condensed states (凝聚態): 包括 liquids and solids!

§10.1

intermolecular forces (分子間的作用力) 使分子"凝聚"

(A) dipole-dipole forces & (B) London Dispersion forces

(A) dipole-dipole forces

Figures 10.2 & 10.3

~~molecul~~ molecules w/ dipole moments can attract each other electrostatically by lining up so that the positive and negative ends are close to each other.

hydrogen bonding (strong dipole-dipole forces)

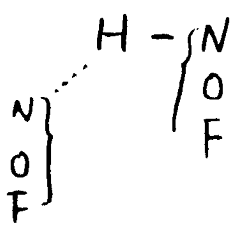


Fig 10.4

H_2O, HF, NH_3 } boiling point 沸點 非常高

∵ 氫鍵強:

① large electronegativity values → very polar X-H bonds

② small size → close approach of the dipoles and strengthening the intermolecular forces

---

London Dispersion Forces

The forces that exist among noble gas ~~molecule~~ atoms and nonpolar molecules → London Dispersion Forces

Fig. 10.5.

Instantaneous dipole induce a similar dipole in a neighboring atom

114
10-3

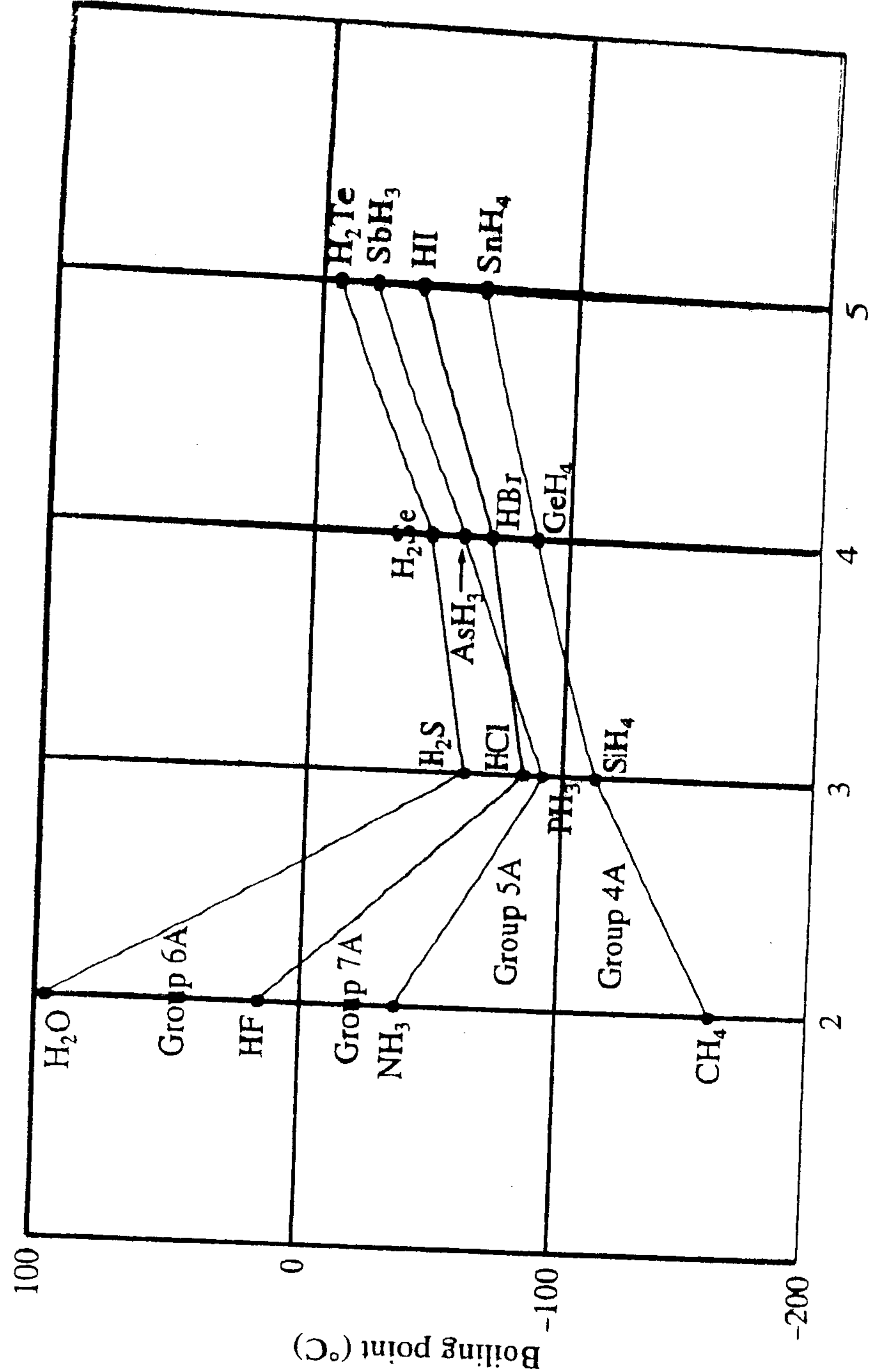


Figure 10.4
The boiling points for various families of hydrides

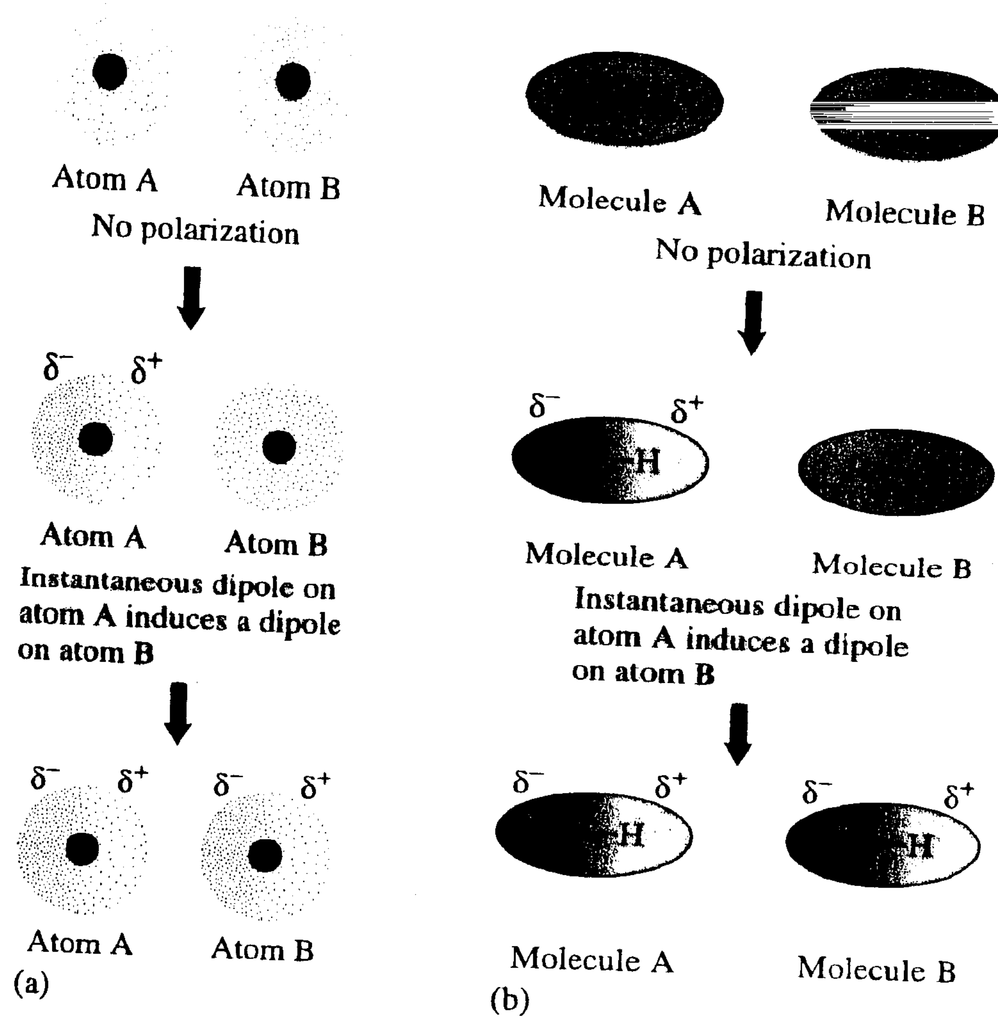


Figure 10.5
London dispersion forces

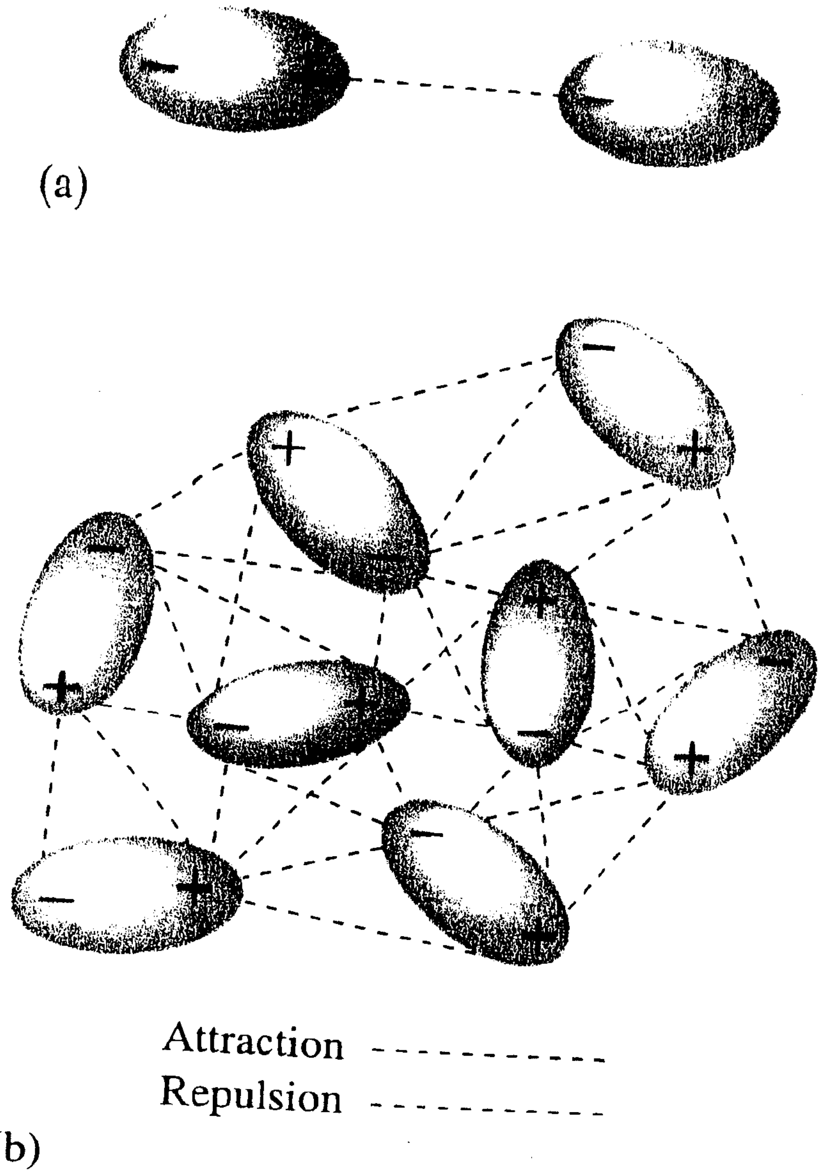


Figure 10.2
Dipole-dipole attractions

Table 10.2

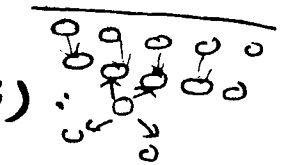
	[illegible]	
He	−269.7	低
Ne	−248.6	↓
Ar	−189.4	
Kr	−157.3	
Xe	−111.9	高

polarizability:

∵ atomic number ↑ → # of electron[s]
→ increase chance of the occuren[ce]
of momentary dipole interactions.

§10.2 The Liquid State

surface tension (表面張力):



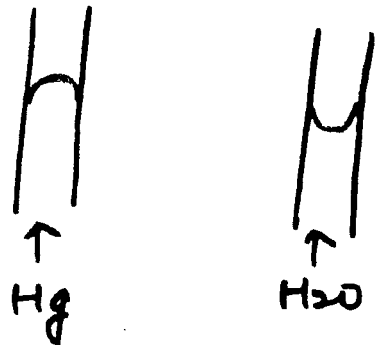
see Fig 10.6

the resistance of a liquid to an increase in its surface area.

capillary action (毛細作用). the Spontaneous rising of a liquid in a narrow tube. 包括 cohesive force: intermolecular forces among liquid molecul[es]

adhesive force ...

Fig 10.7



強對高面 polar

adhesive forces 與 cohesive forces

adhesive → 與容器黏著力

cohesive → 分子間作用力

達平衡 !

§ 10.3 An Introduction to Structures and Types of Solids

amorphous solid : 非結晶狀固體

crystalline solid : 結晶狀固體

Crystalline solids are usually represent by lattice 晶格

lattice : a three dimensional system of points designating the positions of the components (atoms, ions, or molecules) that make up the substance

unit cell (單位晶格): The smallest repeating unit of the lattice

Fig. 10.9.

X-ray Analysis of solids

X-ray diffraction : 繞射

See Fig 10.10 (a) & (b) 建設性與破壞性

constructive destructive

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10-9

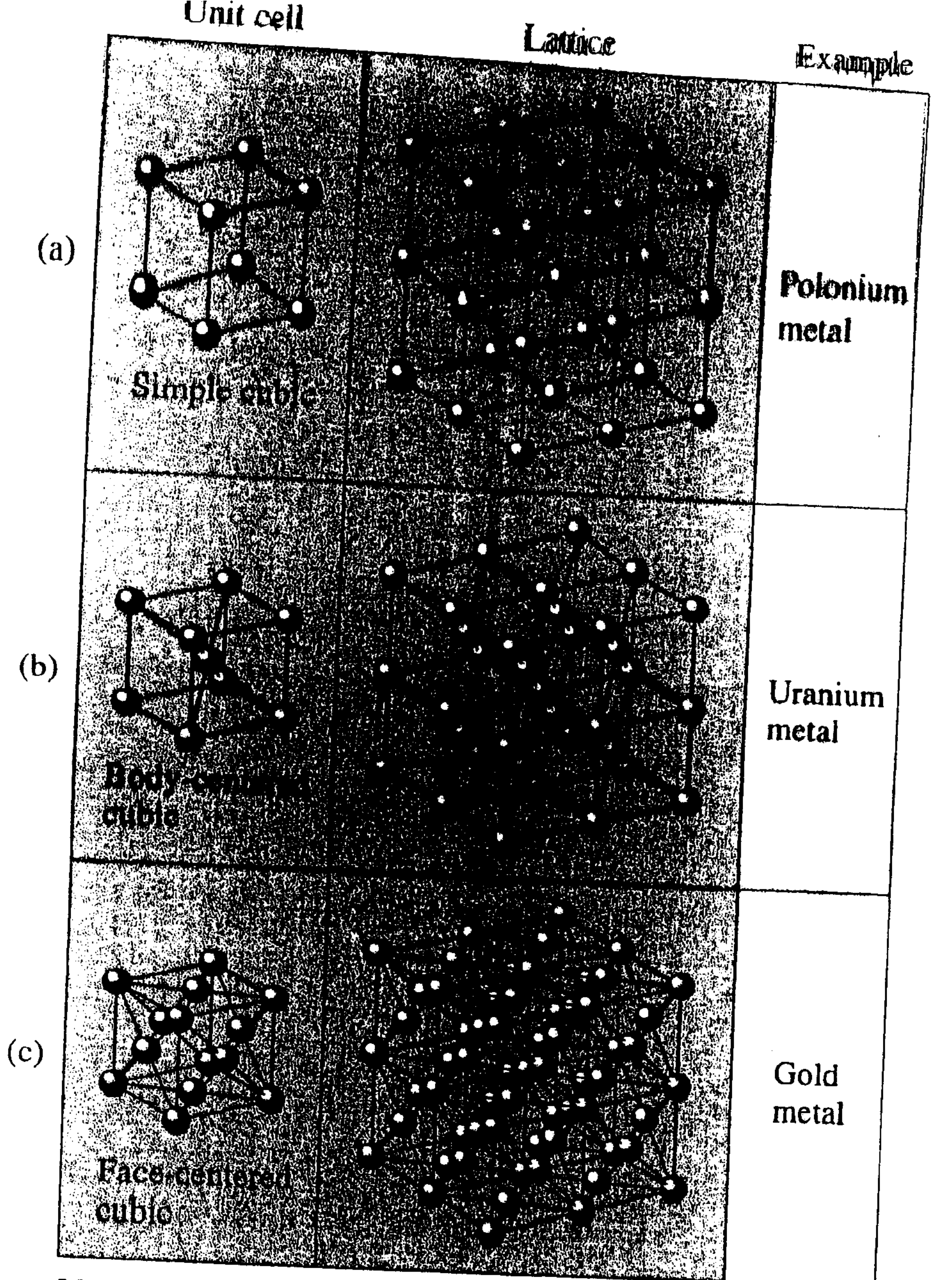


Figure 10.9
Several unit cells and their lattices

See Fig 10.11

$$\boxed{n\lambda = 2d\sin\theta}$$ (0

λ : x-ray 波長 　　 n : 整數

θ : X-ray 入射角度

d : distance between the atoms

(不同"面"上的原子间距)

Ex: 10.1

x-ray 1.54 Å wavelength

19.3° reflected

assuming n = 1, calculate the distance d between the planes of atoms producing thi[s] reflection.

Sol: $n\lambda = 2d\sin\theta$

代入 $1 \cdot 1.54\,\text{Å} = 2d\sin 19.3^\circ$

$d = 2.33\,\text{Å}$

Types of crystalline solids

1. ionic solids : salt (NaCl)
2. molecular solids : sugar, ice
3. atomic solids : diamond

See Fig 10.12

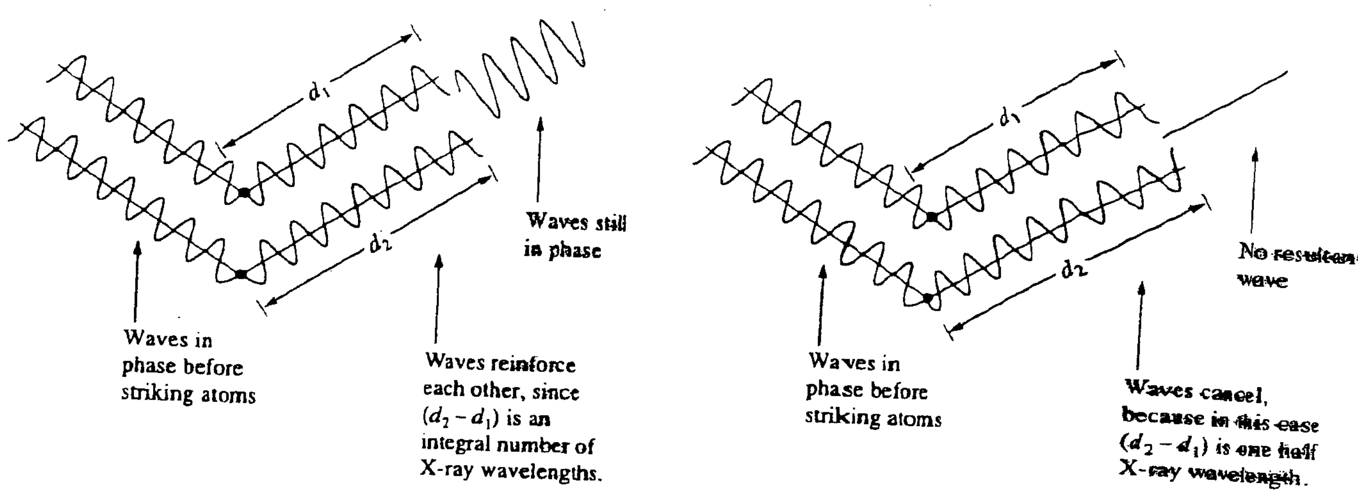


Figure 10.10
Interference of light waves

117 10-11

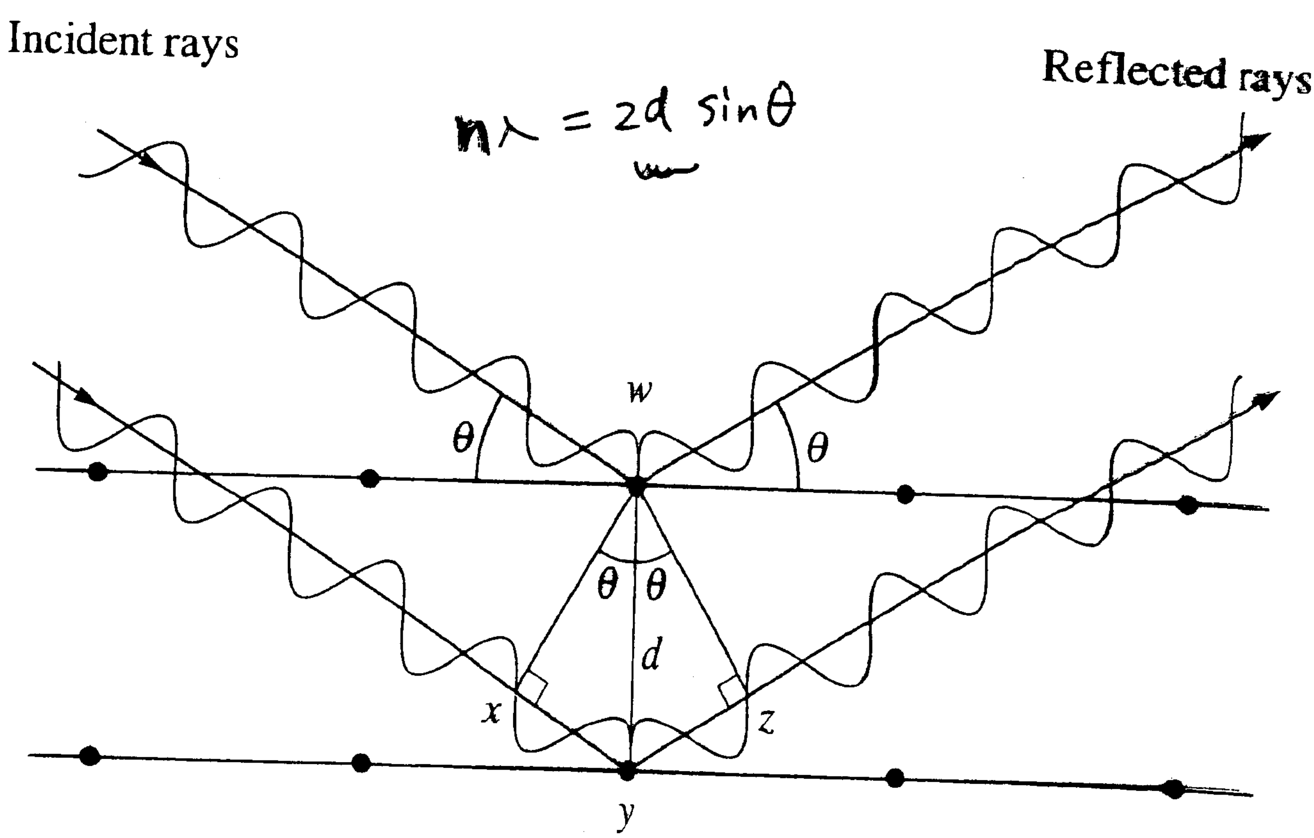


Figure 10.11
Diagram to support the Bragg equation

10-12

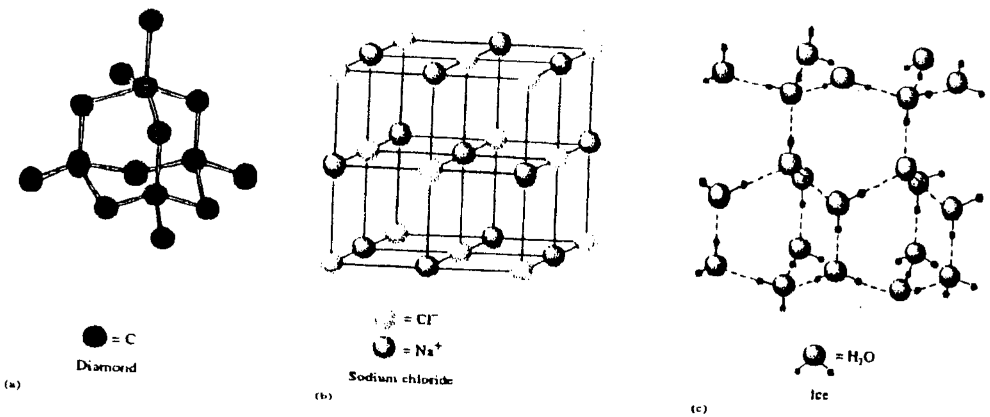


Figure 10.12
The structure of diamond, sodium chloride, and ice

atomic solids 可分為:
1. metallic solids
2. network solids
3. group 8A solids

In metallic solids, delocalized nondirectional covalent bonding

In network solids, the atoms bond to each other w/ strong directional covalent bonds

In group 8A solids, w/ London dispersion forces

See Table 10.3

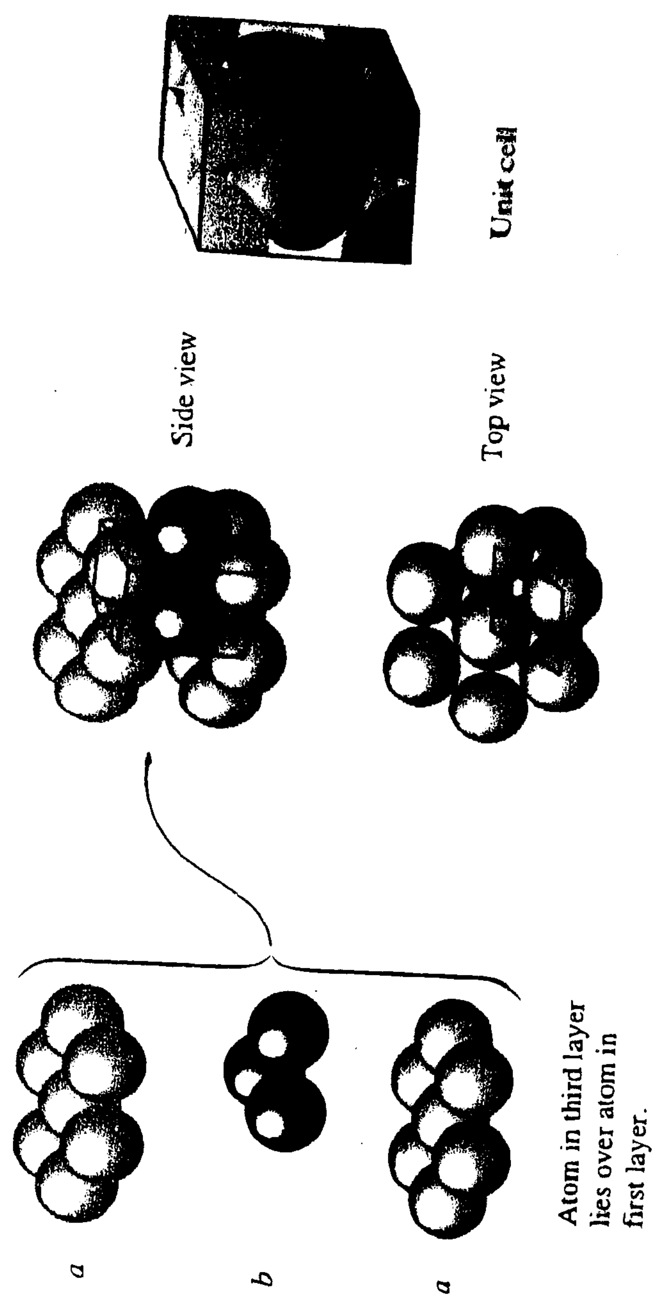
§ 10.4 Structure and Bonding in Metals

closest packing (uniform, hard spheres)

see Fig 10.13

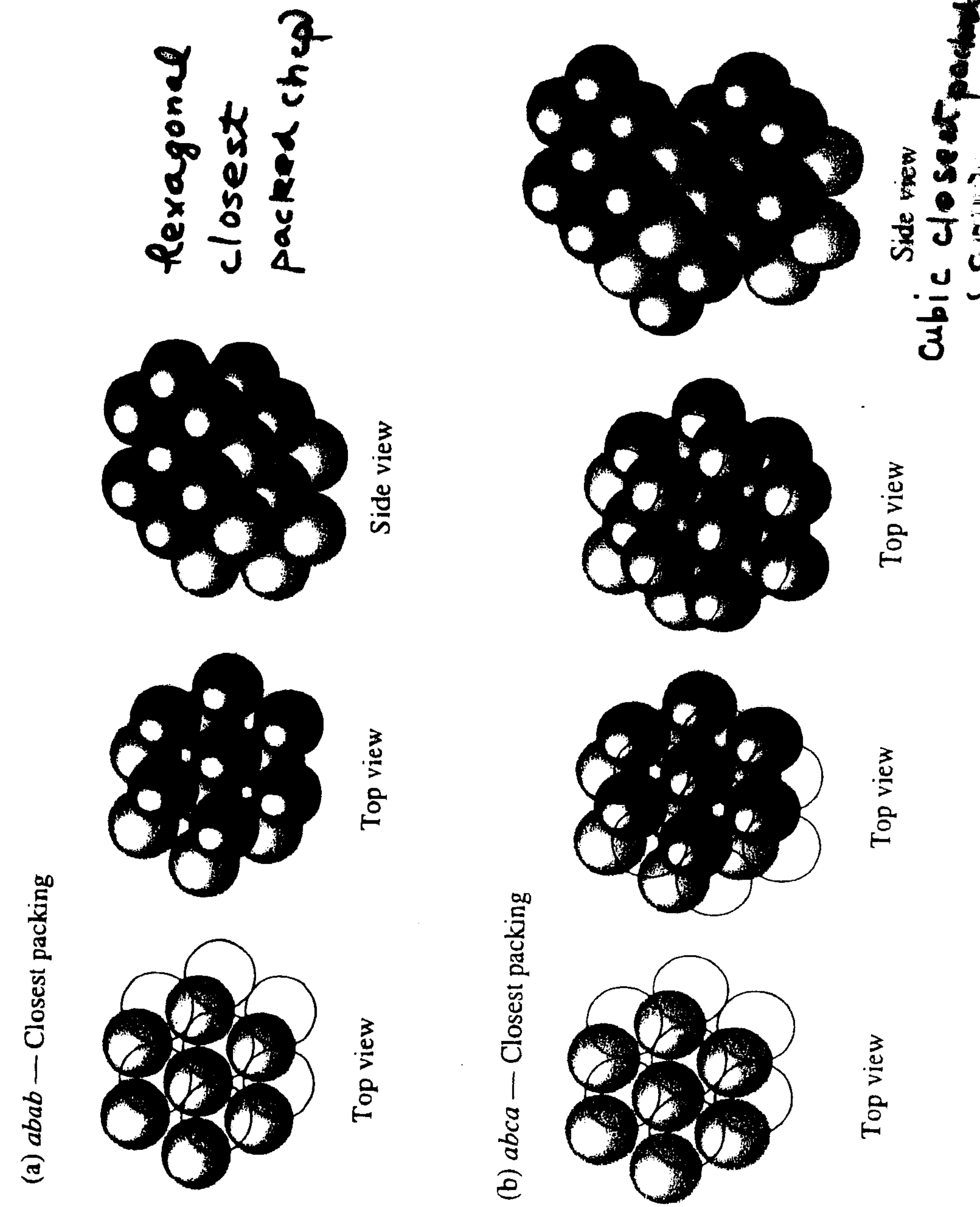
(a) each sphere is surrounded by 6 others
(b) second layer 位於 first layer 的 空隙 上
(c) third layer: 可為 a b a b ... (aba)
or 為 a b c a b c ... (abc)

See Fig 10.14 : (a b a) hexagonal closest packed (hcp)
10.15 : (a b c) → cubic closest packed (ccp)


Unit cell
Side view
Top view
a
b
a
Atom in third layer lies over atom in first layer.

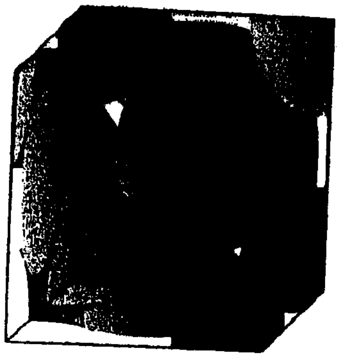
1016

10-13


hexagonal closest packed (hcp)
Side view
Top view
Top view
(a) *abab* — Closest packing
Side view
Cubic closest packed
Top view
Top view
Top view
(b) *abca* — Closest packing

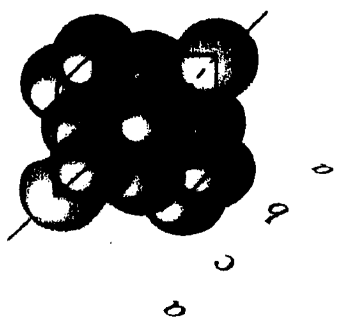
10.15 Cubic closest packing

10-17

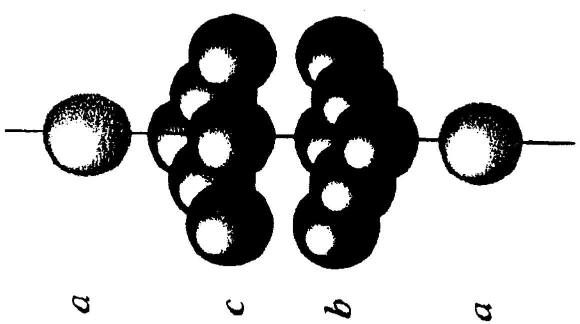


Unit cell

face-centered cubic unit cell

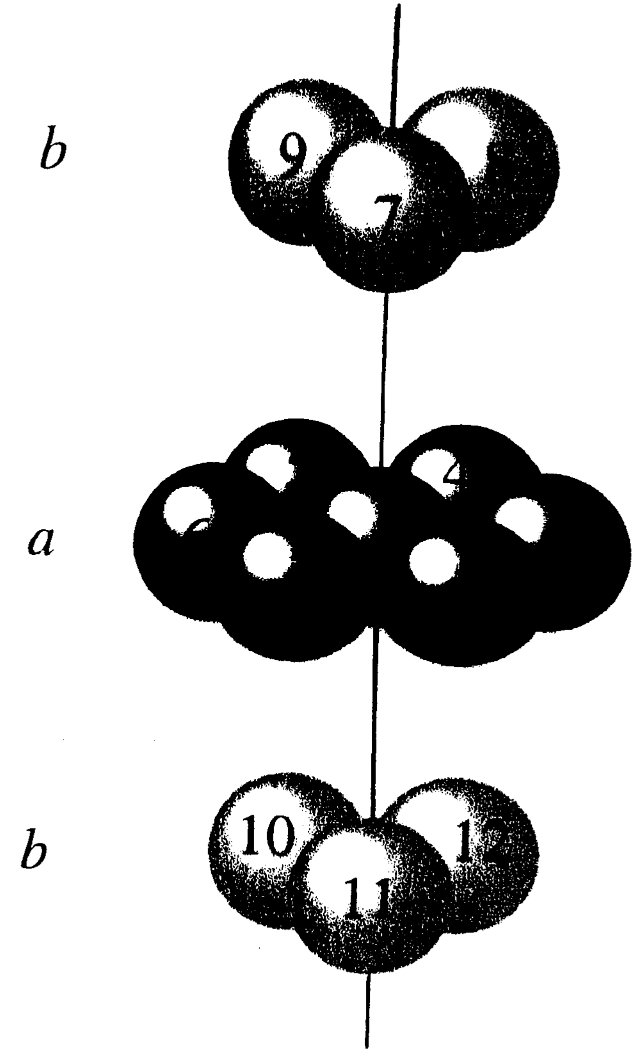


cubic closest packed (ccp)



An atom in every fourth layer lies over an atom in the first layer.

10-18



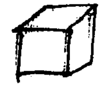
hcp

Figure 10.16

Closest neighbors in closest packed spheres

hexagonal closest packed (hcp) structure

unit cell: hexagonal prism 菱形 (六面体)



ex. Mg, Zn

cubic closest packed (ccp) structure 10-19

unit cell: faced-centered cubic

ex. Al, Fe, Cu, Co, Ni (正方体)

每一个 unit cell 所含原子数目:

(以 ccp 为例)

$$8\times\frac{1}{8} + \left(6\times\frac{1}{2}\right) = 4$$

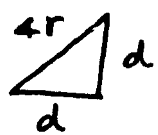
8个角 / 8个晶格 share 1 的角 / 6个面 / 2个晶格 share 1个面

Ex. 10.2 計算密度(晶体)

Silver (銀) radius = 144 pm

structure: ccp ; M.W = 107.9 g/mol

sol: ccp 的一面



$d^2+d^2=(4r)^2$

$\therefore d = \sqrt{8}\,r = \sqrt{8}\cdot 144\,pm = 407\,pm$

每一晶格 volume $= d^3 = (407\,pm)^3$

$= (4.07\times10^{-12}\,m)^3$

mass 每一晶格 4 atoms $= 4\times(107.9\,g/mol \div 6.022\times10^{23}\,atoms/mol)$

$D = \dfrac{mass}{volume} = \dfrac{4\left(\frac{107.9}{6.022\times10^{23}}\right)g}{(4.07\times10^{-12}\,m)^3}$

$= 10.6\,g/cm^3$

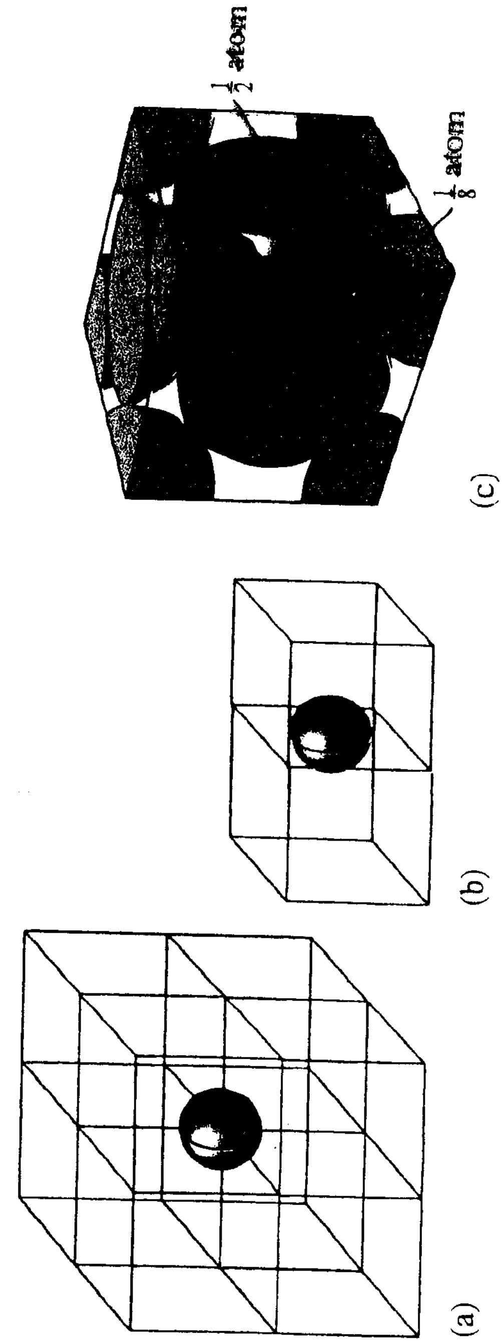


Figure 10.17
Net spheres on faces and corners of unit cell

12
(0-2

Bonding in metals: strong and nondirectional

electron sea model:

(see Fig 10.18)

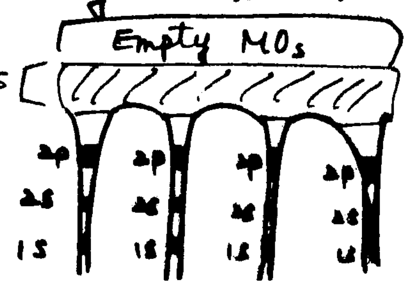
a regular array of metal cations in a "sea" of valence electrons

band model or molecular orbital (MO) model:

the electrons are assumed to travel around the metal crystal in molecular orbitals formed from the valence atomic orbitals of the metal atoms (see Fig 10.19) page 467

(n = # of interacting orbitals)

see Fig. 10.20



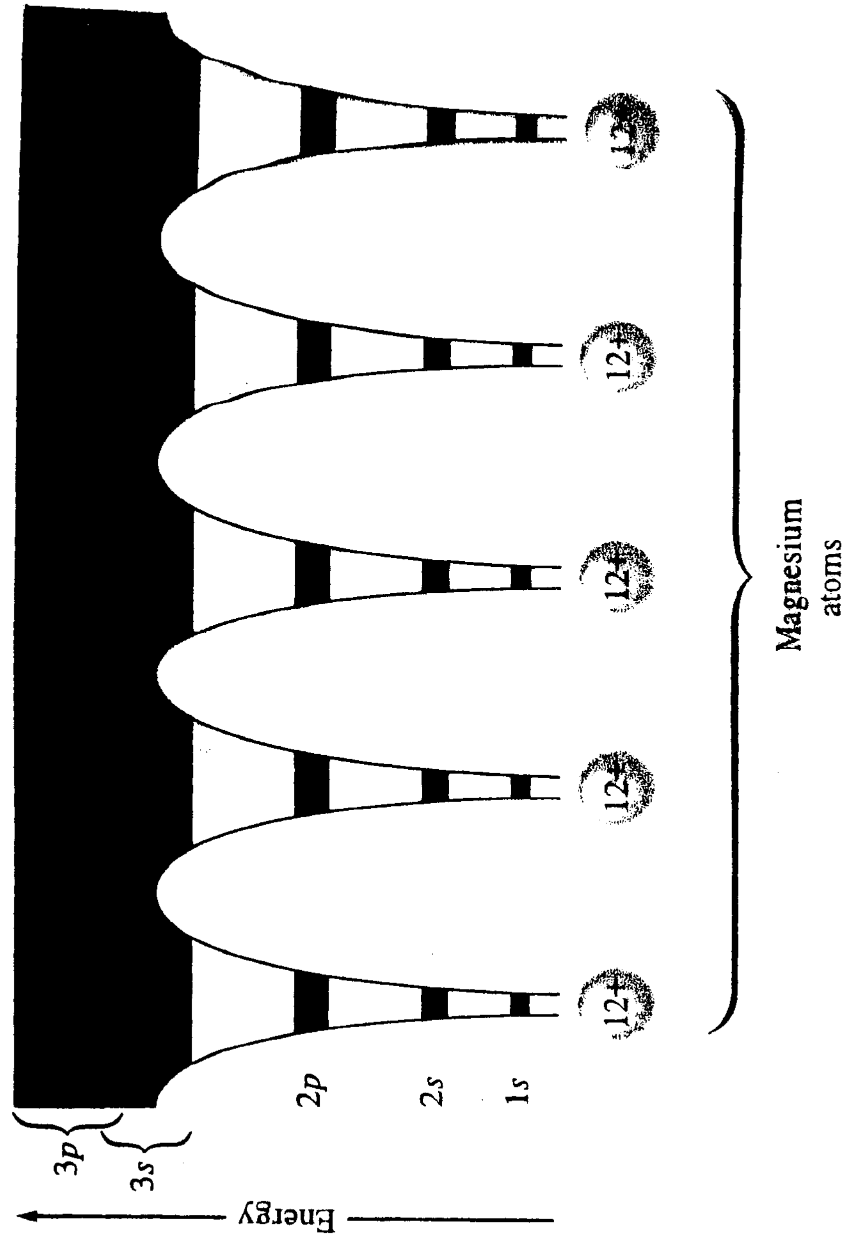


Figure 10.20
The band model for magnesium

alloys : substances that contain mixtures of elements and have metallic properties

分為 1. substitutional alloy (置換) 青銅……

2. interstitial alloy (填塞 隙)

see Fig 10.21

interstitial alloy : 如 填 C into iron

改變金屬性質 : ∵ C and iron form "directional" bonding

↓

steel 鋼 (% of C ↑, 硬度 ↑)

Table 10.4 alloy steel

§ 10.5 Carbon and Silicon : Network Atomic Solids

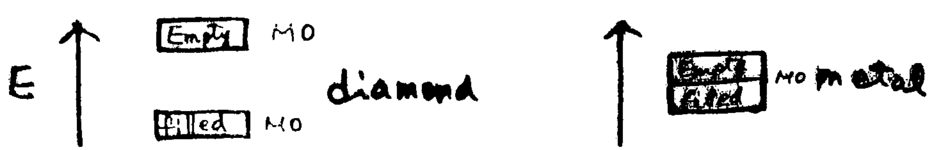
strong directional covalent bonds to form a "giant molecule" — network solids

不導电 or 熱

Carbon : 鑽石

石墨

Fig. 10.22 & 10.23



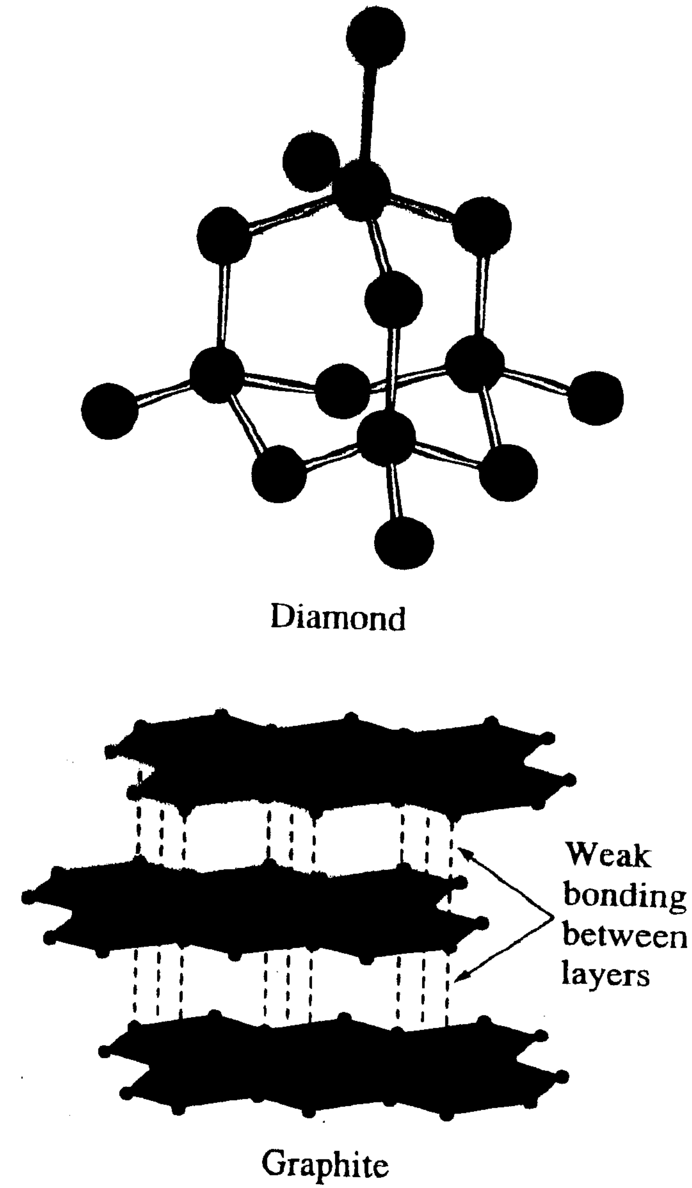


Figure 10.22
Diamond and graphite structures

From 10.23

there is large energy gap between the filled and the empty levels in diamond
→ good electrical insulator.

diamond　carbon 以 [sp³] 軌道重疊成 σ bond

graphite 石墨　carbon 以 sp^2-sp^2 〃 σ bonds
以 p − p 〃 π bonds

see Fig 10.26

π molecular orbitals w/ their delocalized electrons account for the electrical conductivity of graphite

graphite …　lubricant in locks

graphite $\xrightarrow[2800°C]{150,000\,atm}$ diamond

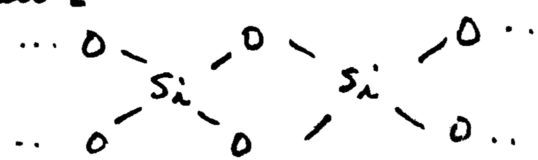
Silicon (Si)

Silica (SiO_2) : quartz

O = C = O

sp of C

π bonding



(晶體式 SiO_2)

Silicates : Si / O 化合物
含 silicon-oxygen anions

see Fig 10.27

SiO_4^{4-}, $Si_2O_7^{6-}$, $Si_3O_9^{6-}$, $(Si_4O_{11})_n^{6n-}$

glass : 非晶体, 而似溶液

不同的玻璃為 SiO_2 加入不同添加物.

(see Table 10.5 on page 474)

<u>Ceramics</u> (陶瓷)

a glass is a "homogeneous", non-crystalline "frozen solution"

a ceramic is "heterogeneous"

含 two phases : { "minute crystals of silicates" suspended in a "glassy cement"

feldspar 長石 ($K_2O \cdot Al_2O_3 \cdot 6SiO_2$, $Na_2O\ Al_2O_3\ 6SiO_2$) + water CO_2 → clay 陶土 · 泥土
含 kaolinite $Al_2Si_2O_5(OH)_4$ (高嶺石)
↓ H_2O
黏土 + 水 ↑ (塑膠性)
→ 高溫 → Silicate + cations
→ glass + tiny crystal of kaolinite

See Fig 10.23

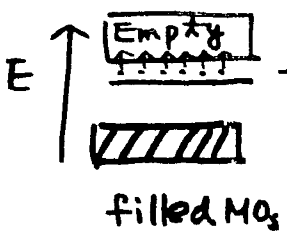
diamond: large energy gap between the filled and empty molecular orbitals

silicon: energy gap smaller than it in diamond
(semiconductor)

Temp ↑ conductivity ↑

n-type semiconductor: silicon doped w/ atoms having more valence electrons (e.g. As 砷)

See Fig 10.29 (a) & 10.30 (a)



→ "excess" valence electron from "donor" impurity

The extra electrons lie close in energy to the conduction bands and easily be excited into these bands.

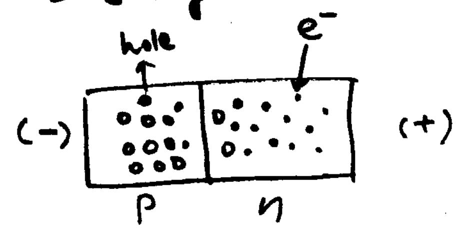
P-type semiconductor: semiconductors are doped w/ atoms having fewer valence electrons than the atoms of the host crystal

See Fig 10.29(b) & 10.30(b)

one less valence e^- → electron "vacancy" or "hole"

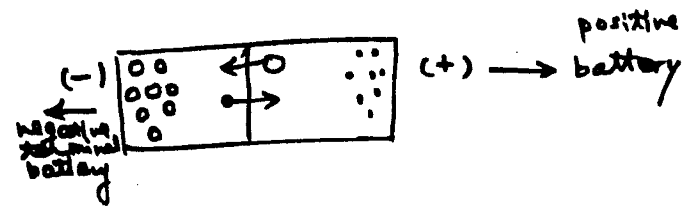
P-n junction (整流器)

See Fig 10.31

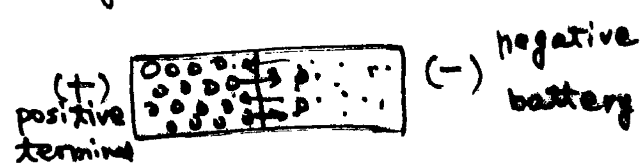


junction potential

Apply electric potential



Reverse bias



forward bias

§ 10.6 Molecular Solids

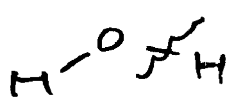
Fig. 10.32 S_8 molecule

P_4 molecule (存水中.
會和 O_2 作用)

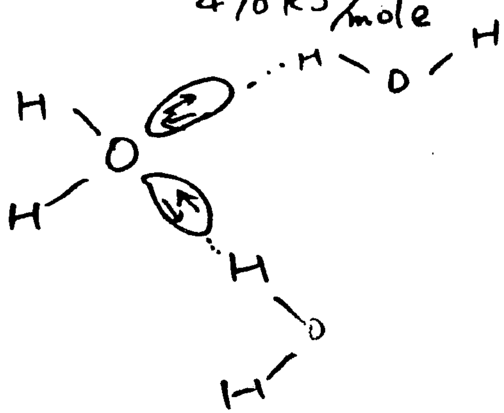
Table 10.6

	solid	distance in molecule	closest distance between molecule in the solid
無 dipole moment	P_4	220 pm	380 pm
	S_8	206 pm	370 pm
	Cl_2	199 pm	360 pm

有 dipole moment H_2O 与 H_2O
6 KJ/mole



470 KJ/mole



§ 10.7 Ionic solids

Fig 10.33 在晶體中的空隙

trigonal hole

tetrahedral hole

octahedral hole

- e.g. ZnS ionic solid

~~Zn^{2+}~~ S^{2-} 以 faced centered cubic 排列
(cubic closest packed)

將 ~~S^{2-}~~ Zn^{2+} 排在 ~~Zn^{2+}~~ S^{2-} 所成的 tetrahedral hole 內.

↓

Fig 10.34

Ex. 10.3 & 10.4

NaCl

Na ↑ ccp 排列; Cl ↖ octahedral hole 內

Table 10.7 Types and properties of solids

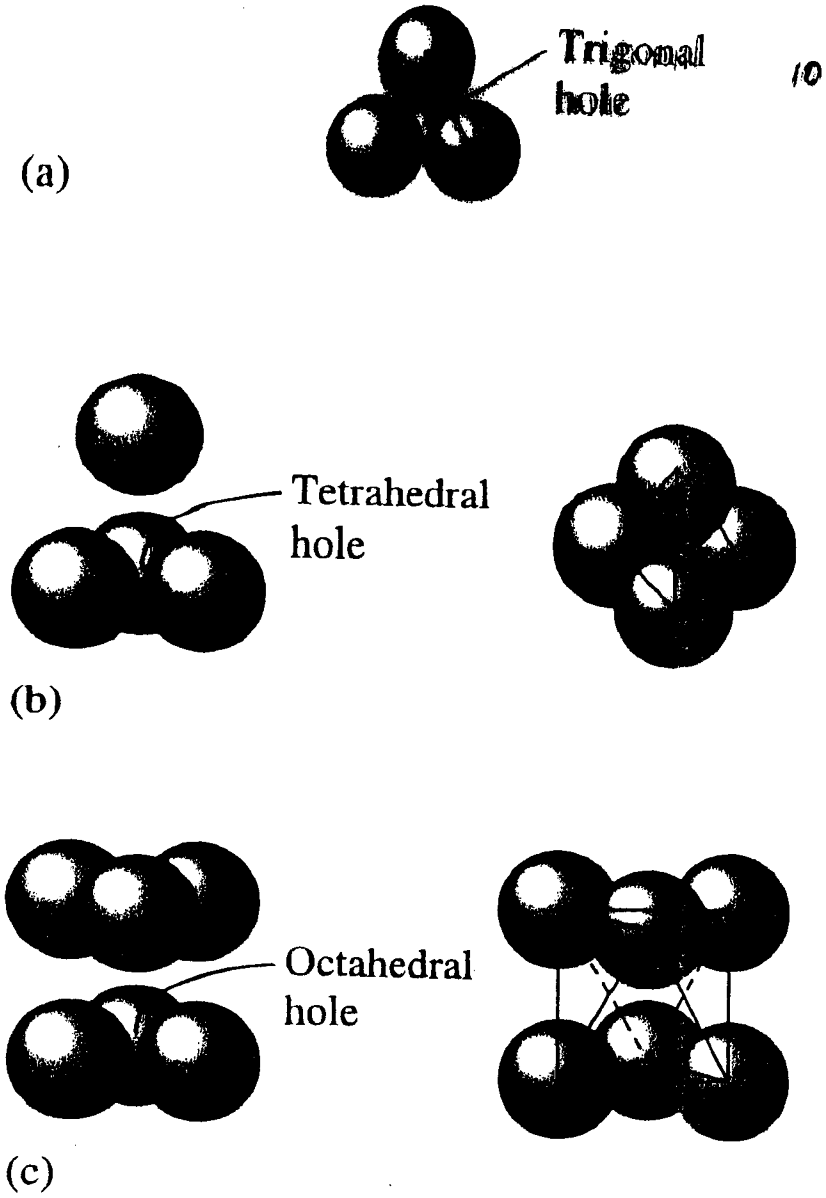


Figure 10.33
Trigonal, tetrahedral, and octahedral holes

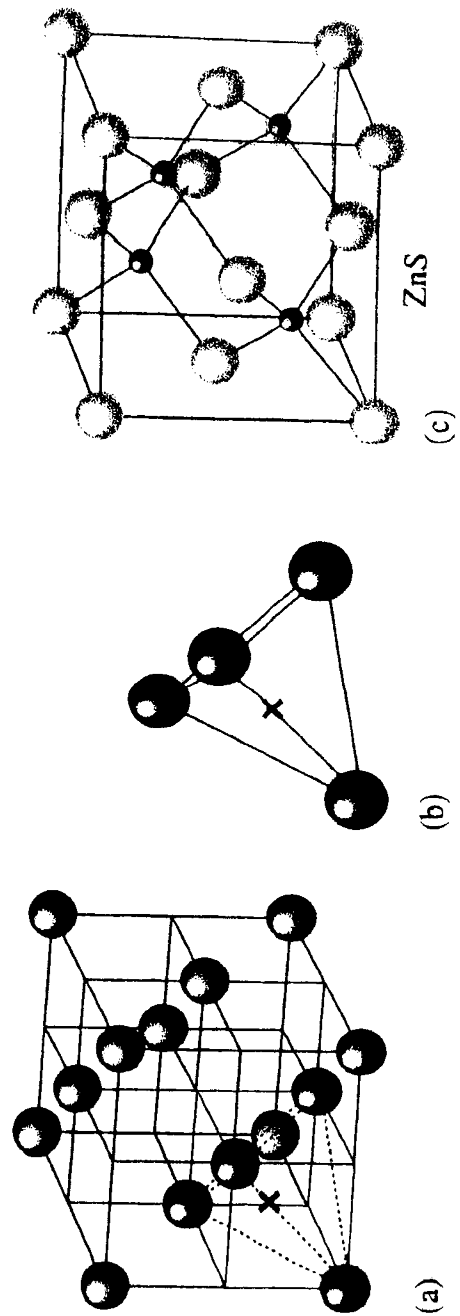
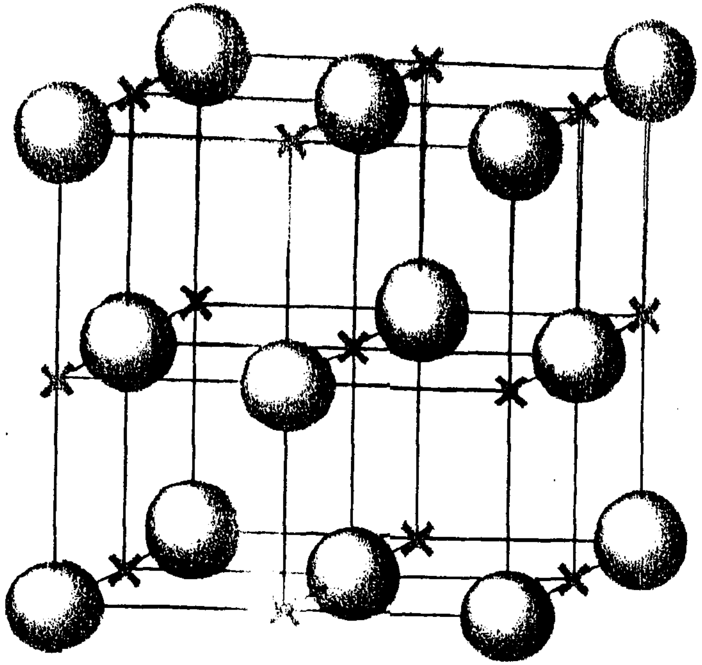
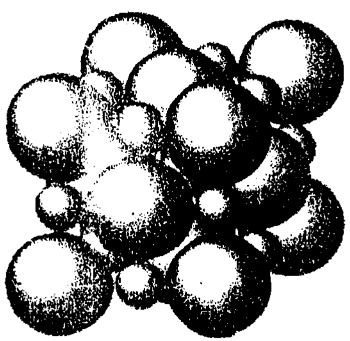


Figure 10.34
Position of tetrahedral holes in face-centered cubic unit cell



(a)



(b)

Figure 10.35
Cubic closest packing in NaCl

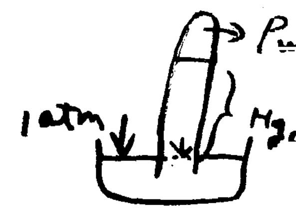
§ 10.8 Vapor Pressure and changes of state

ΔH_{vap} : the energy required to vaporize 1 mole of a liquid at 1 atm.

heat of vaporization
or enthalpy of vaporization

Fig. 10.36 & 10.37
↑
vapor pressure

Fig 10.38.



$P_{atmosphere} = P_{vapor} + P_{Hg\ column}$

$P_{vapor} = P_{atmosphere} - P_{Hg\ column}$

$\therefore P_{vapor}(H_2O) < P_{vapor}(C_2H_5OH)$ ethanol

$< P_{vapor}(C_2H_{5}{}_2O)$ ether

(与 放 一 美 floating on the mercury)

10.35

Vapor pressure & Temp.

同一種 molecule

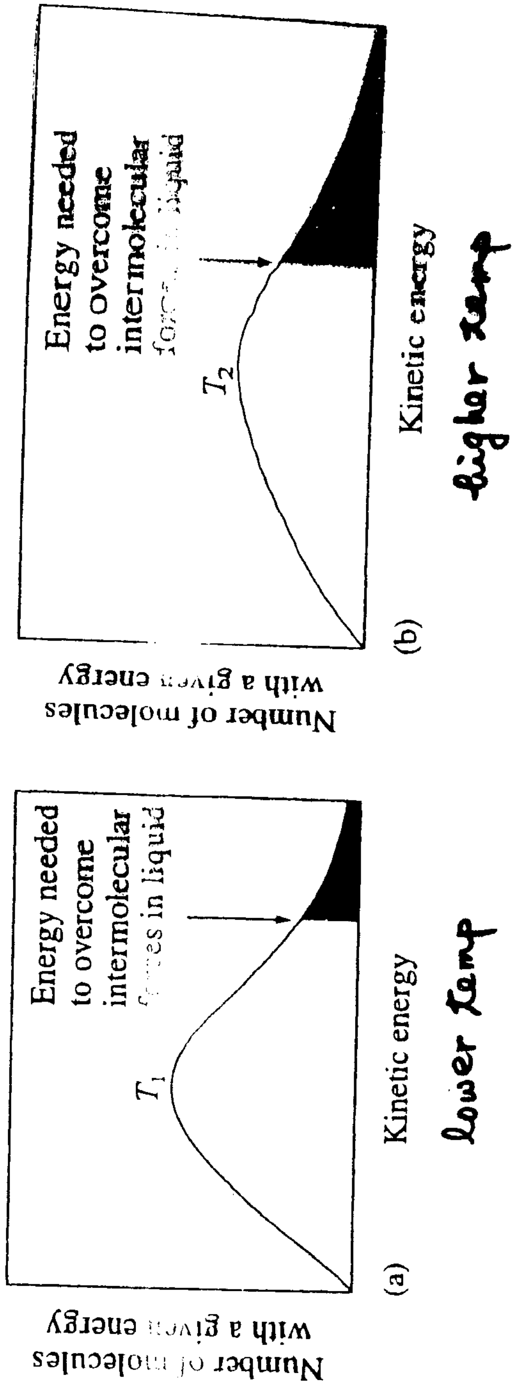


Figure 10.39 **Diagrams showing the reason vapor pressure depends on temperature**

∴ T↑, vapor pressure ↑ see Table 10.8

$$\ln(p^{vap}) = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T}\right) + C \qquad 10.36$$

↑ vapor pressure

$$y = mx + b$$

$y = \ln(p^{vap})$

$x = \frac{1}{T}$ } 作圖

$m =$ slope (斜率) $= -\frac{\Delta H_{vap}}{R}$

$b =$ intercept (截距) $= C$

Ex. 10.5 & 10.6

$$\ln(p^{vap}_{T_1}) - \ln(p^{vap}_{T_2}) = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

10-37

Heating curve of H_2O

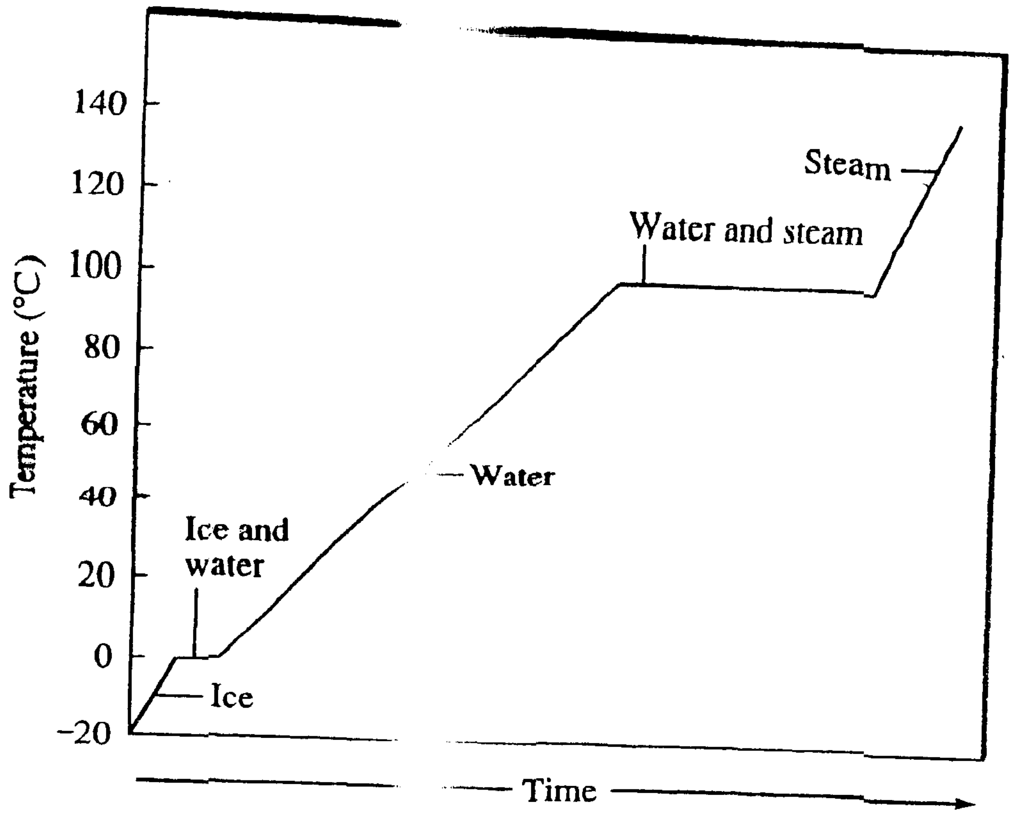


Figure 10.42

Heating curve for wat

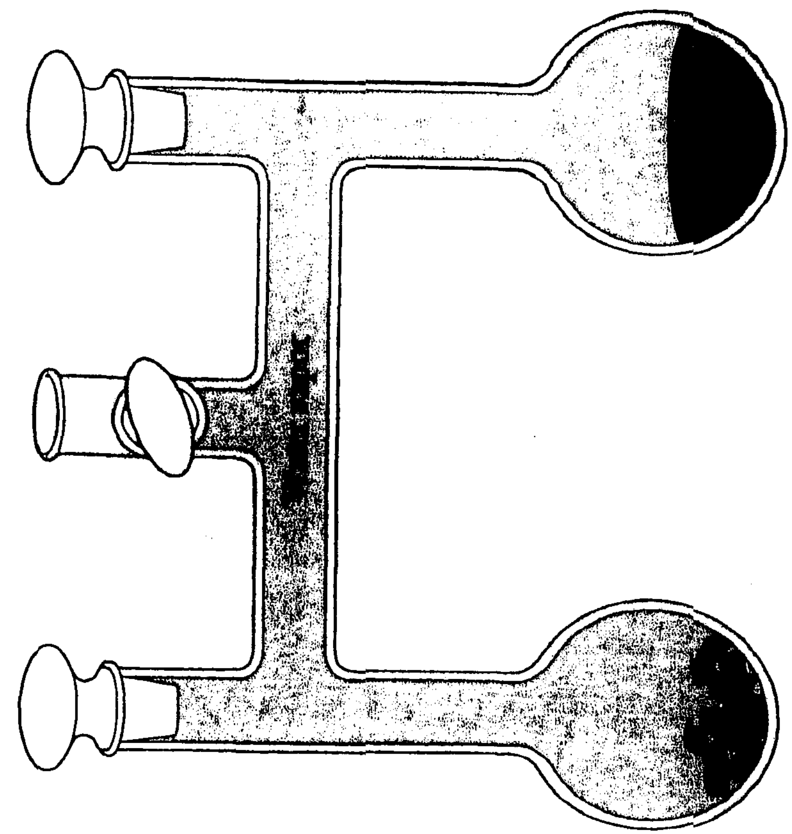


Figure 10.44

Solid and liquid phases in equilibrium with the vapor phase

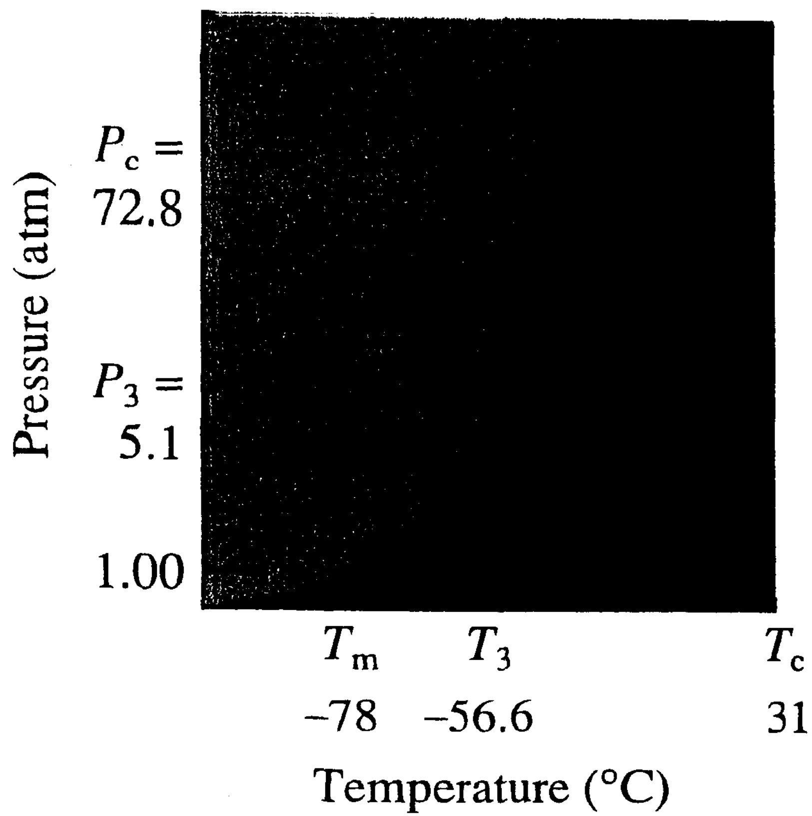


Figure 10.52
Phase diagram for carbon dioxide

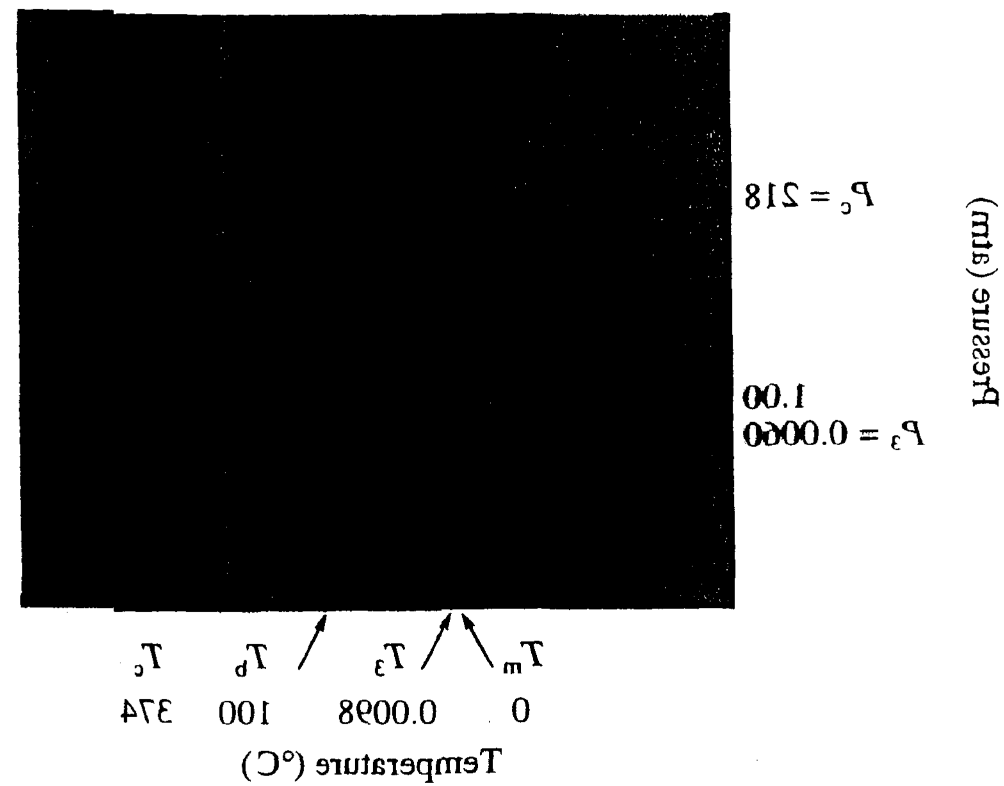
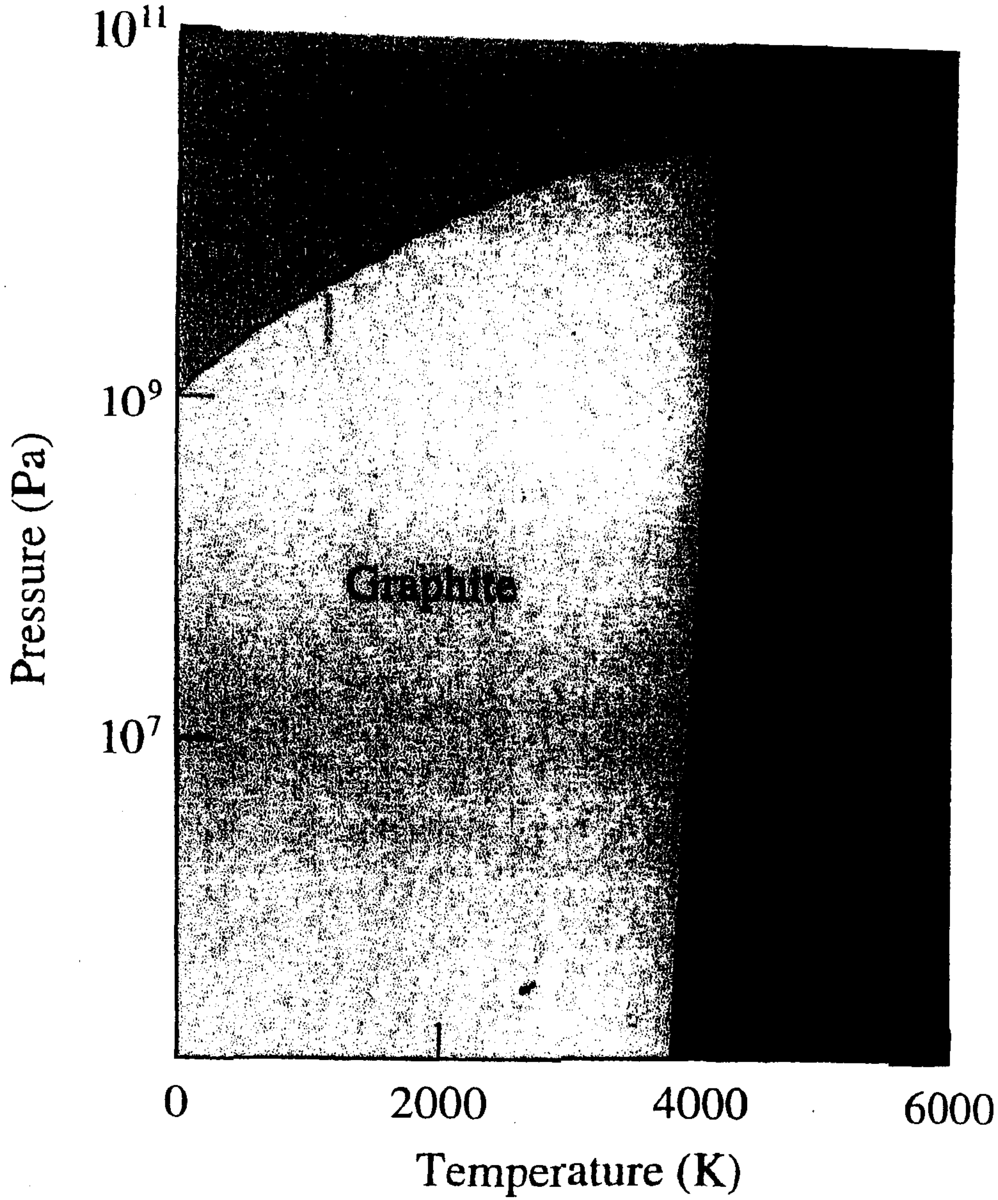
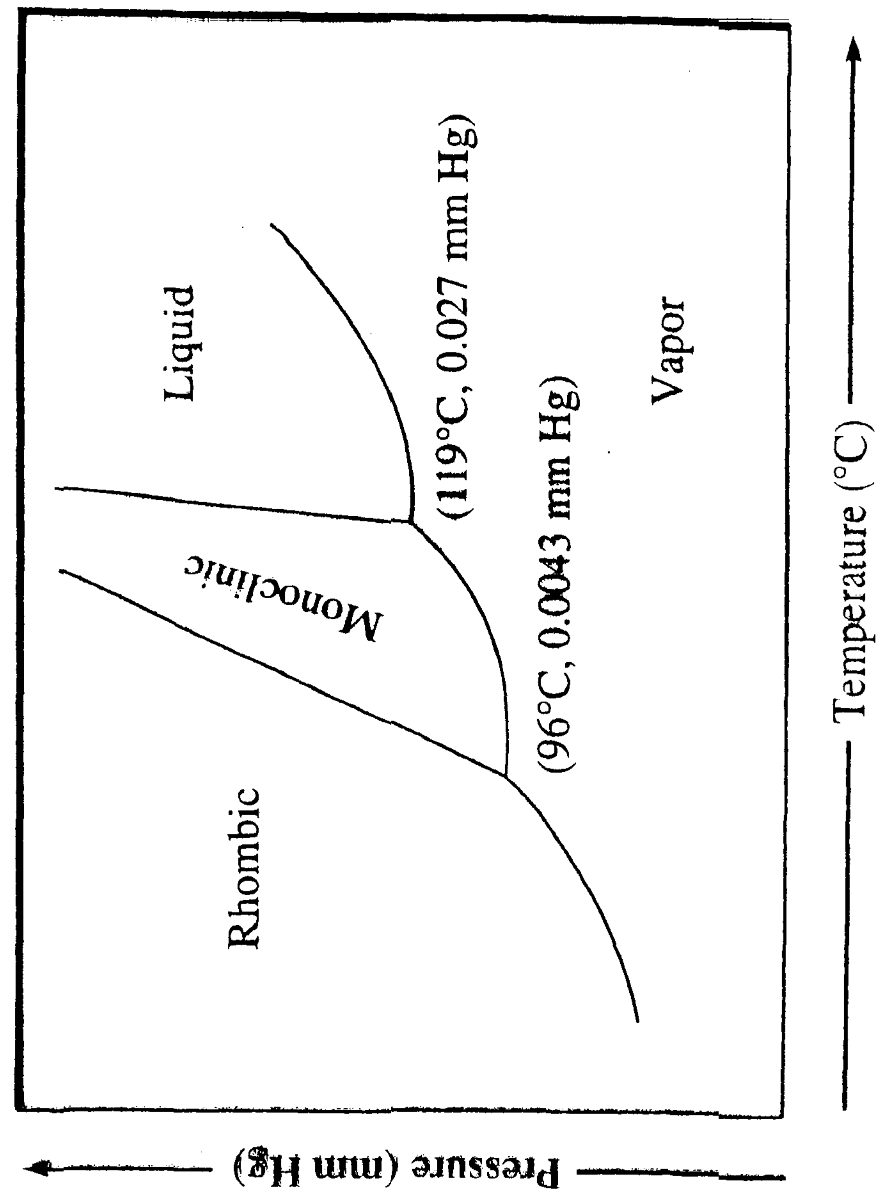


Figure 10.47
Phase diagram for water



Phase diagram for carbon



hase diagram for sulfur