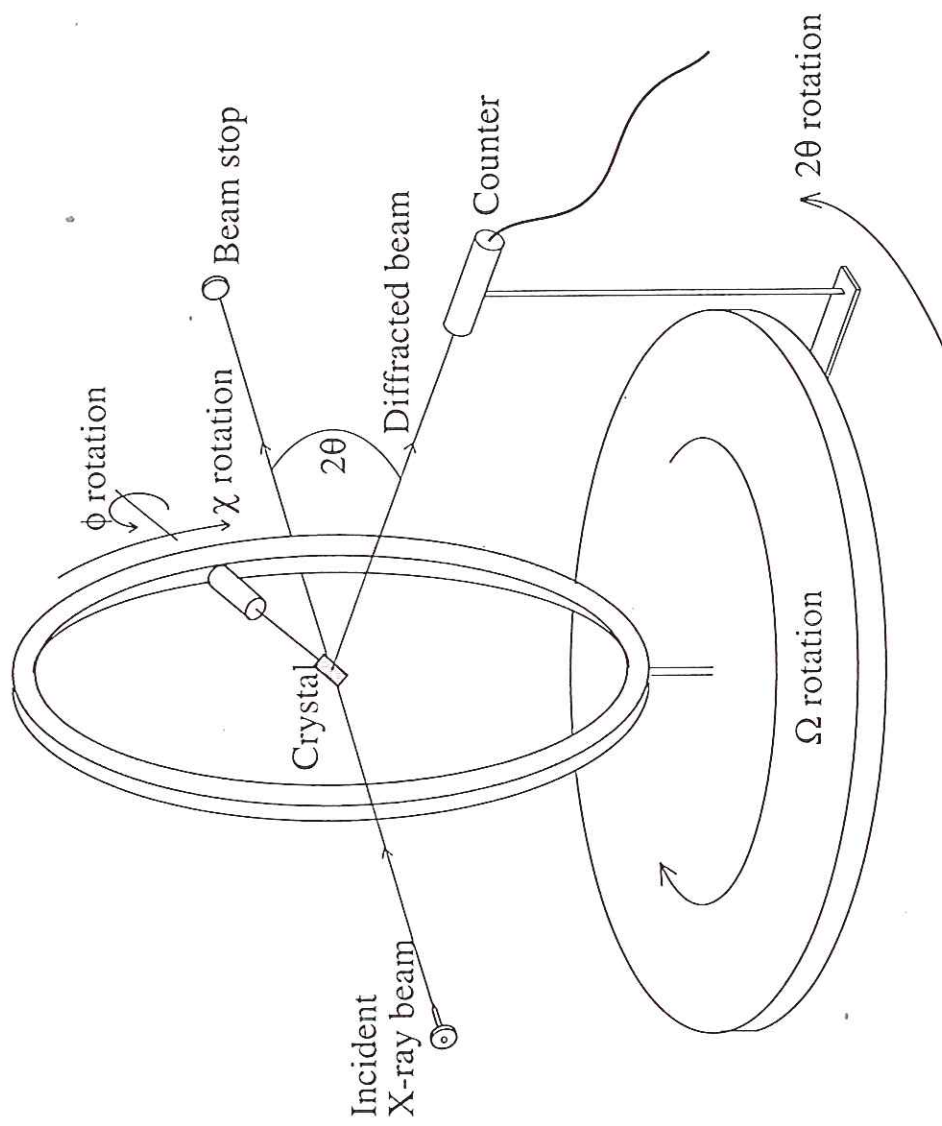
Fig 3.13

plus 3.12

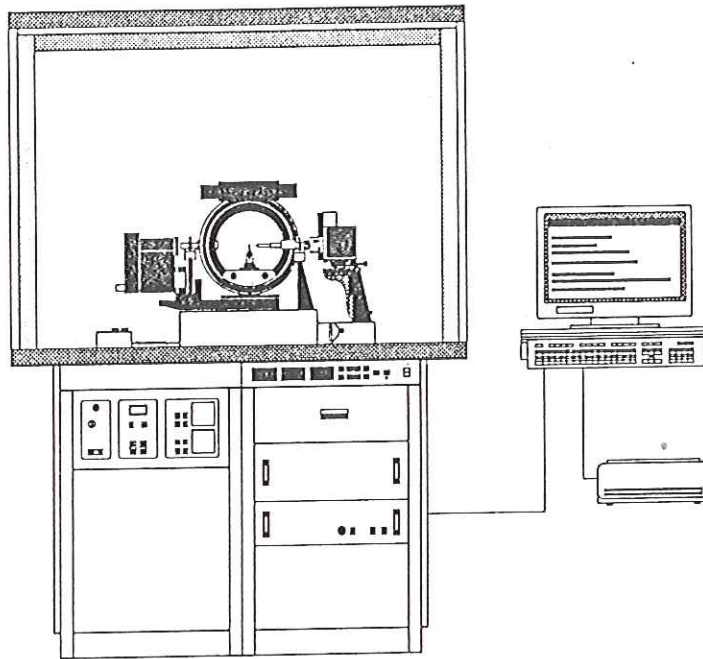
random orientation guarantees  
every hkl will be present  
in diffraction pattern as  
a diffraction cone Fig 3.13

Simplest case — a cubic xtal  
such as NaCl or CsCl

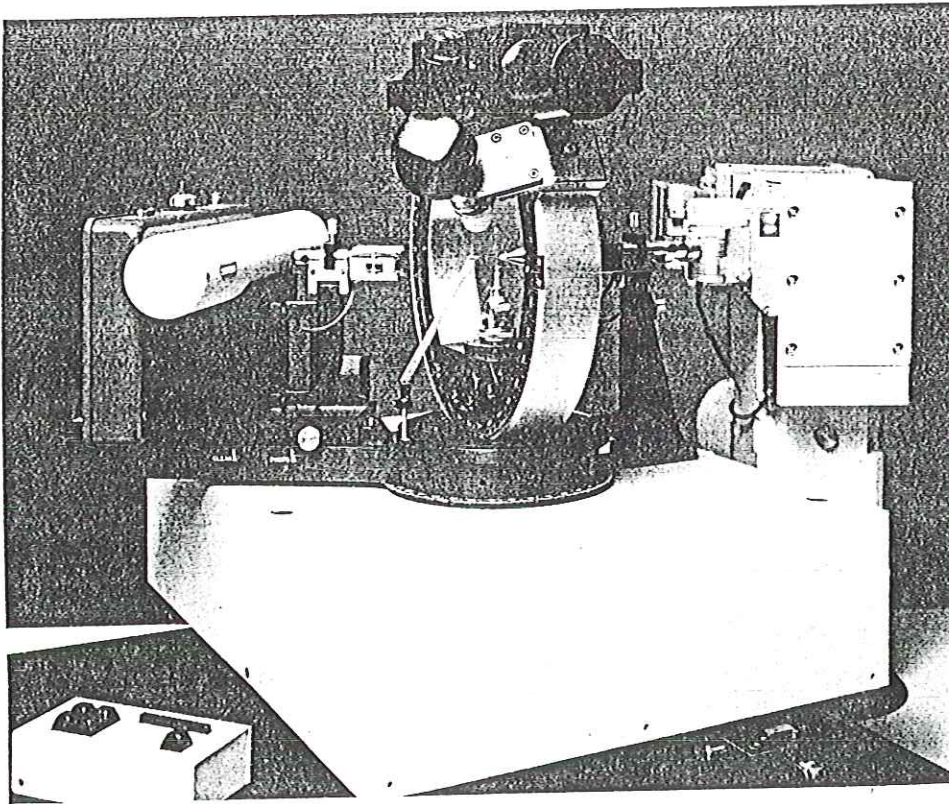
Fig 1.14



**Figure 3.24.** A schematic figure of a four-circle single crystal diffractometer, in which a crystal, centrally mounted in a circular ring can be automatically rotated around three different axes: the  $\phi$ ,  $\chi$  and  $\Omega$  rotations, while the detector moves on the  $2\theta$  rotation. This instrument enables the positions and intensities of several thousand  $hkl$  reflections to be recorded automatically.



(a)



(b)

FIG. 7.12. (a) Schematic illustration of the P4 single-crystal X-ray diffractometer manufactured by Siemens Industrial Automation, Inc. (b) Close-up of the four-circle goniometer for controlling the orientation of the single crystal (in center of photograph). To the right is the X-ray tube, and to the left is the X-ray detector, a scintillation counter. (Courtesy of Siemens Industrial Automation, Inc., Madison, Wis.)



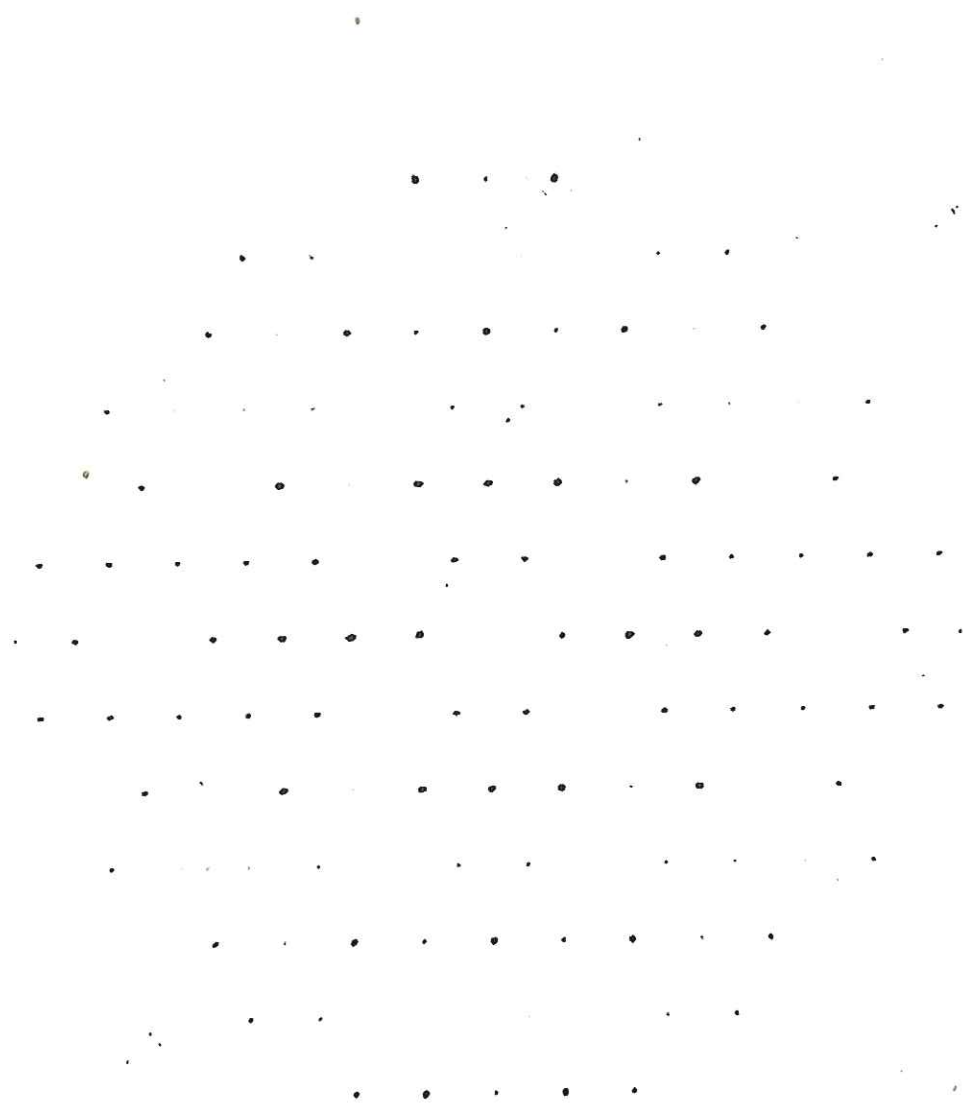
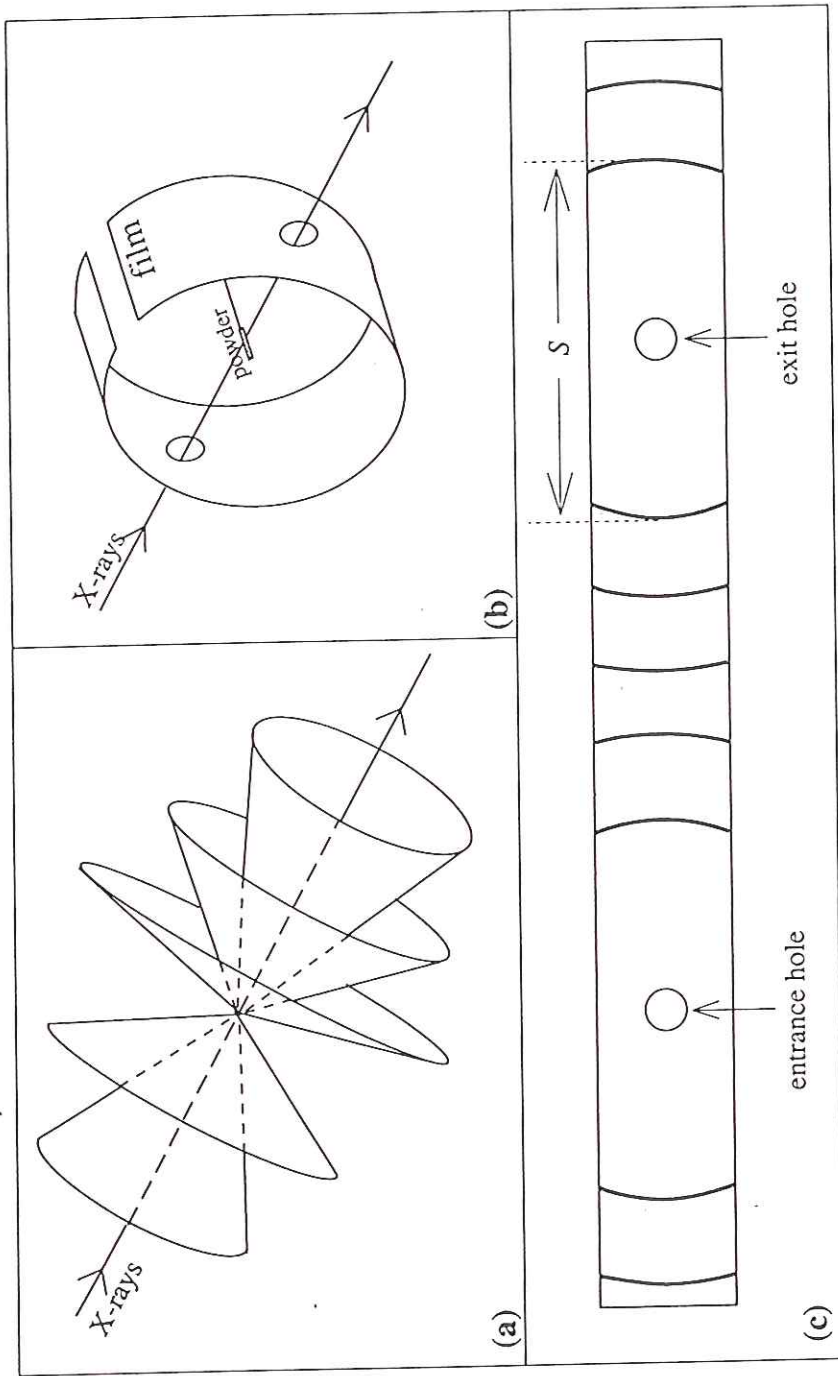
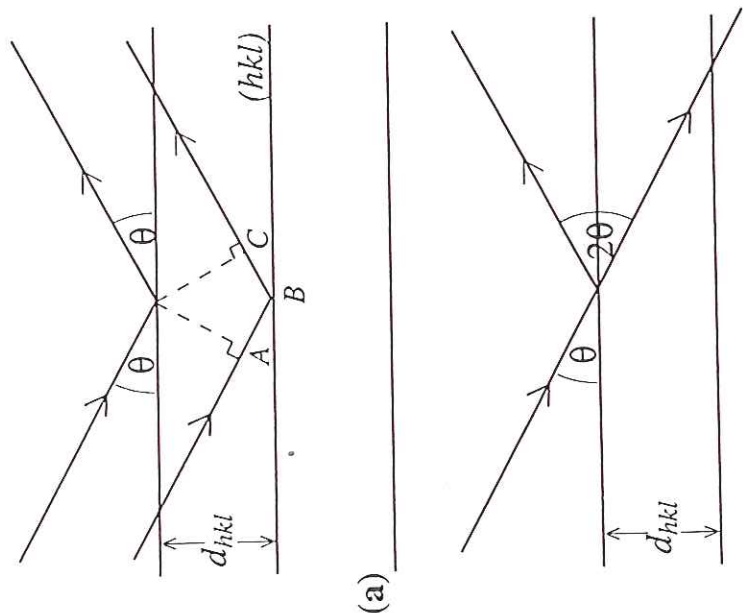


Figure 3.23. An X-ray precession photograph of the tetragonal mineral vesuvianite, precession axis [001]. The diffraction pattern is an undistorted  $a^*c^*$  section of the reciprocal lattice.



**Figure 3.13.** (a) When X-rays are incident on a powder, the diffracted rays form cones coaxial with the incident beam. Each cone of diffracted rays represents Bragg reflection from a set of lattice planes in the sample. (b) In a powder camera a cylindrical strip of film directs the diffracted beams. (c) When the strip of film is laid flat, the intersections of the cones of diffraction with the film form pairs of arcs around the exit and entrance holes through which the X-rays pass.



(b)

Figure 3.11. The condition for Bragg reflection from planes  $hkl$  with spacing  $d_{hkl}$ . (a) The path difference between X-rays 'reflected' from successive planes is  $AB+BC$ . (b) X-rays incident on a set of planes at the Bragg angle  $\theta$  are diffracted through an angle  $2\theta$ .

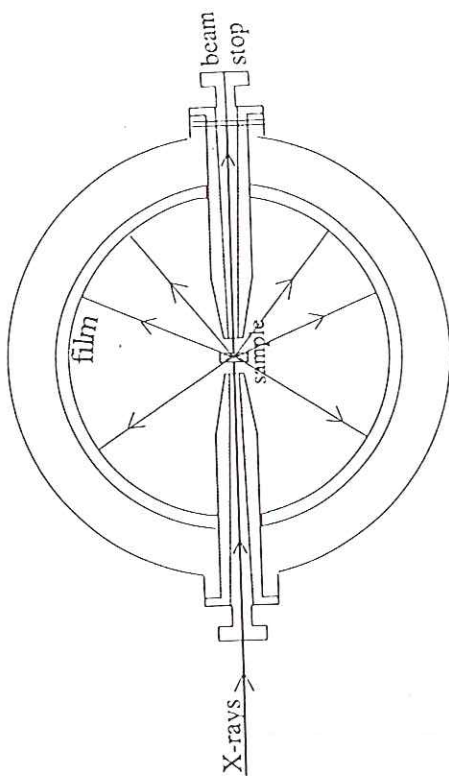


Figure 3.12. Schematic diagram of an X-ray powder diffraction camera. The X-rays enter a cylindrical metal chamber with the sample held at the centre and a strip of film around the inside wall.

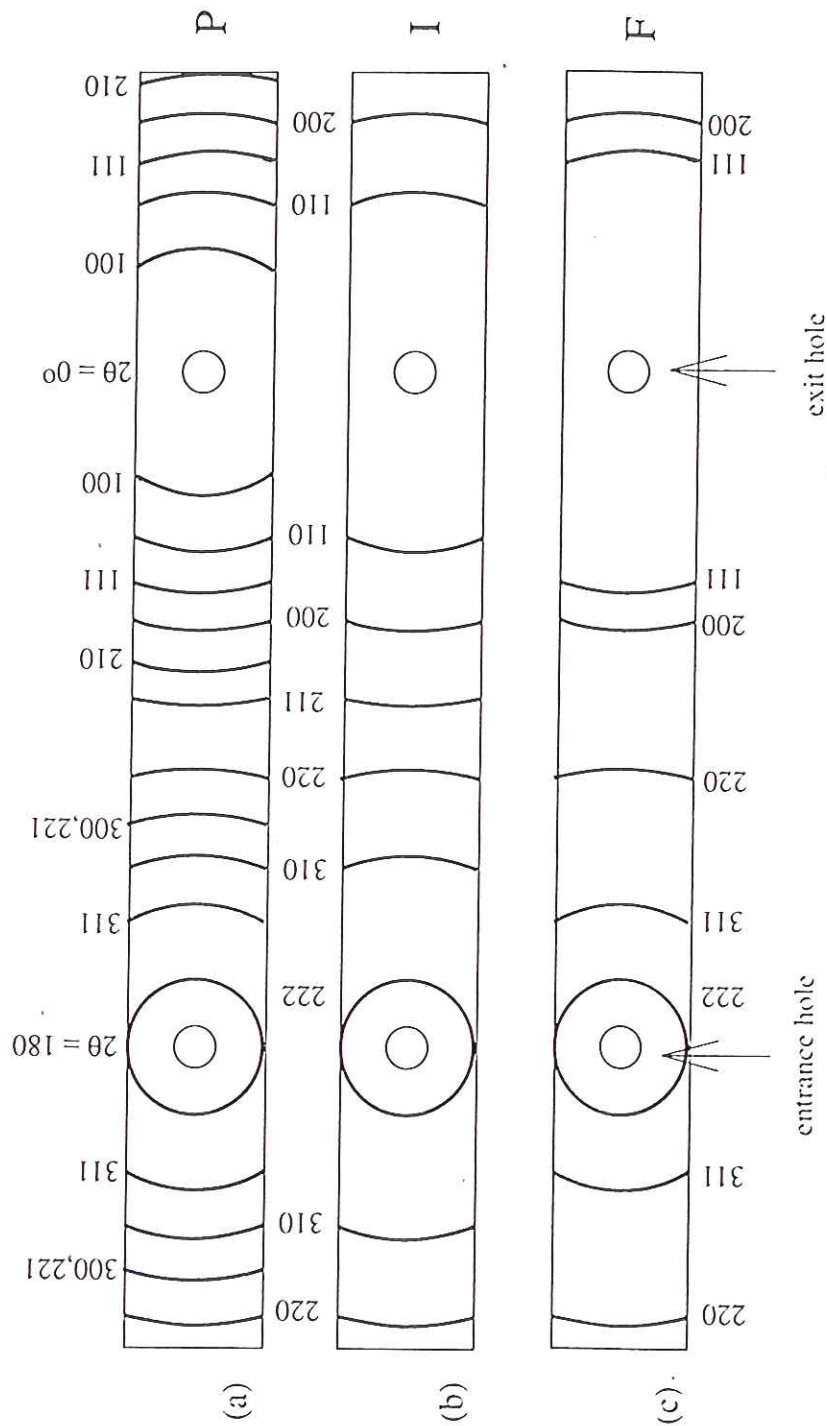


Figure 3.14. Powder diffraction patterns from cubic crystals. (a) When the unit cell is primitive (P) all values of  $h, k$  and  $l$  are allowed; (b) for a body-centred (I) unit cell  $h+k+l$  must be even, and (c) for a face-centred (F) unit cell only reflections for which  $h, k$  and  $l$  are all even or all odd are allowed. The diffraction patterns in this figure have been calculated for X-rays of wavelength  $\lambda = 1.54 \text{ \AA}$  incident onto a material with a cubic cell with lattice parameter  $a = 2.7 \text{ \AA}$ . This is unrealistically small for a real mineral structure. For a larger lattice parameter, more lines out to higher values of  $h^2+k^2+l^2$ , will be present in the powder patterns.



# geometry

$$a = d_{hkl} \sqrt{h^2 + k^2 + l^2}$$

unit cell size

Fig 3.14

Fig 3.15 actual pattern for magnetite (lodestone — primitive compasses)  $\text{Fe}_3\text{O}_4$

440 reflection marked — actually off ~~220~~ with  $n = 2$  waves

$$\lambda = 2d_{hkl} \sin \theta = \frac{2a \sin \theta}{\sqrt{h^2 + k^2 + l^2}}$$

$$a = \frac{\lambda \sqrt{h^2 + k^2 + l^2}}{2 \sin \theta}$$

check: 220 should be at  $2\theta = 38^\circ$

Measure  $2\theta = 82^\circ$   
 $\theta = 41^\circ$

$$a = \frac{1.94 \text{ \AA} \sqrt{32}}{2 \sin 41^\circ} = 8.4 \text{ \AA} \text{ — size of magnetite unit cell}$$

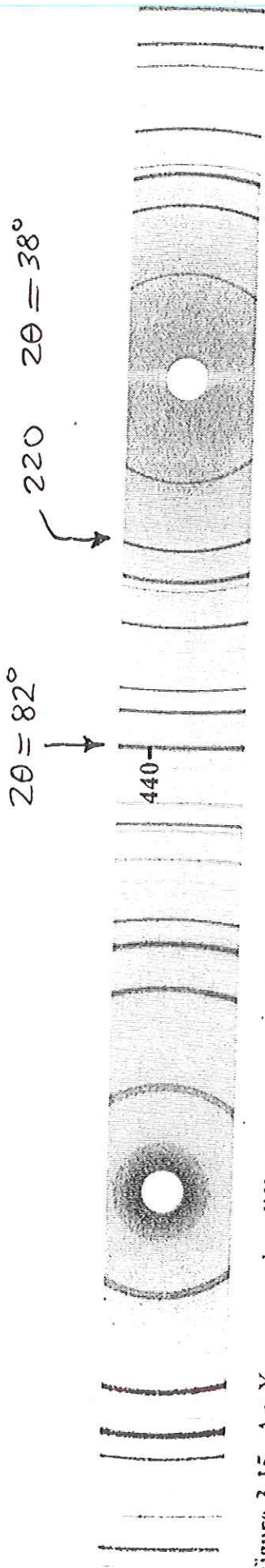


Figure 3.15. An X-ray powder diffraction pattern of magnetite,  $\text{Fe}_3\text{O}_4$ , which has a cubic F cell with lattice parameter  $a = 8.4\text{\AA}$ . The radiation used was  $\text{Fe } K_{\alpha 1}$   $1.936\text{\AA}$ ,  $\text{Fe } K_{\alpha 2}$   $1.940\text{\AA}$ .

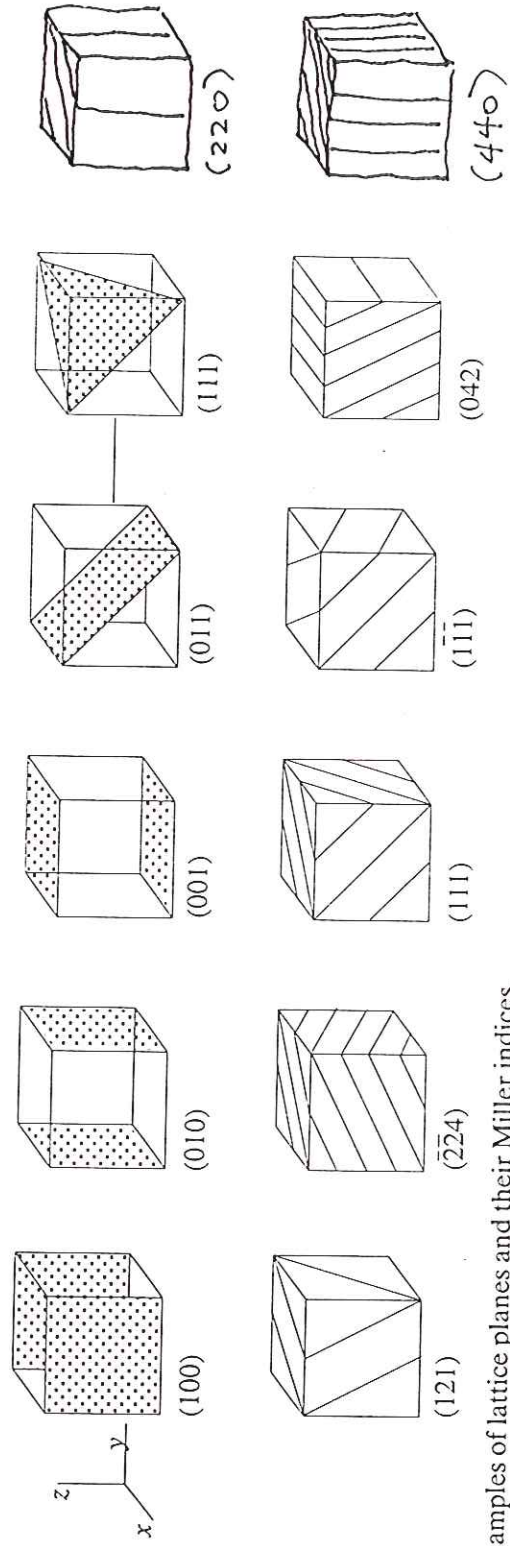


Figure 1.14. Examples of lattice planes and their Miller indices.

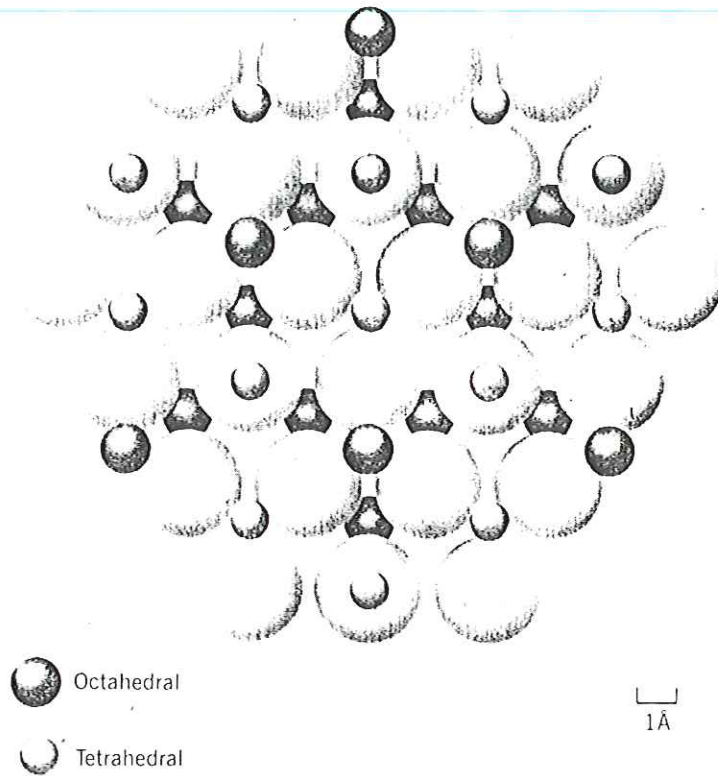
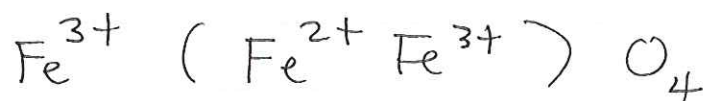


FIG. 11.6. An oxygen layer in the spinel structure, projected onto the (111) plane. See Fig. 11.5 for the position of such planes in the structure. The large circles are oxygen in approximate cubic closest packing. The cation layers on either side of the oxygen layer are shown as well. (Redrawn after Lindsley, D. H., 1976, The crystal chemistry and structure of oxide minerals as exemplified by the Fe-Ti oxides, in *Oxide Minerals, Reviews in Mineralogy*, v. 3. Mineralogical Society of America, Washington, D.C.)

Table 11.2  
**END MEMBERS OF THE  
 SPINEL GROUP ( $XY_2O_4$ )**

	Normal Spinel Structure		Inverse Spinel Structure
Spinel	$MgAl_2^{3+}O_4$	Magnetite	$Fe^{3+}(Fe^{2+}Fe^{3+})O_4$
Hercynite	$FeAl_2^{3+}O_4$	Magnesioferrite	$Fe^{3+}(Mg^{2+}Fe^{3+})O_4$
Gahnite	$ZnAl_2^{3+}O_4$	Jacobsite	$Fe^{3+}(Mn^{2+}Fe^{3+})O_4$
Galaxite	$MnAl_2^{3+}O_4$	Ulvöspinel	$Fe^{2+}(Fe^{2+}Ti^{4+})O_4$
Franklinite	$ZnFe_2^{3+}O_4$		
Chromite	$Fe^{2+}Cr_2^{3+}O_4$		
Magnesiochromite	$Mg^{2+}Cr_2^{3+}O_4$		

Structure of magnetite — shown  
in Fig. 11.6



8  $\text{Fe}^{3+}$  in tetrahedral ~~sites~~ sites  
8  $\text{Fe}^{3+}$  in octahedral sites  
8  $\text{Fe}^{2+}$  in other octahedral sites

Fig 7.19 shows powder pattern  
for quartz  $\text{SiO}_2$  — hexagonal  
symmetry rather than cubic

Powder patterns are very distinctive —  
like fingerprints

Makes mineral identification a cinch.

Used by many prior to other  
investigations.

Tom Duffy estimates that 10-20%  
of minerals "identified" by  
distinguished Princeton professors  
of geology before development of  
x-rays are incorrect.



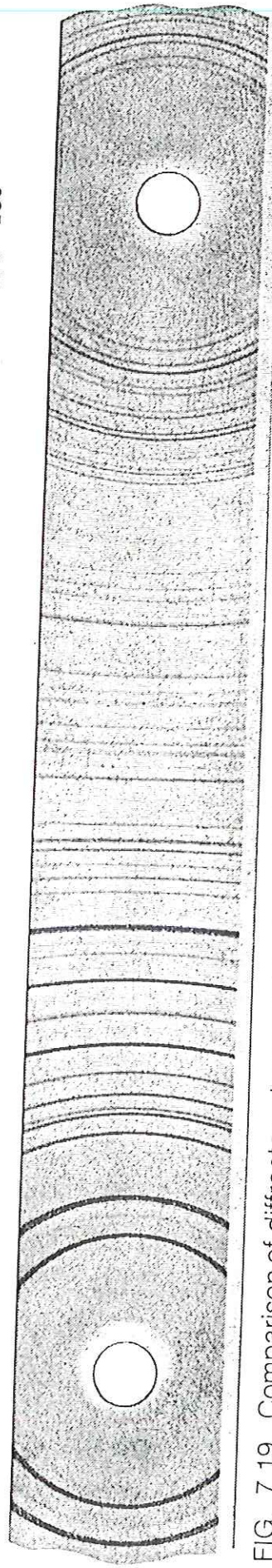
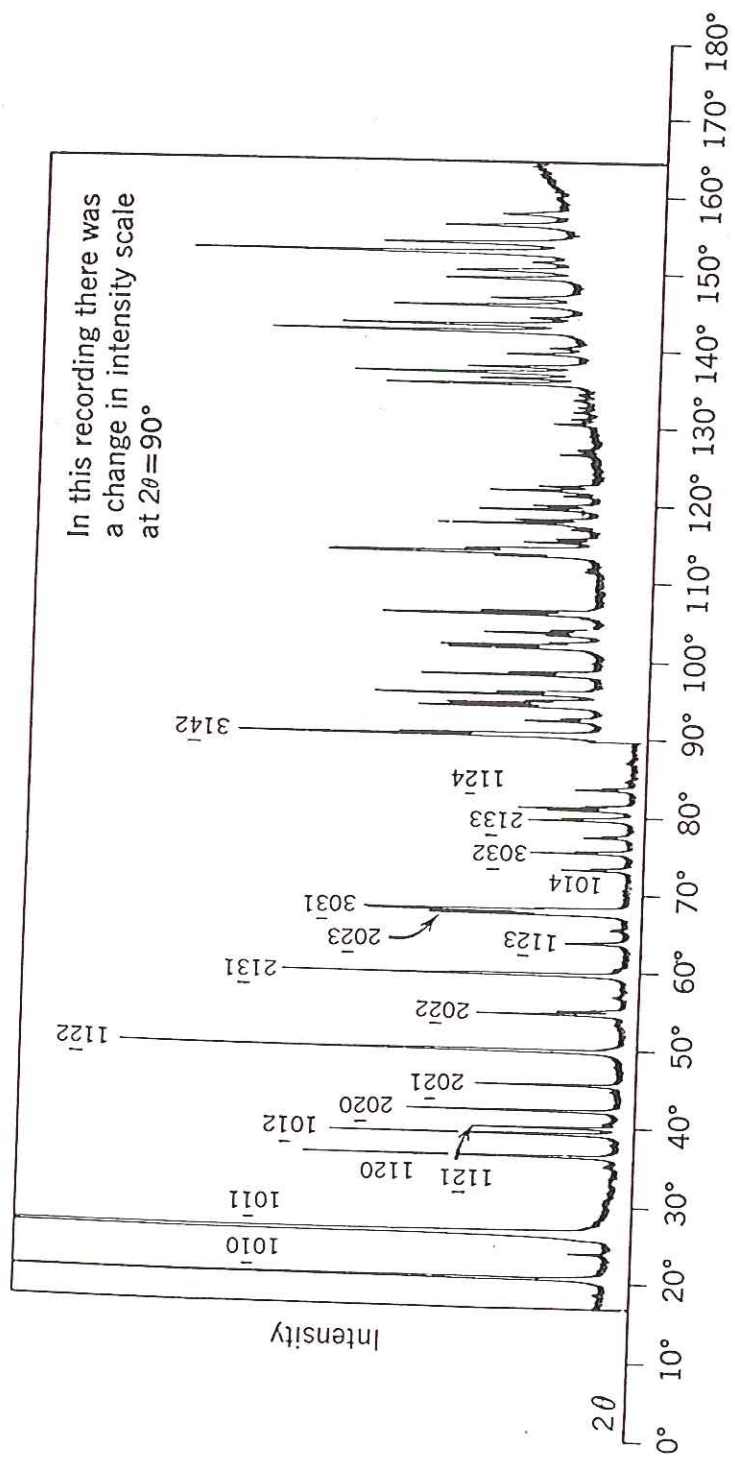


FIG. 7.19. Comparison of diffractometer record and powder film of quartz. On the diffractometer recording are given the Miller indices of the crystal planes that gave rise to the various low-angle diffraction peaks. (Courtesy of Philips Electronic Instruments, Inc., Mahwah, N.J.)