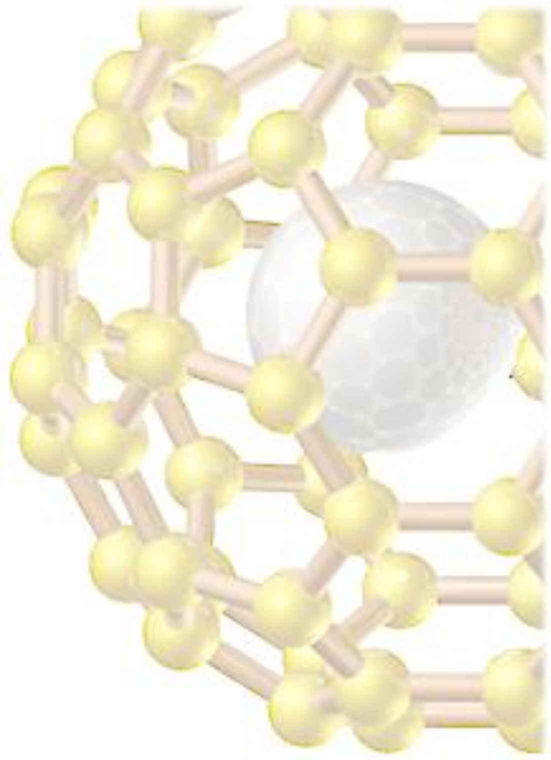
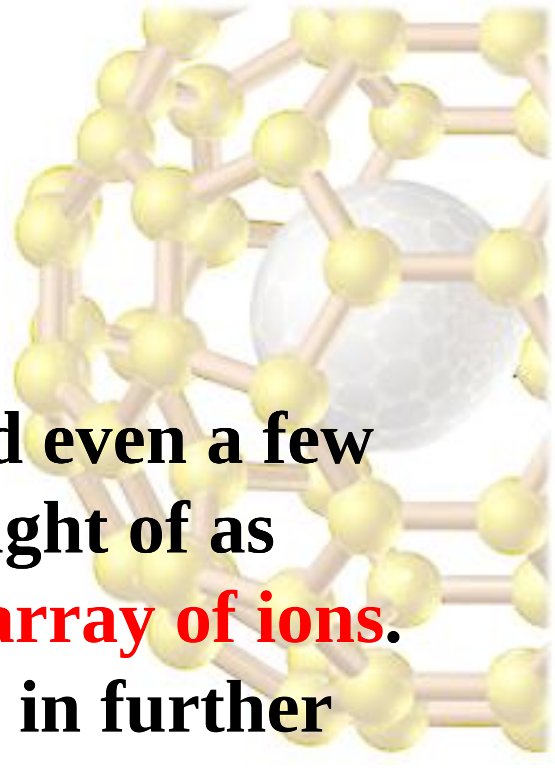


离子晶体结构

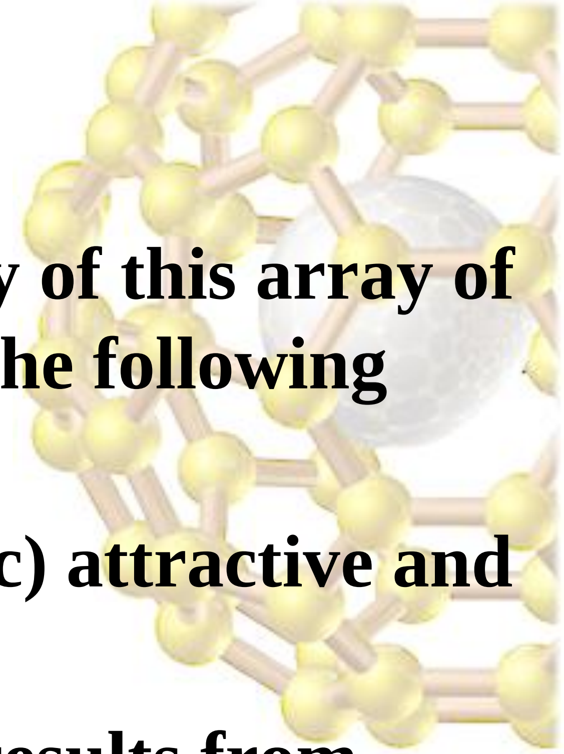
Chapter 4 Ionic solids

Introduction



- **A great many inorganic solids, and even a few organic ones, can usefully be thought of as consisting of a three-dimensional array of ions. This ionic model can be developed in further detail in two main ways.**

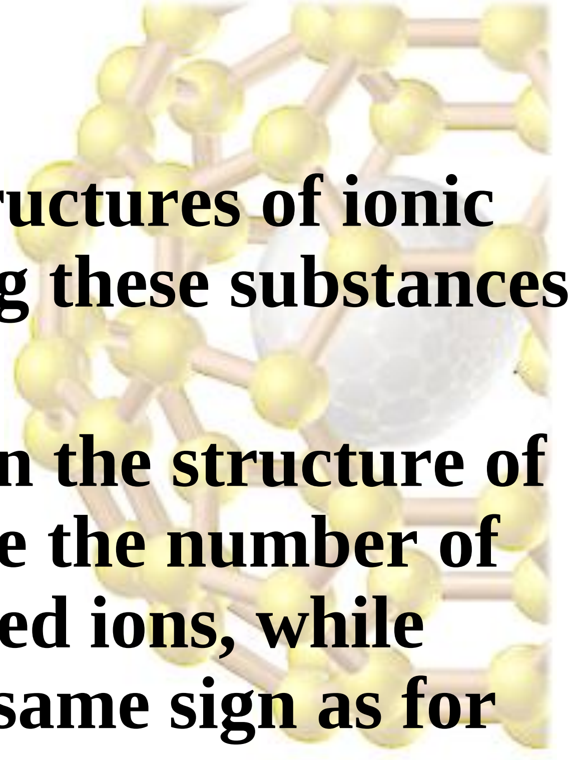
Introduction



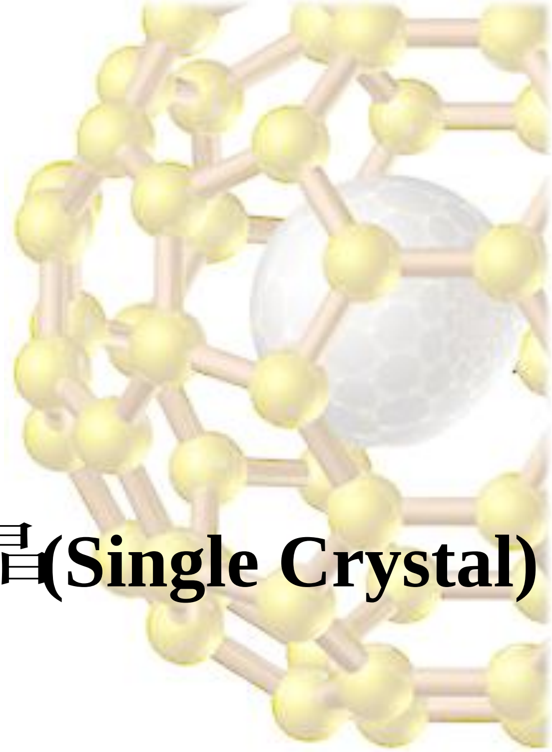
First, it is assumed that the energy of this array of ions can be treated as the sum of the following contributions:

- **Coulombic(库仑的）（electrostatic) attractive and repulsive energies.**
- **Additional repulsive energy that results from repulsion between the overlapping outer electron density of adjacent ions.**
- **A variety of minor energy terms, mainly van der Waals and zero point vibrational energy.**

Introduction



- **Second, the main features of the structures of ionic solids can be understood by treating these substances as efficiently packed arrays of ions.**
- **To be efficient the packing of ions in the structure of and ionic compound must maximize the number of contracts between oppositely charged ions, while simultaneously keeping ions of the same sign as for apart as possible.**
- **A set of radii for the different ions, together with a geometrical and electrostatic analysis, can enable us to understand why , for example, NaCl, CsCl, and CuCl all have different structures.**

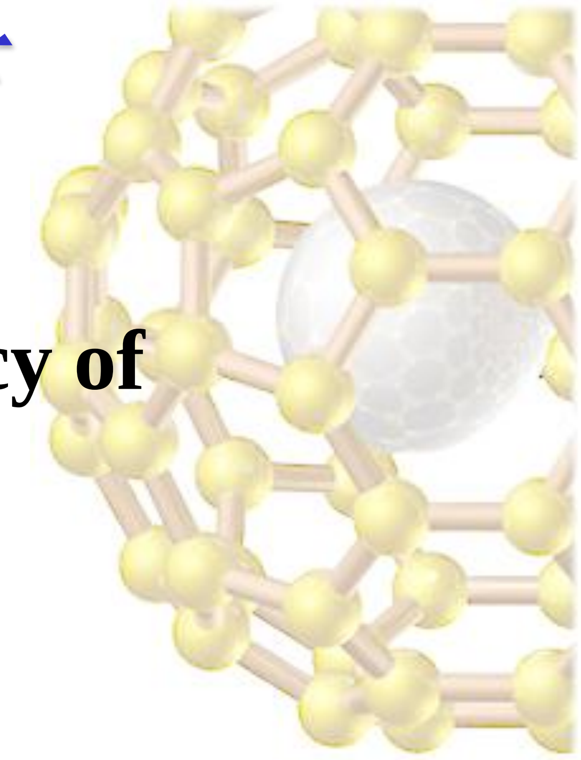


14.1 晶体结构的分类和宏观特征

14.1.1 固体物质的分类

- 晶体
  - 单晶**(Single Crystal)**
  - 多晶**(Poly crystal)**
- **(amorphous substance)**
  无定形物质

14.1.2 固体物质的宏观特征



- 晶体的特征

1. 晶面角守恒定律(law of constancy of interfacial angle)
2. 有固定的熔点(melting point)
3. 各向异性(anisotropy)
4. 具有对称性(symmetry)

- 无定形物质的特征

1. 没有固定的外形
2. 没有固定的熔点
3. 各向同性(isotropy)

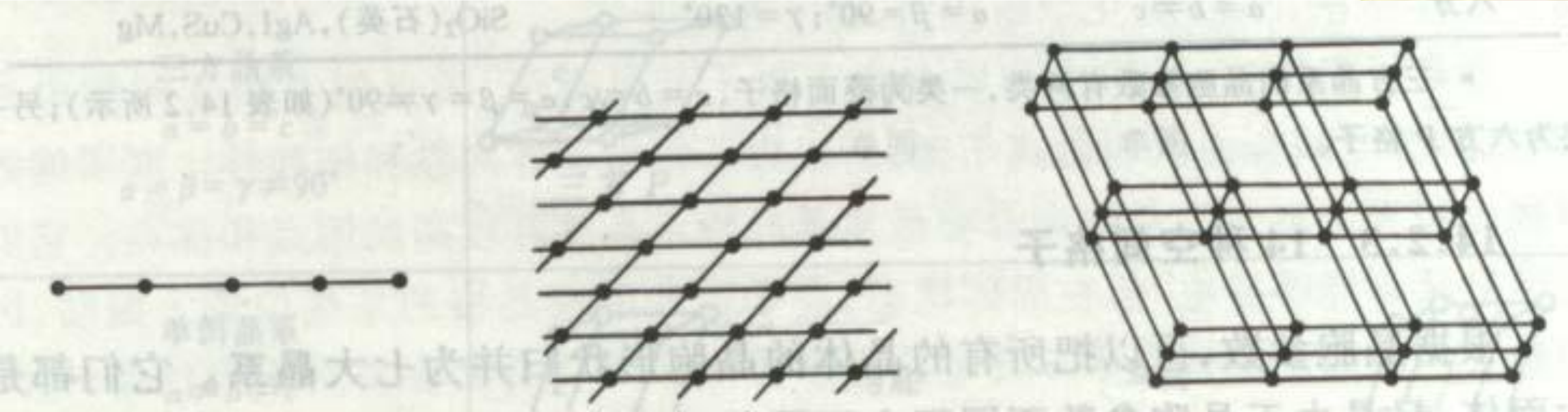
14.2 晶体的微观点阵结构

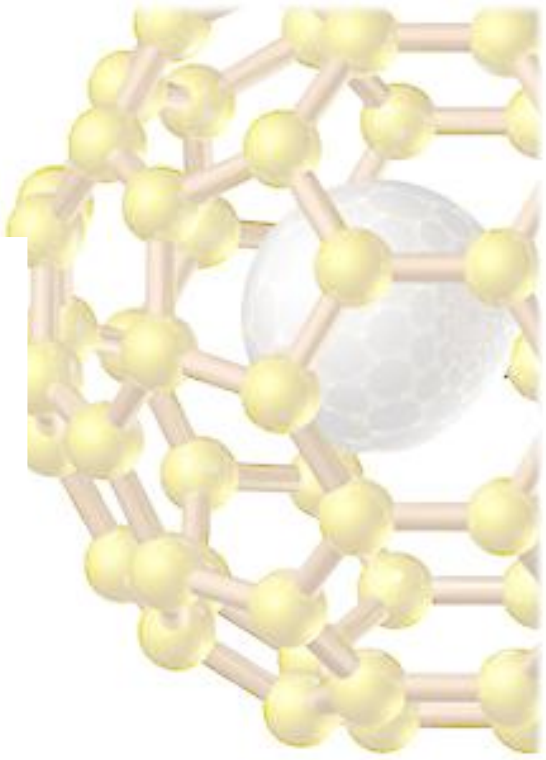
- **14.2.1 晶体与点阵(Crystal and lattice)**

直线点阵(图14.2)

平面点阵(图14.3

空间点阵(space lattice) (图14.4)





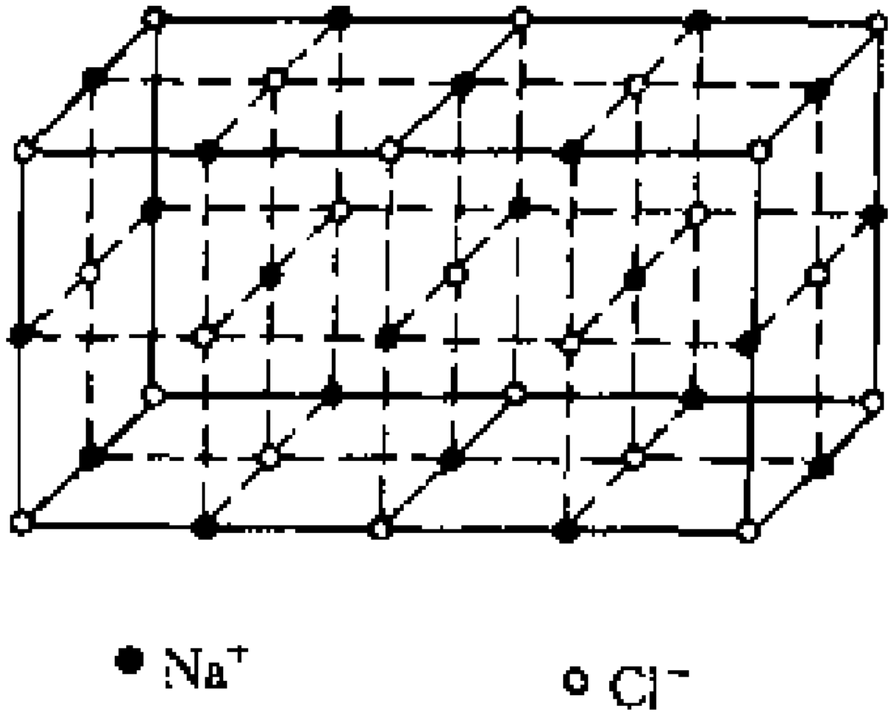
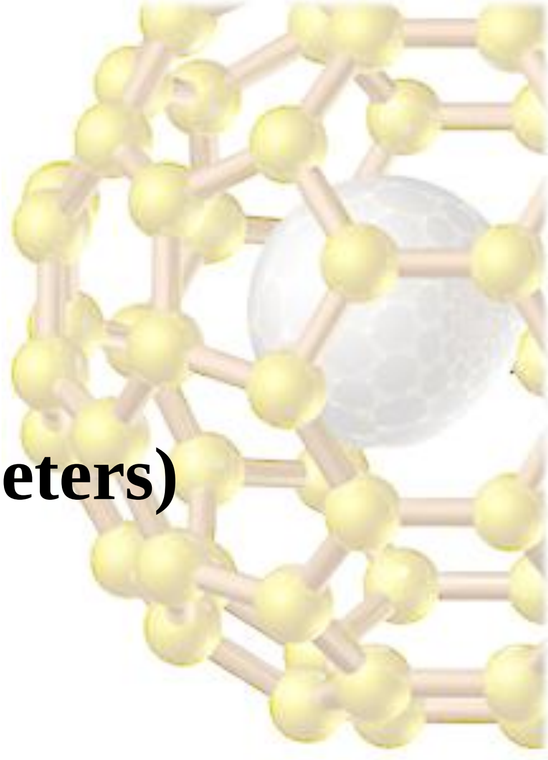


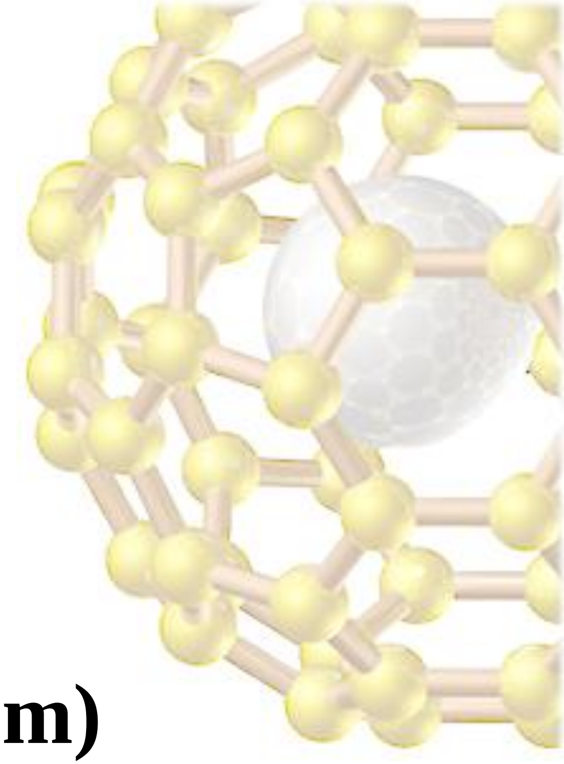
图 14.1　NaCl 晶体结构示意图

14.2.2 晶胞和七个晶系



- 结点(joint)
- 晶胞(unit cell)
- 晶胞参数(点阵参数，lattice parameters)

七个晶系(见表14.1)



- 立方晶系(cubic system)
- 四方晶系(tetragonal system)
- 正交晶系(rhombic system)
- 三方晶系(rhombohedral system)
- 六方晶系(hexagonal system)
- 单斜晶系(monoclinic system)
- 三斜晶系(reiclinic system)

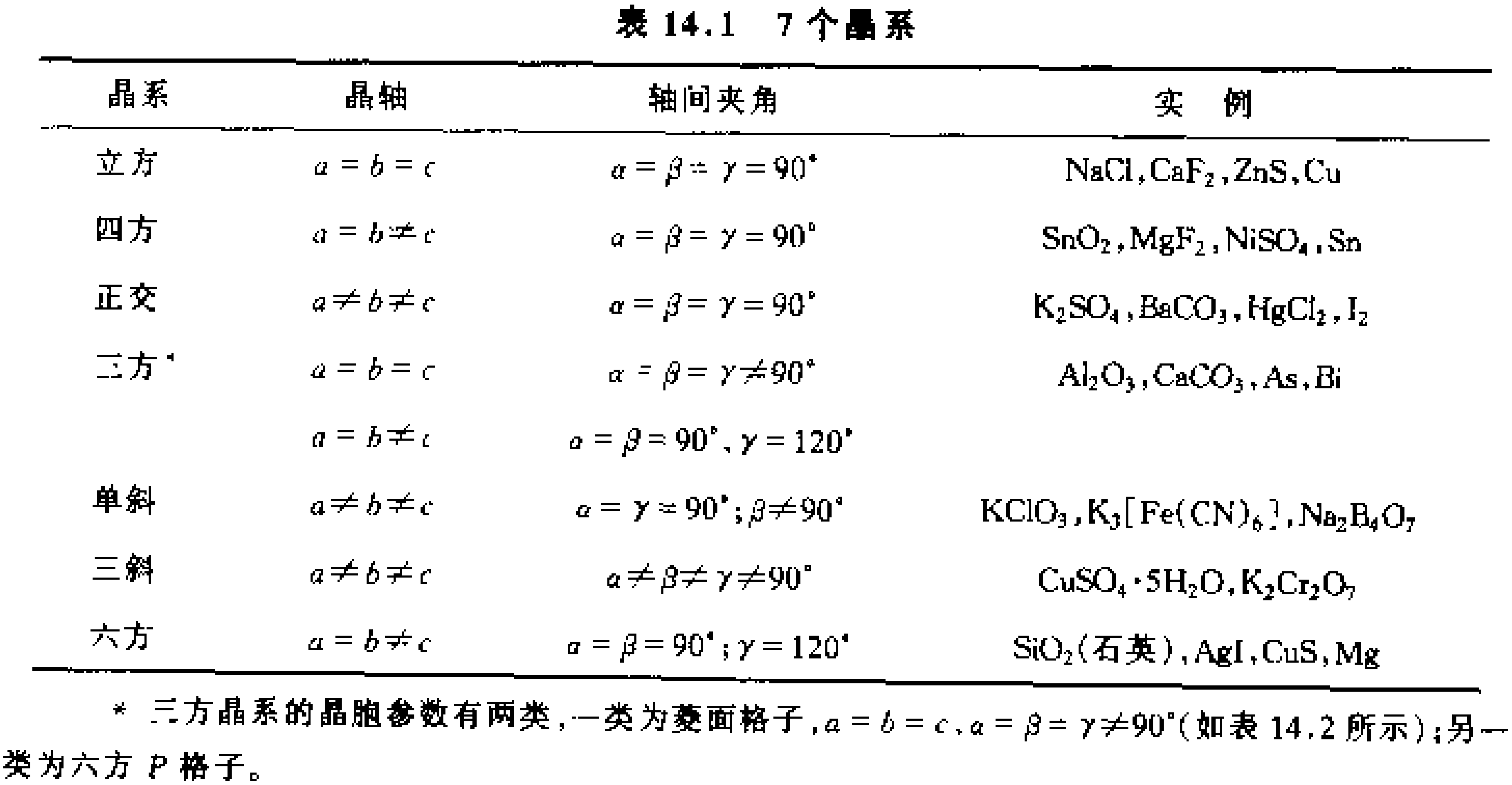
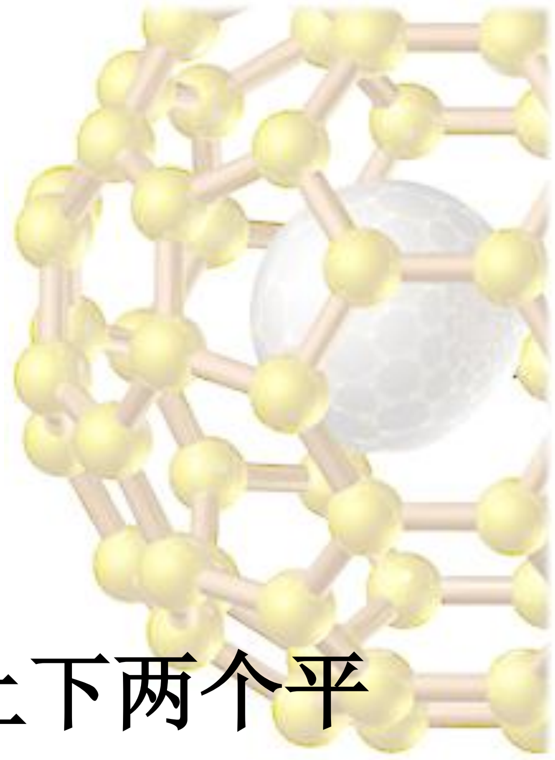


表 14.1　7 个晶系

晶系	晶轴	轴间夹角	实　例
立方	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	NaCl，CaF_2，ZnS，Cu
四方	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	SnO_2，MgF_2，$NiSO_4$，Sn
正交	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	K_2SO_4，$BaCO_3$，$HgCl_2$，I_2
三方*	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	Al_2O_3，$CaCO_3$，As，Bi
	$a = b \neq c$	$\alpha = \beta = 90^\circ$、$\gamma = 120^\circ$	
单斜	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ$；$\beta \neq 90^\circ$	$KClO_3$，$K_3[Fe(CN)_6]$，$Na_2B_4O_7$
三斜	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	$CuSO_4 \cdot 5H_2O$，$K_2Cr_2O_7$
六方	$a = b \neq c$	$\alpha = \beta = 90^\circ$；$\gamma = 120^\circ$	SiO_2（石英），AgI，CuS，Mg

* 三方晶系的晶胞参数有两类，一类为菱面格子，$a = b = c$、$\alpha = \beta = \gamma \neq 90^\circ$（如表 14.2 所示）；另一类为六方 P 格子。

14.2.3 14种空间格子

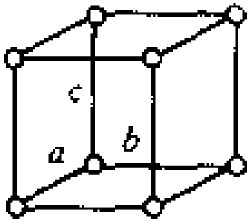
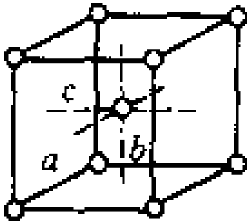
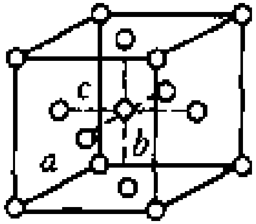
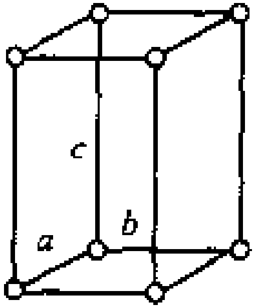
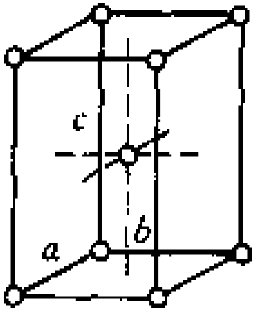
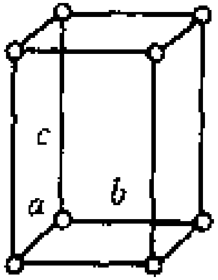
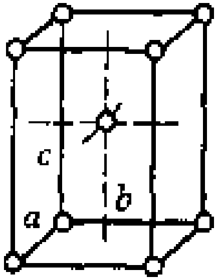
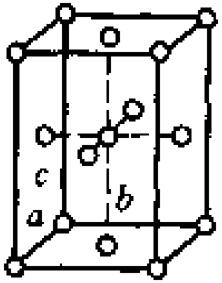
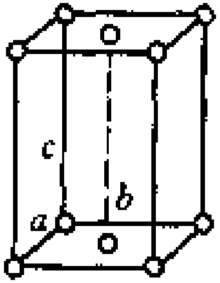


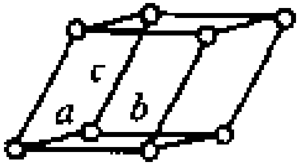
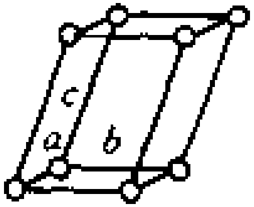
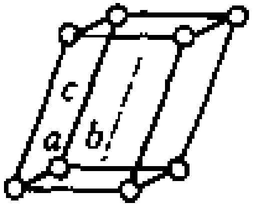
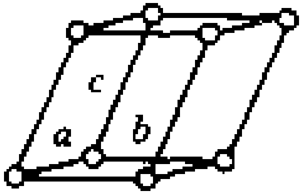
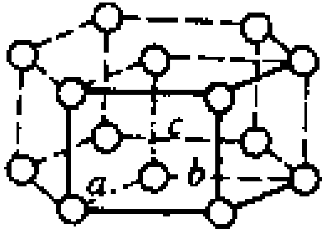
- **4 种格子**

1. **简单格子P(simple cubic)**
2. **底心格子C(除8个顶角外，上下两个平面的中心各个一个结点)**
3. **体心格子I(body-centered cubic)**
4. **面心格子F(face-centered cubic)**

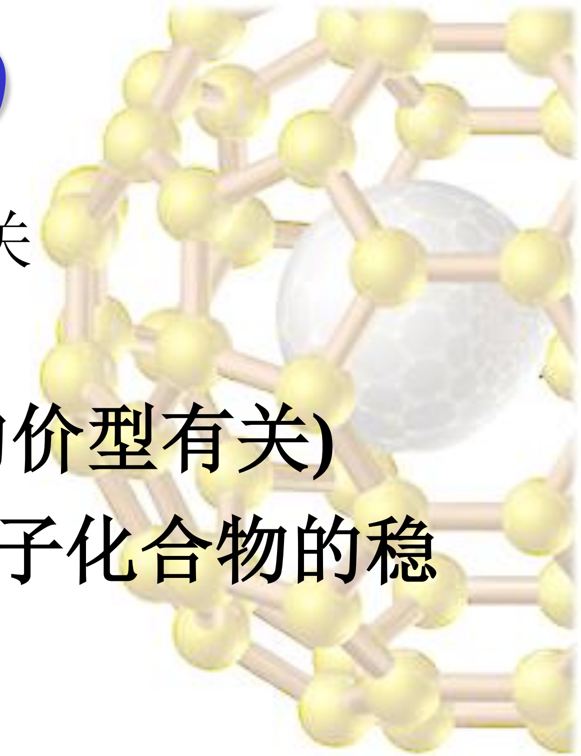
- **14种格子见表14.2**

表 14.2 7个晶系和14种晶格

	简单格子	体心格子	面心格子	底心格子
立方晶系 $a=b=c$ $\alpha=\beta=\gamma=90°$	 立方P	 立方I	 立方F	—
四方晶系 $a=b\neq c$ $\alpha=\beta=\gamma=90°$	 四方P	 四方I	与体心同	与简单同
正交晶系 $a\neq b\neq c$ $\alpha=\beta=\gamma=90°$	 正交P	 正交I	 正交F	 正交C

三方晶系 $a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$	 三方 P	与简单同	与简单同	—
单斜晶系 $a \neq b \neq c$ $\alpha = \gamma = 90^\circ$ $\beta \neq 90^\circ$	 单斜 P	与底同	与简单同	 单斜 C
三斜晶系 $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$	 三斜 P	与简单同	与简单同	与简单同
六方晶系 $a = b \neq c$ $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	—	—	—	 六方 P

14.3 离子晶体(ionic crystal)



在离子晶体中离子如何排布与以下因素有关

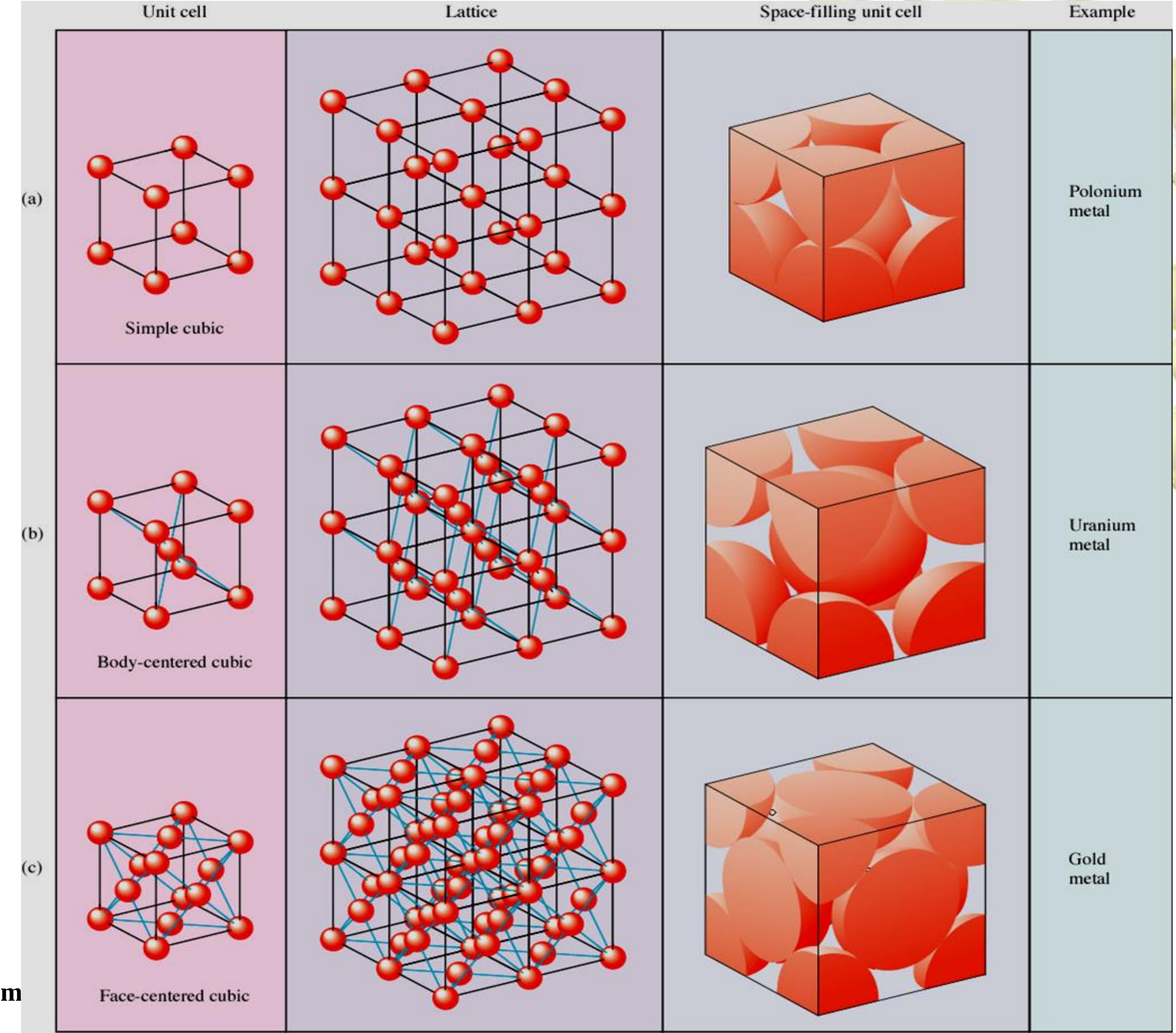
- 离子所带的电荷(与离子化合物的价型有关)

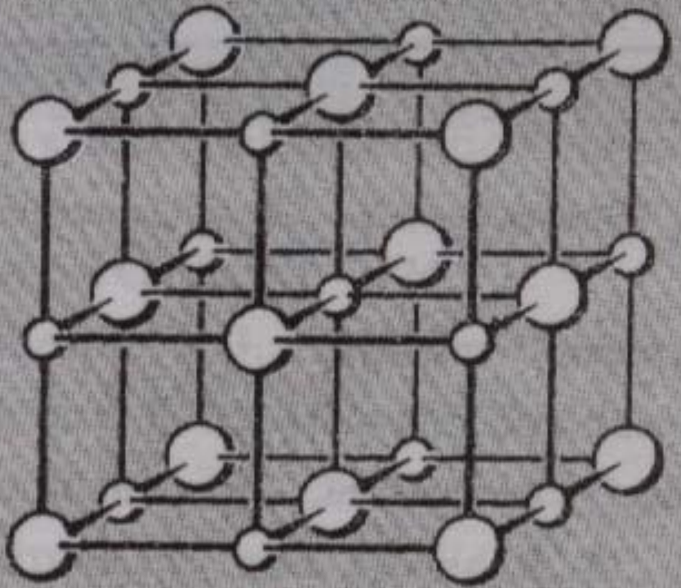
离子晶体的晶格能的大小能影响离子化合物的稳定性、熔点、沸点、硬度

- 离子晶体的离子半径比

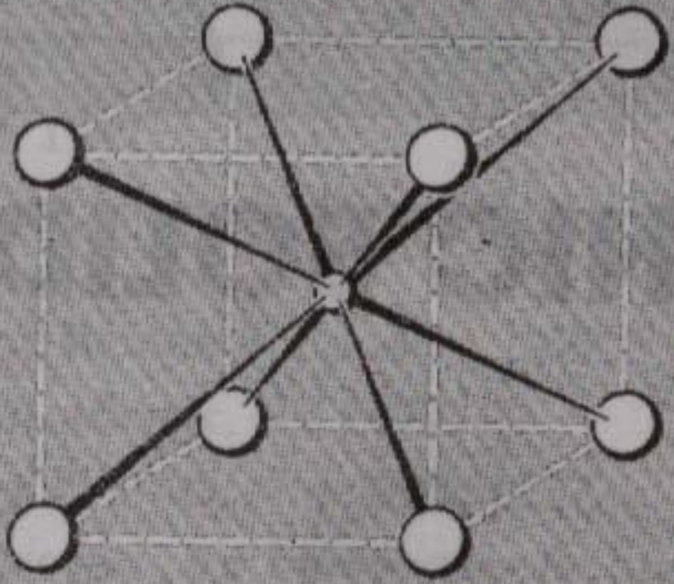
半径比	配位数	晶体结构	实例
0.225-0.414	**4**	**ZnS**	**ZnS ZnO BeS Cucl**
0.414-0.732	**6**	**NaCl**	**NaCl KCl NaBr**
0.732-1	**8**	**CsCl**	**CsCl CsBr CsI TlCl**

14.3.3离子晶体最简单的几种构型

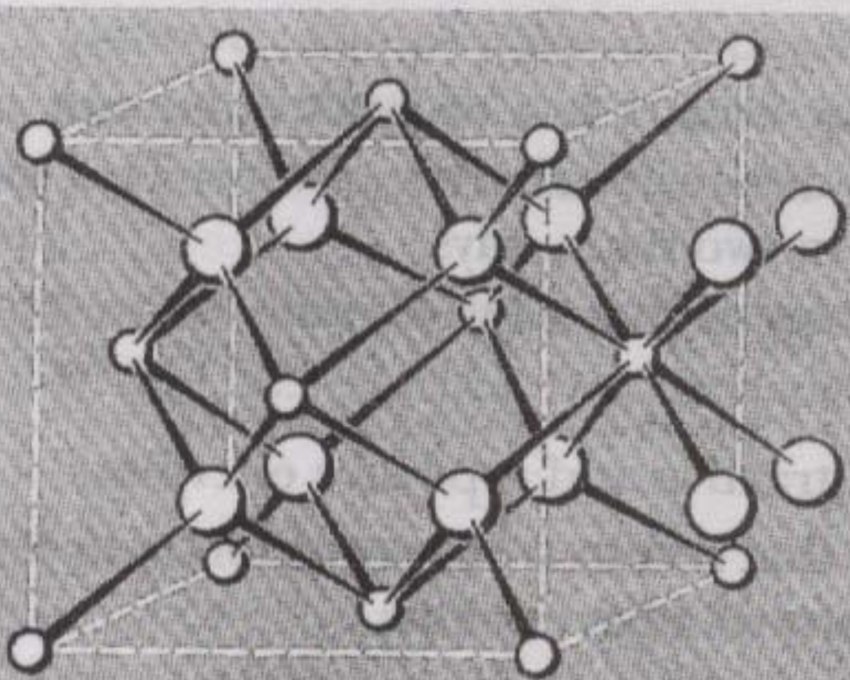




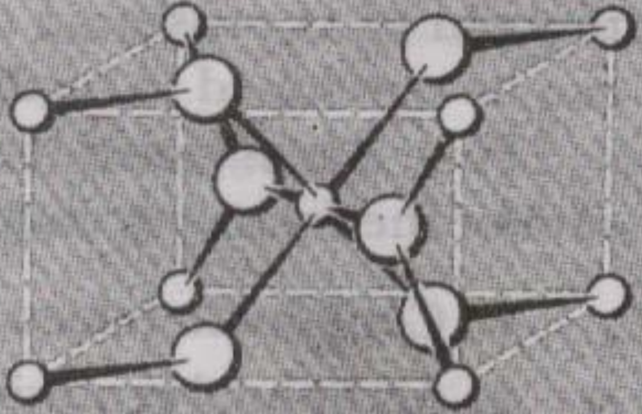
Rock-salt (NaCl)



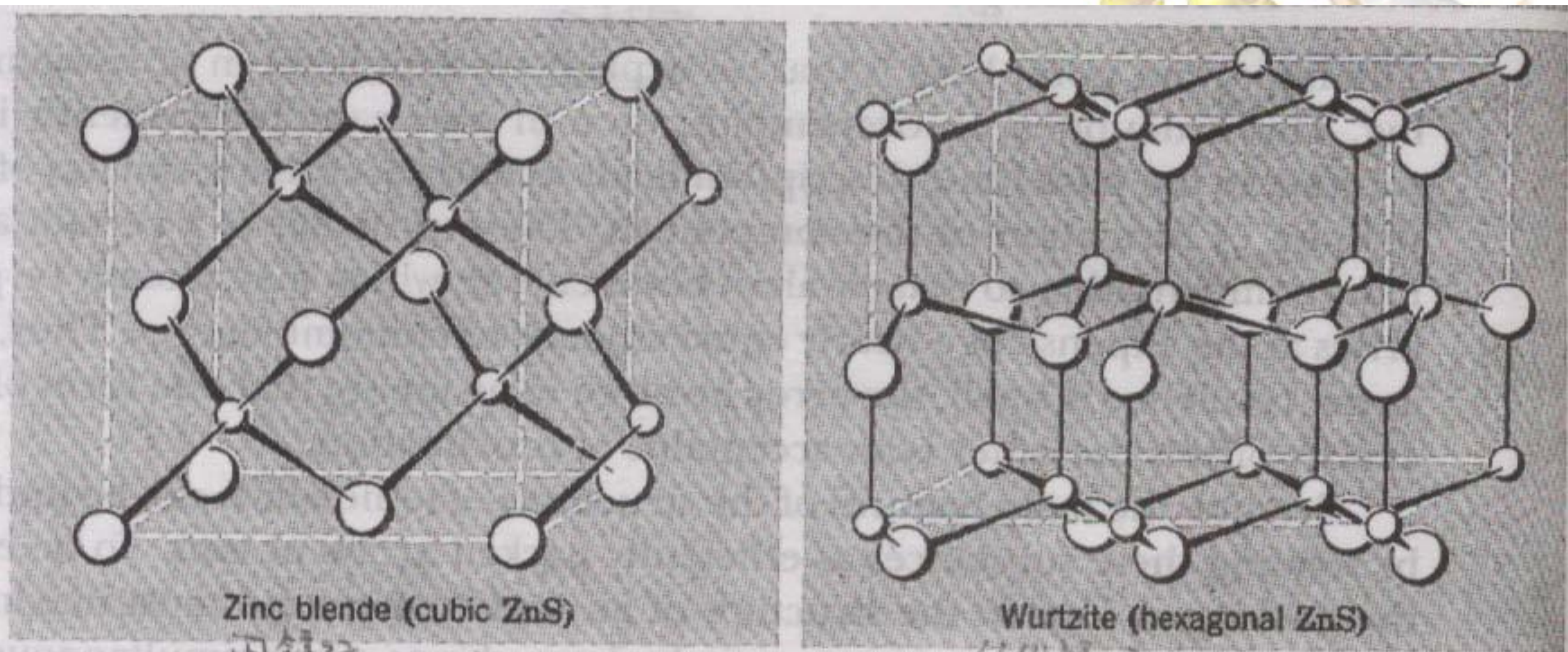
Cesium chloride (CsCl)



Fluorite (CaF_2)



Rutile (TiO_2)



Zinc blende (cubic ZnS)

闪锌矿

Wurtzite (hexagonal ZnS)

纤维锌矿

Figure 4-1 Six important ionic structures. Small circles denote metal cations and large circles denote anions.

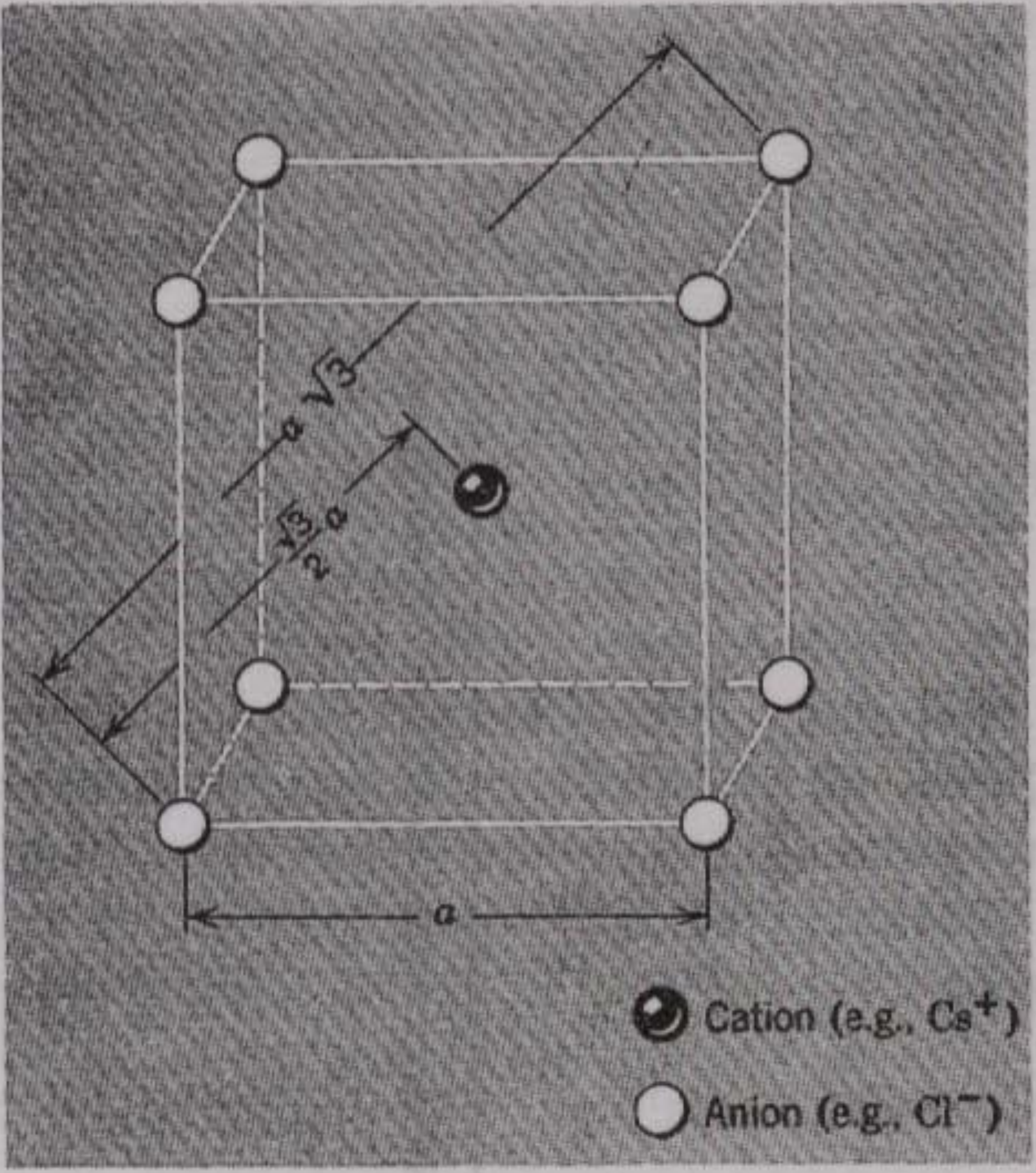
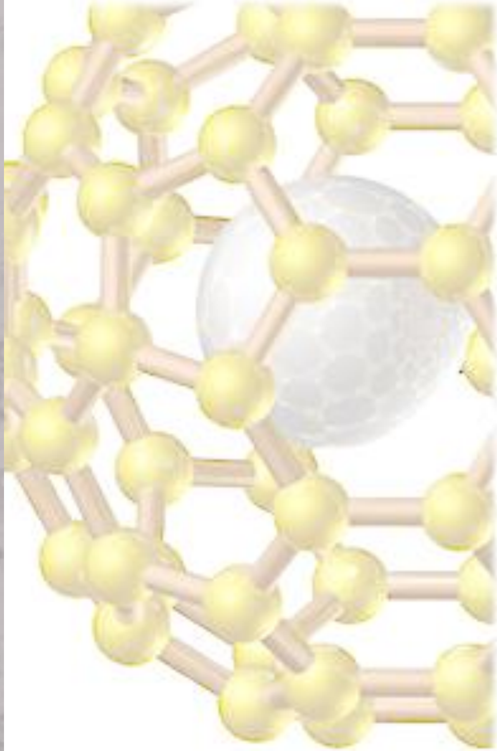
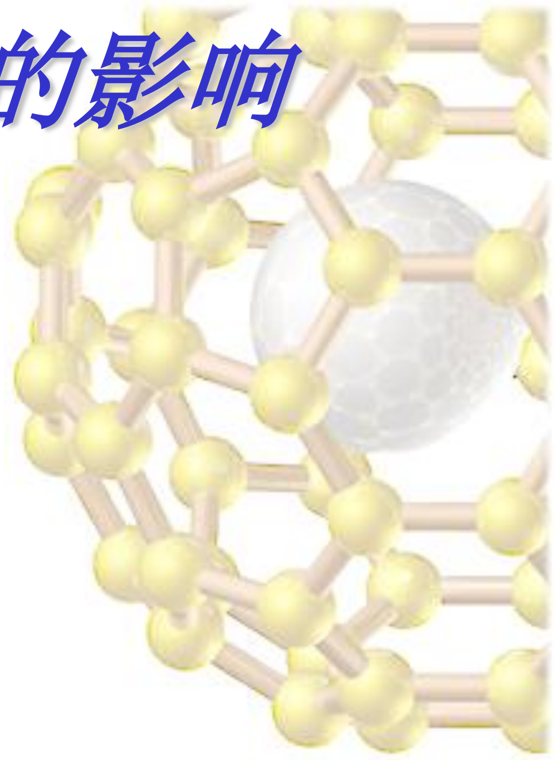


Figure 4-3 The geometry of the crystal lattice for CsCl.



14.3.4 离子极化对晶体结构的影响



- 离子极化作用和变形性

1. 极化作用的强弱
2. 变形性的大小
3. 附加极化作用

- 离子极化作用对化合物性质的影响

1. 熔点和沸点降低
2. 溶解度降低
3. 化合物的颜色
4. 离子化合物的晶型

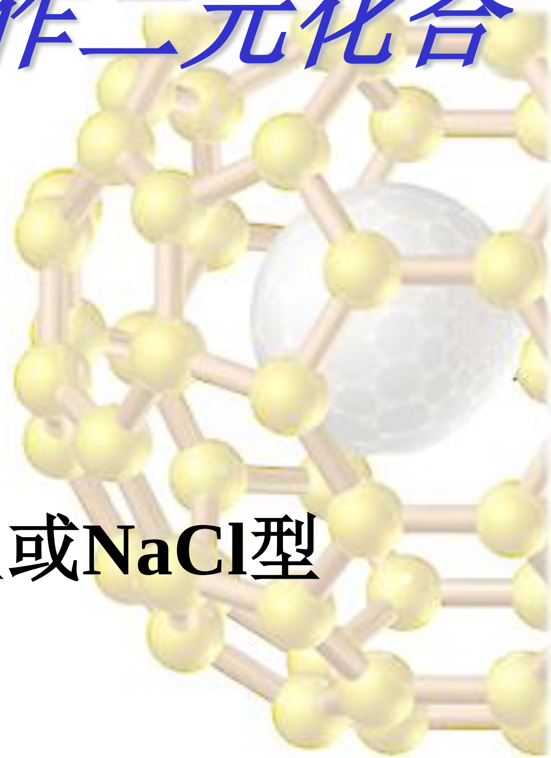
子构型。离子电荷愈高，半径愈小，极化作用愈强。正离子的电子层结构对极化作用也有影响。其作用的次序是：外层具有 8 个电子（稀有气体构型）时，极化能力最小（如 Na^+，Mg^{2+}，Ca^{2+} 等），外层具有 9～17 个电子，即不饱和电子层时，具有较大的极化能力（如 Mn^{2+}，Fe^{2+}，Fe^{3+} 等），外层具有 18，18＋2 或 2 个电子时，极化能力最强（如 Hg^{2+}，Sn^{2+}，Li^+，Be^{2+} 等）。

●变形性的大小。离子的半径愈大，变形性愈大。变形性也与电子构型有关，外层具有 9～17 个电子的离子变形性比稀有气体构型的要大得多。

虽然正离子和负离子都有极化作用和变形性，但一般地说，负离子电荷低，离子半径大，极化作用比较弱，变形性大。而正离子恰恰相反，具有较强的极化作用，变形性却不大。因此我们讨论离子相互极化时，主要是指正离子的极化作用和负离子的变形性。

●附加极化作用。通常考虑离子间相互作用时，一般考虑正离子的极化作用和负离子的变形性。但正离子也有被极化的可能，当负离子被极化后，在一定程度上增强了负离子对正离子的极化作用，结果使正离子变形而被极化，正离子被极化后，又增加了它对负离子的极化作用。这种加强的极化作用称为附加极化。每个离子的总极化作用应是它原来的极化作用和附加极化作用的加和。相互增强的极化作用使正、负离子都发生显著的极化现象。通常离子的d电子数愈多，电子层数愈多，附加极化作用也愈大。

14.3.5 某些多元化合物可看作二元化合物的衍生物(P598)



- NaCl型与CsCl型 的衍生结构

1. NH_4X(X=Cl、Br、I)-------CsCl型或NaCl型
2. CaC_2-----------NaCl型
3. RbO_2 BaO_2 与CaF_2

方解石$CaCO_3$可看成是变形的NaCl

- ZnS型的衍生结构

1. 黄铜矿$CuFeS_2$

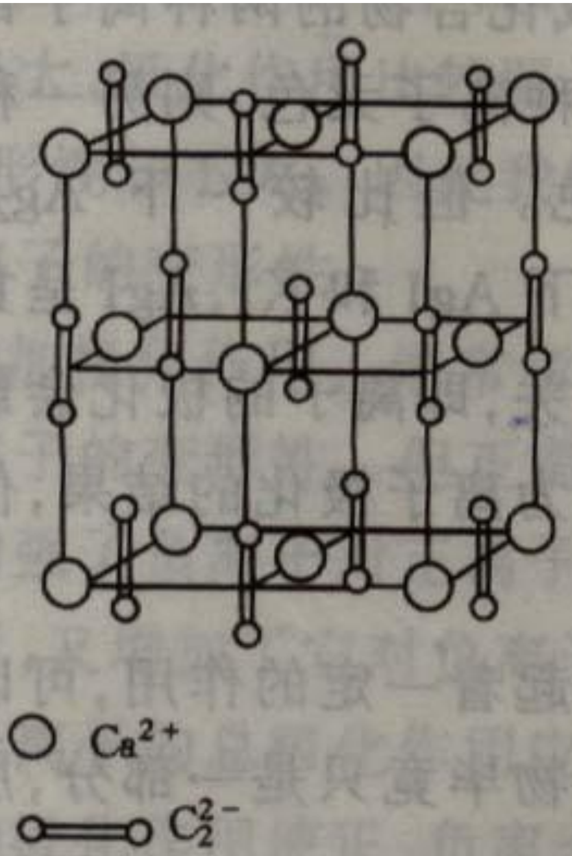


图 14.10 CaC_2 型结构

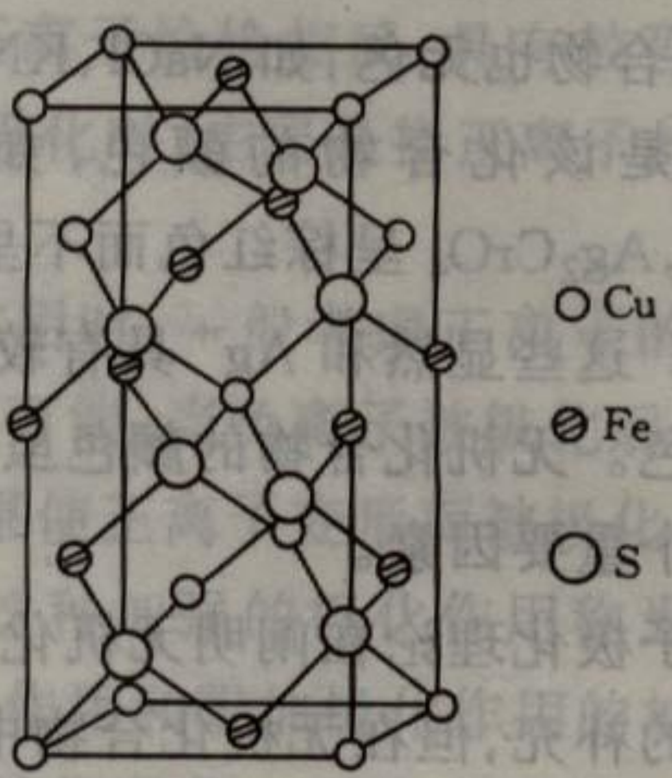
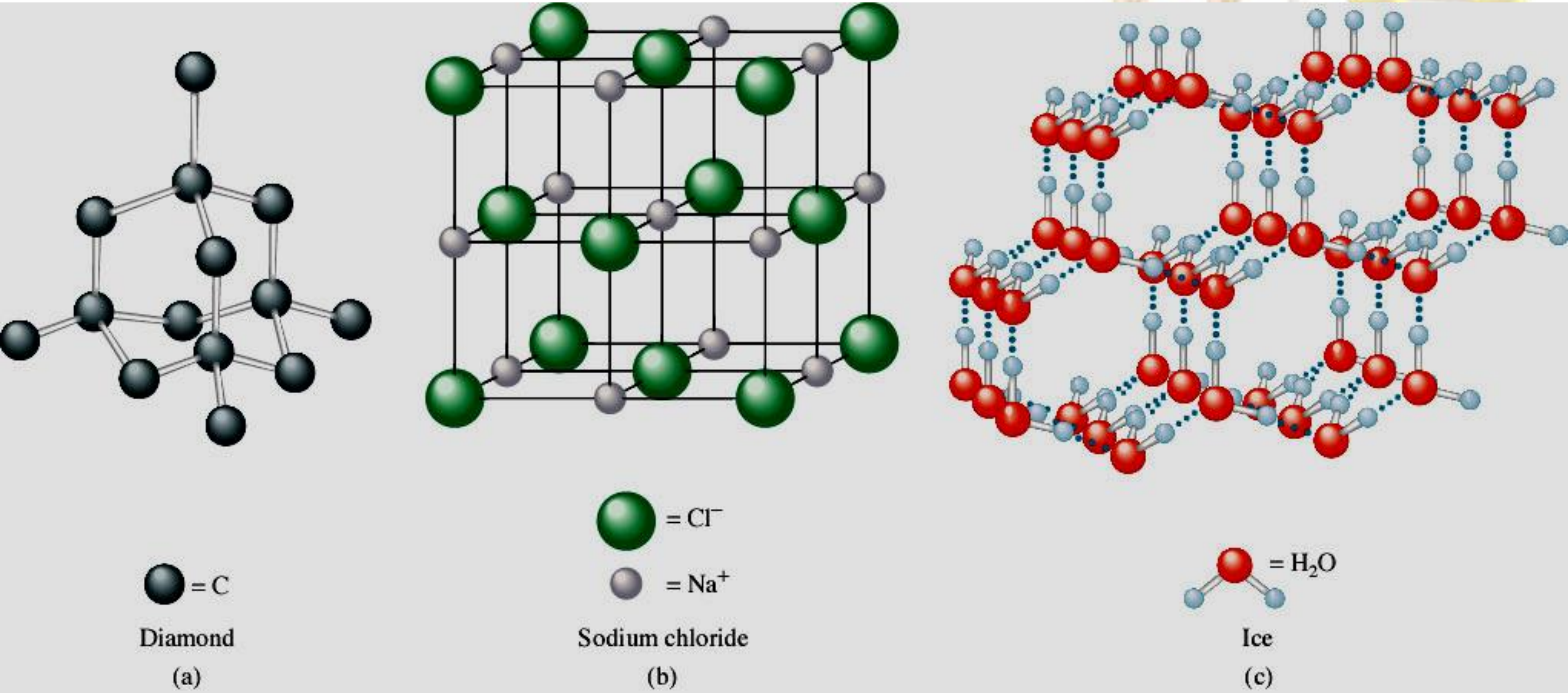


图 14.11 黄铜矿 $CuFeS_2$ 的结构

Examples of Three Types of Crystalline Solids



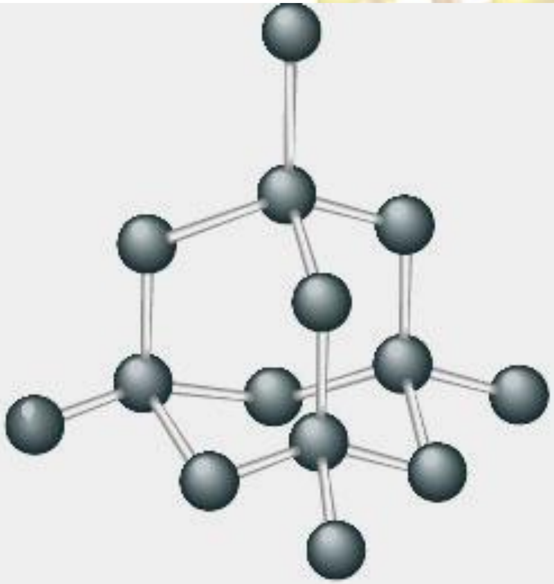
Diamond (a)

Sodium chloride (b)

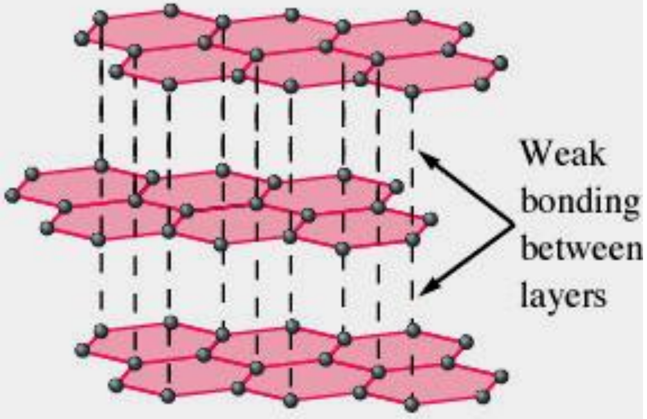
Ice (c)

14.4 原子晶体和分子晶体

The Structures of Diamond and Graphite



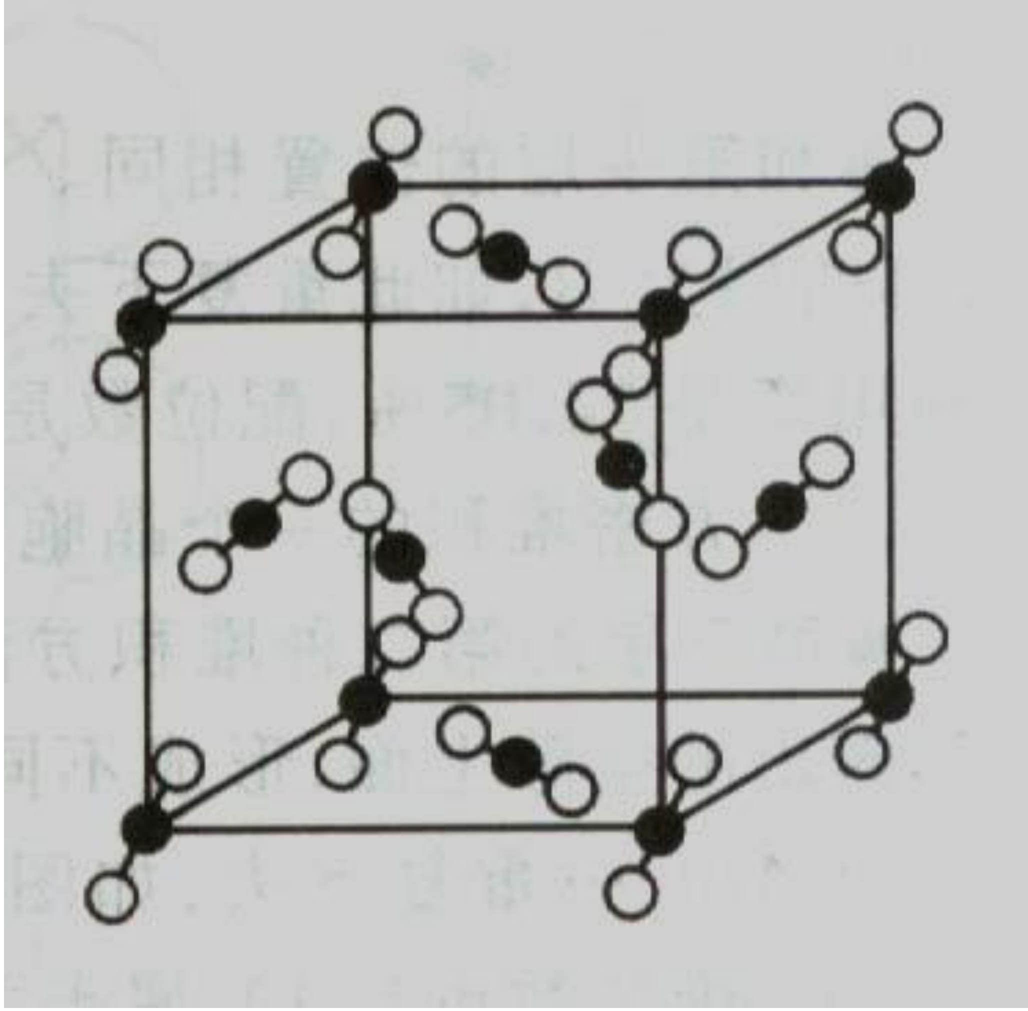
(a) Diamond

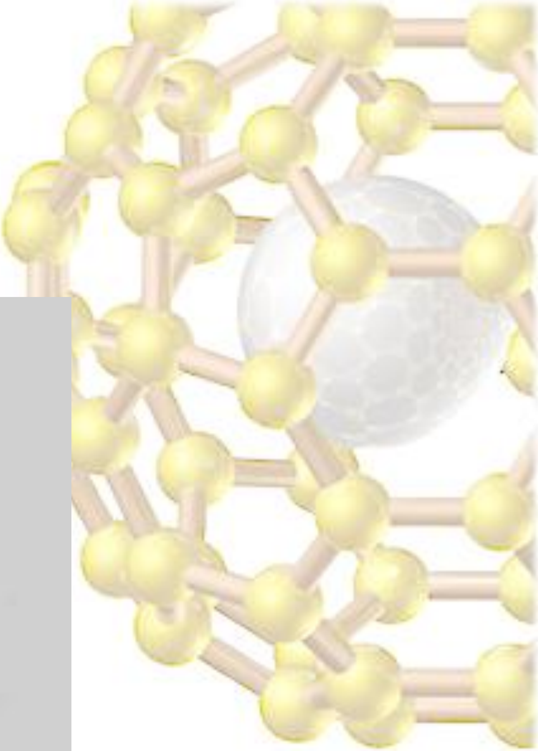


(b) Graphite

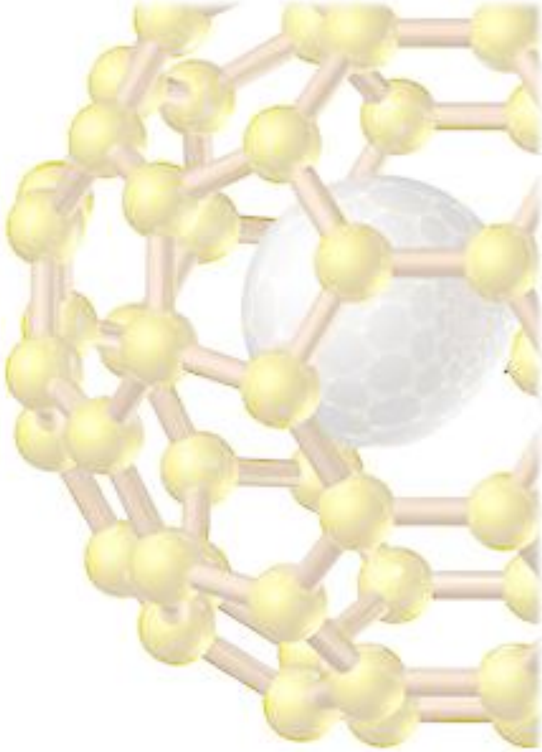
14.4.2 分子晶体

- CO_2分子的晶胞P599



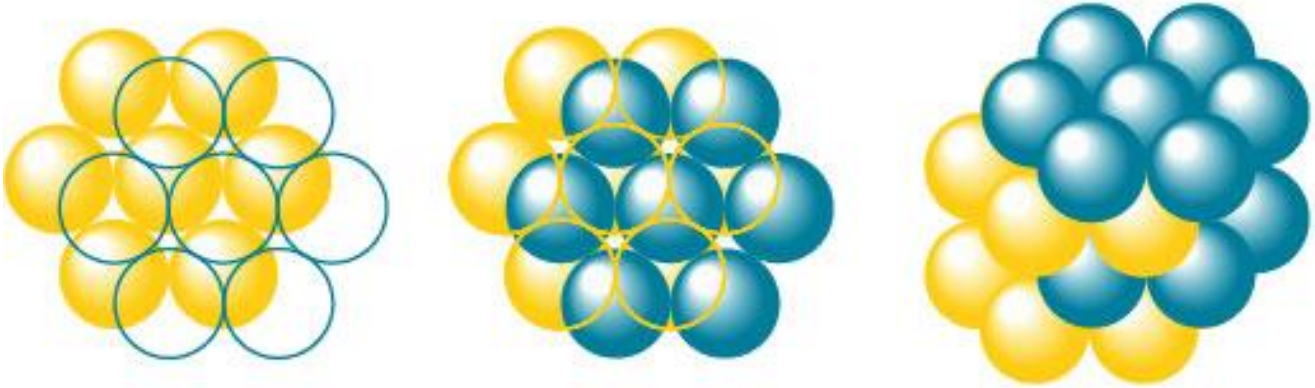


14.5 金属晶体



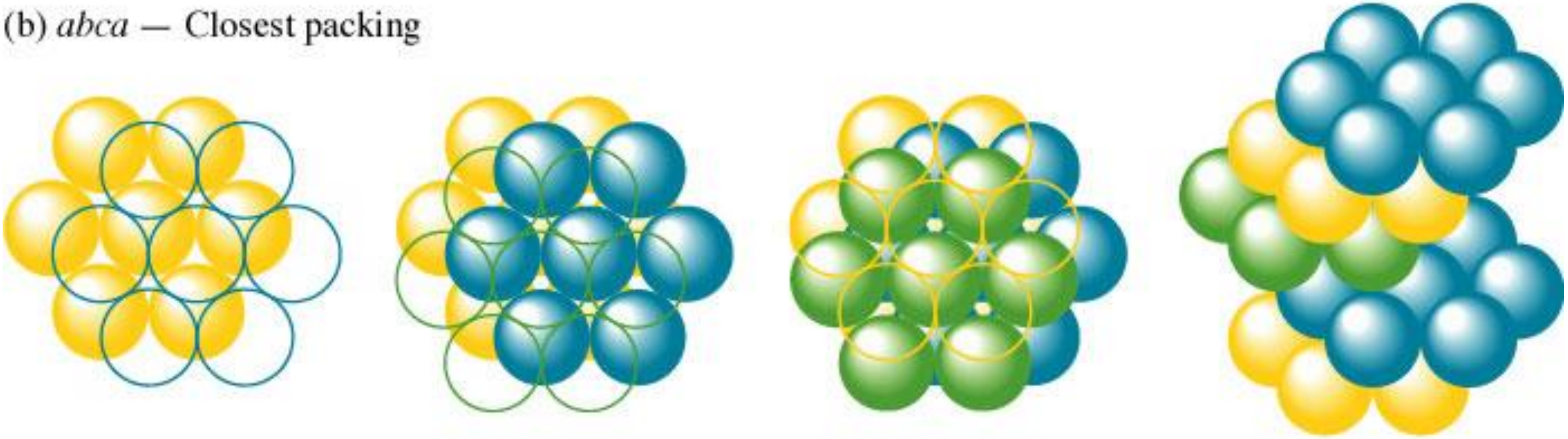
The Closest Packing Arrangement of Uniform Spheres

(a) *abab* — Closest packing



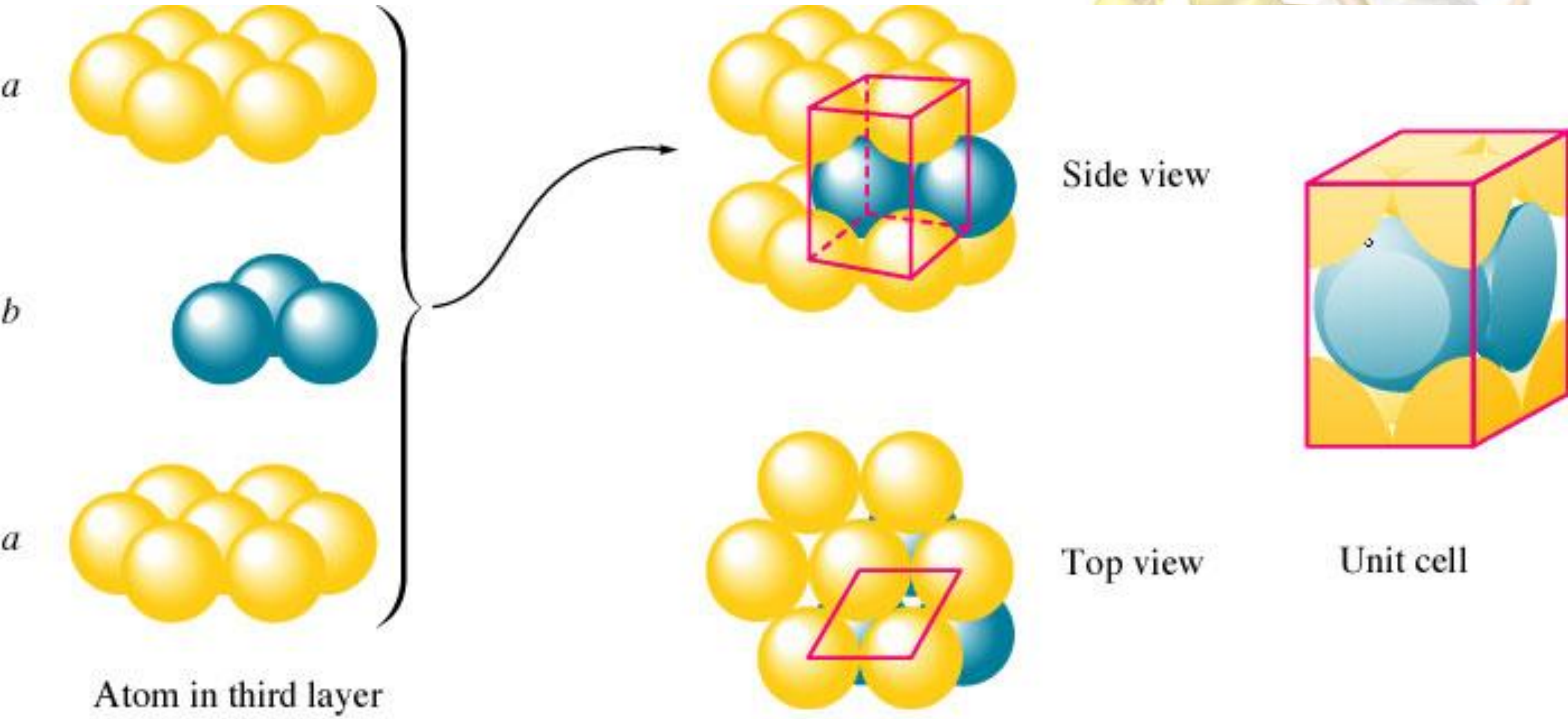
Top view Top view Side view

(b) *abca* — Closest packing



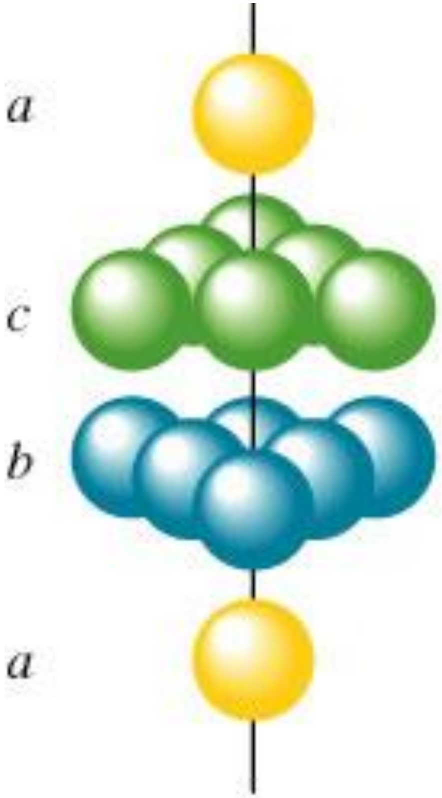
Top view Top view Top view Side view

Hexagonal Closest Packing(HCP)

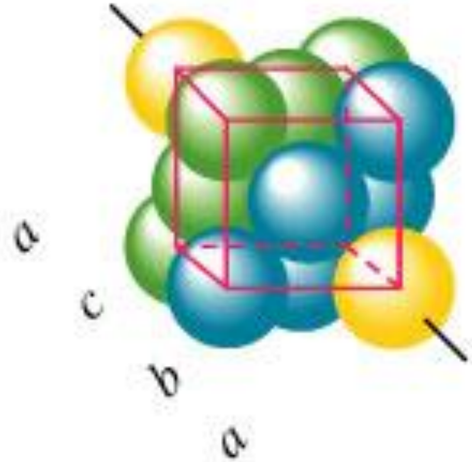


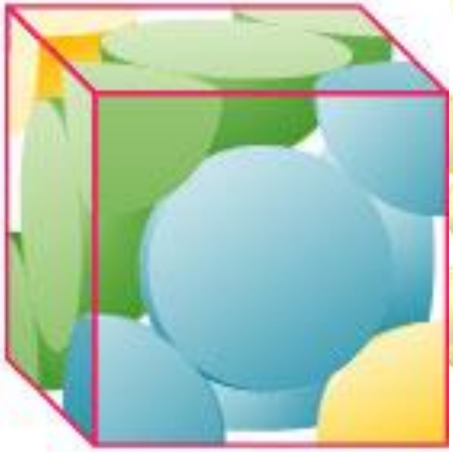
Atom in third layer lies over atom in first layer.

Cubic Closest Packing(CCP)



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

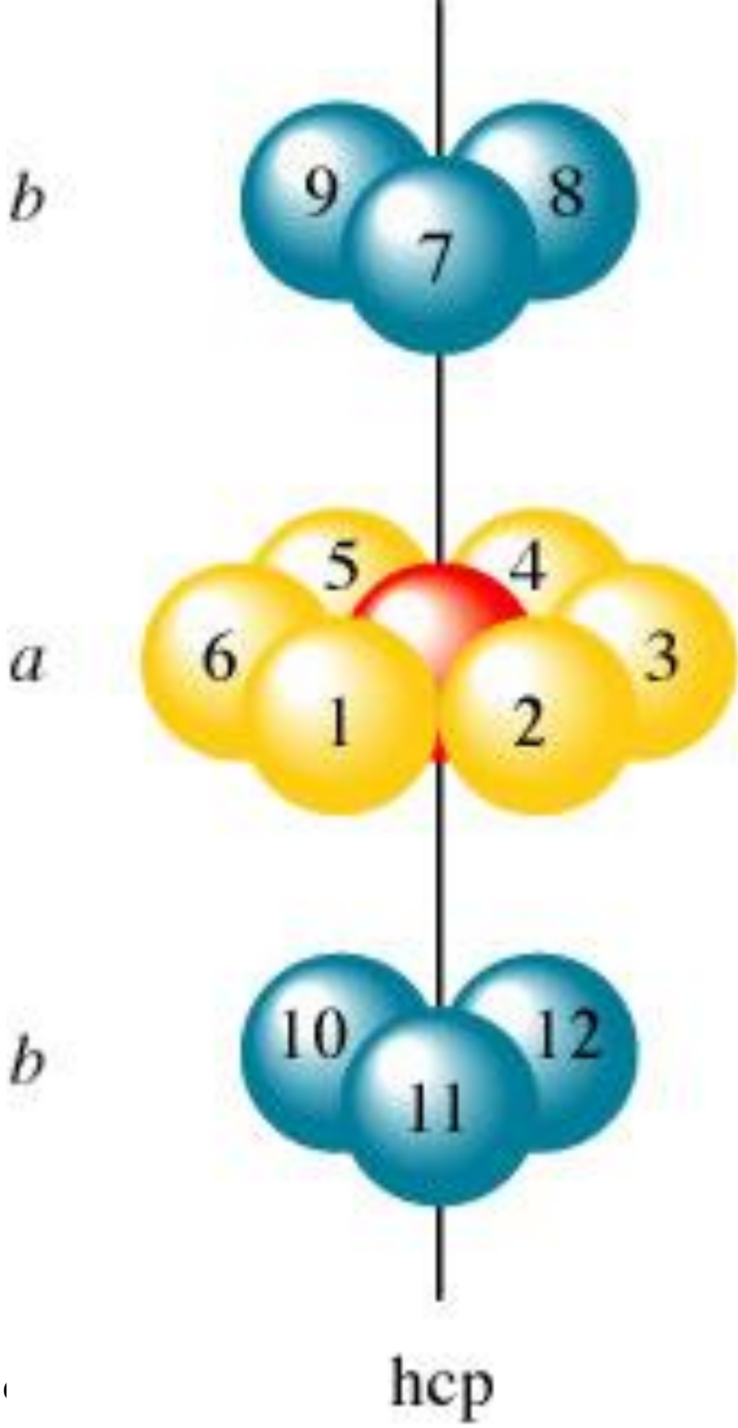




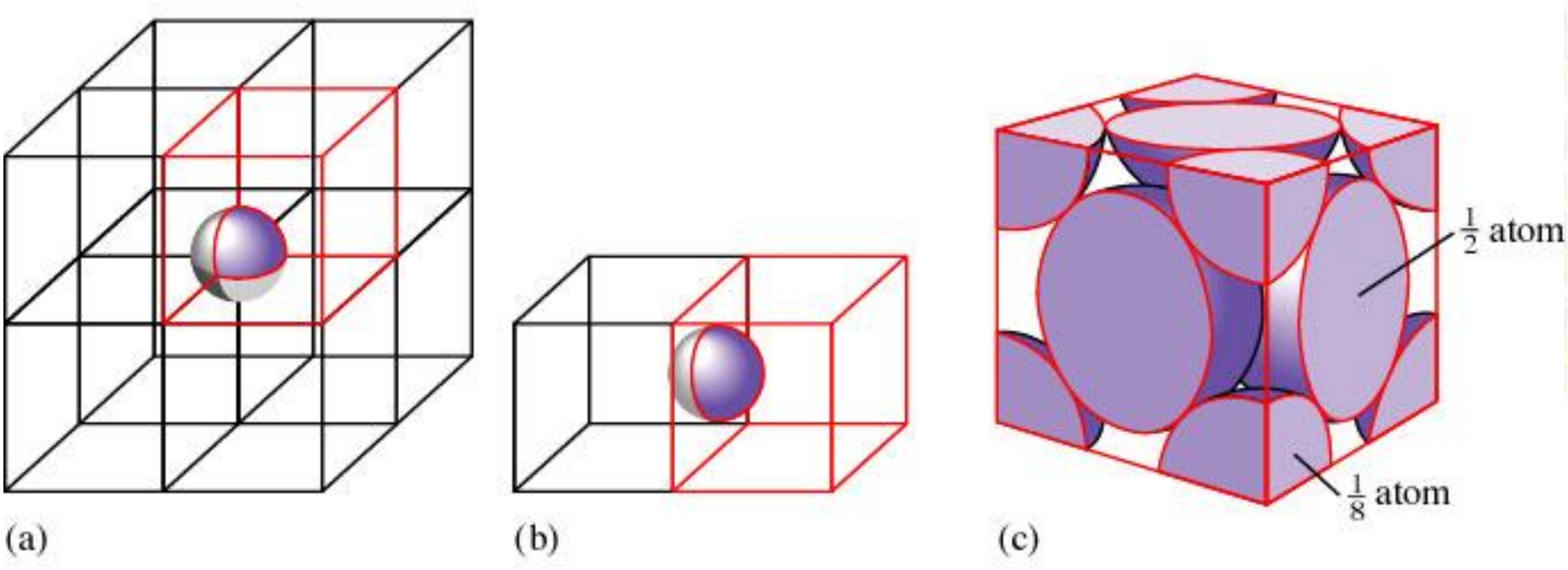
Unit cell

The Indicated Sphere

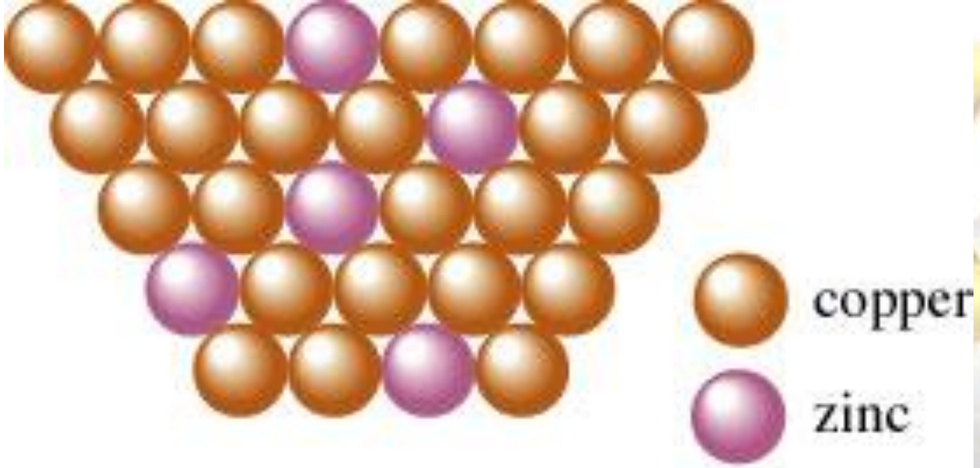
Has 12 Nearest neighbors



The Net Number of Spheres in a Face-Centered Cubic Unit Cell

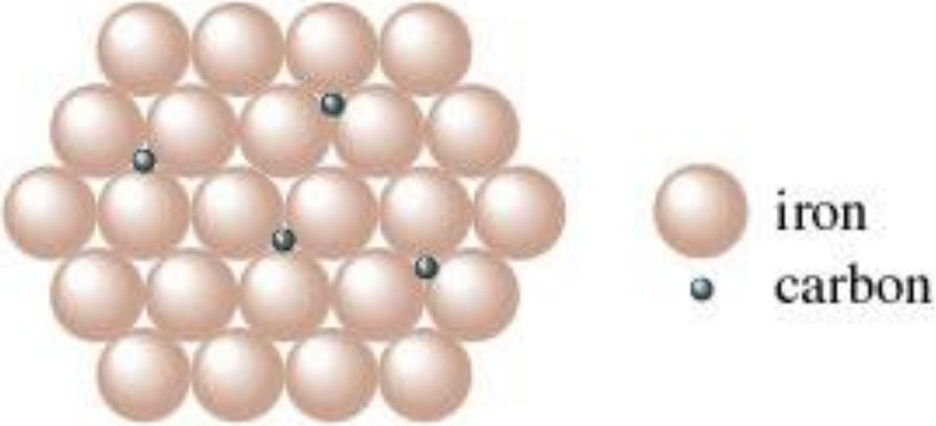


Two Types of Alloys



Brass

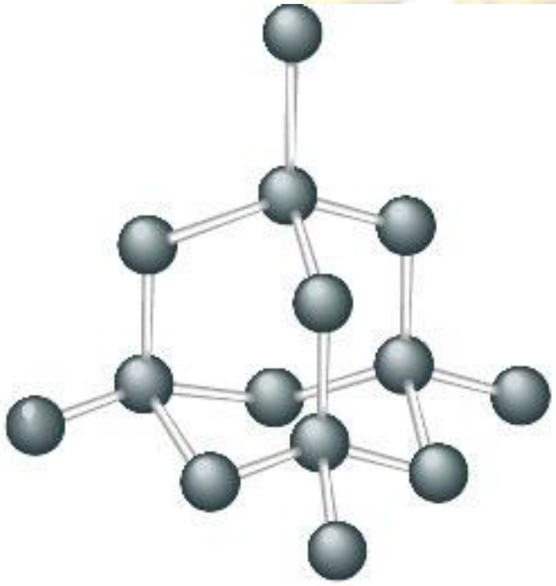
(a)



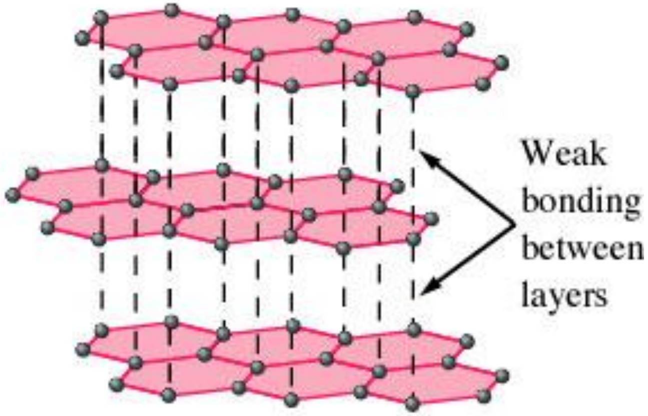
Steel

(b)

14.6 混合键型的晶体

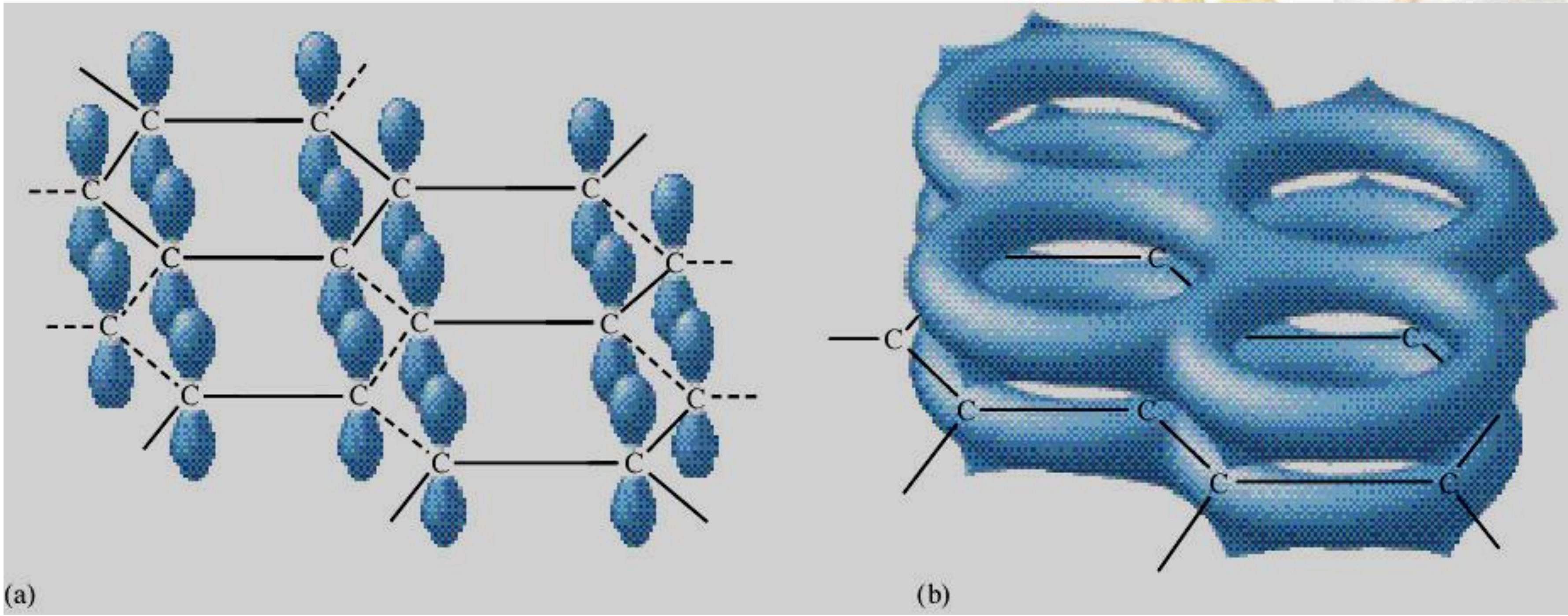


(a) Diamond

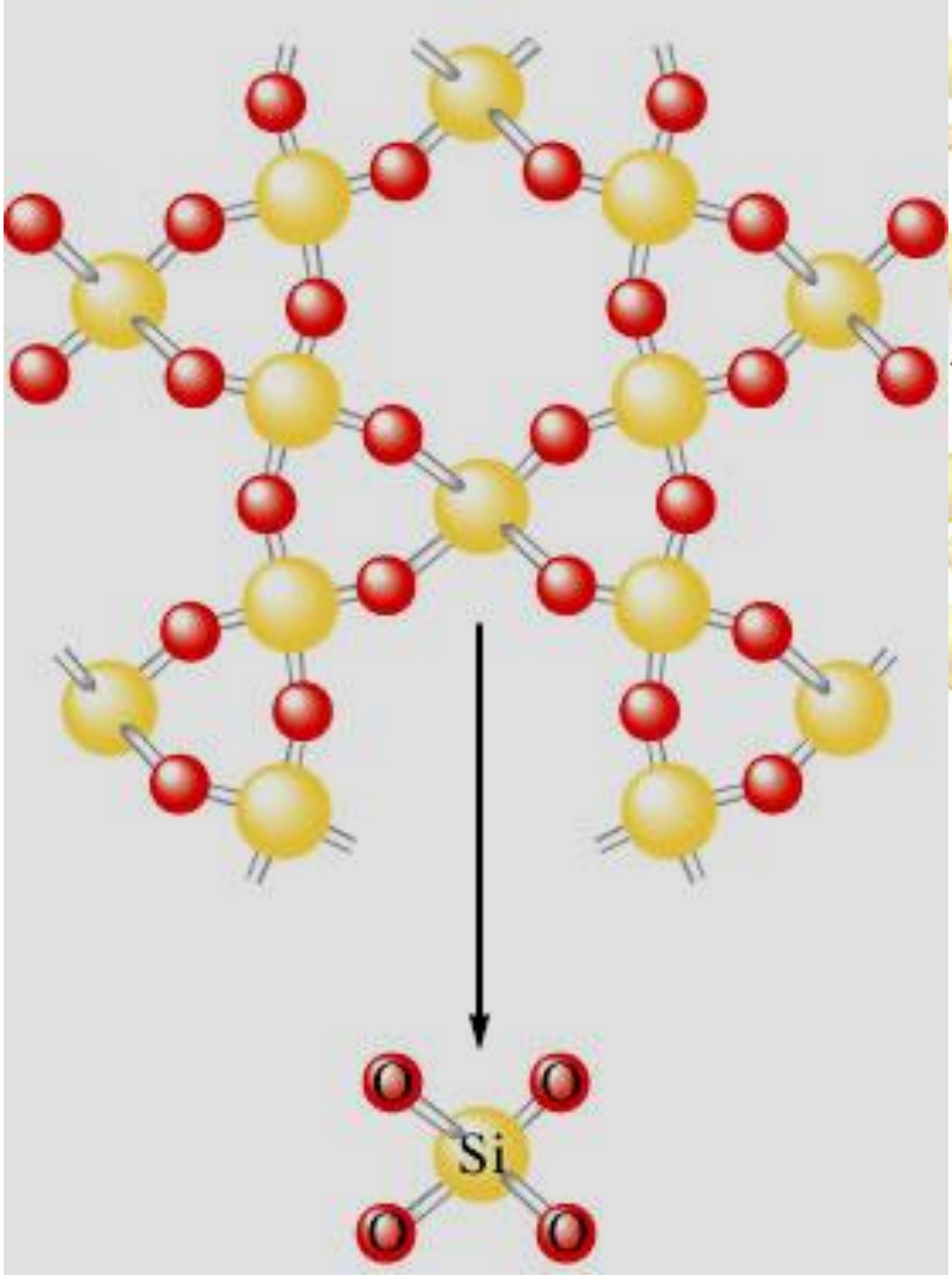


(b) Graphite

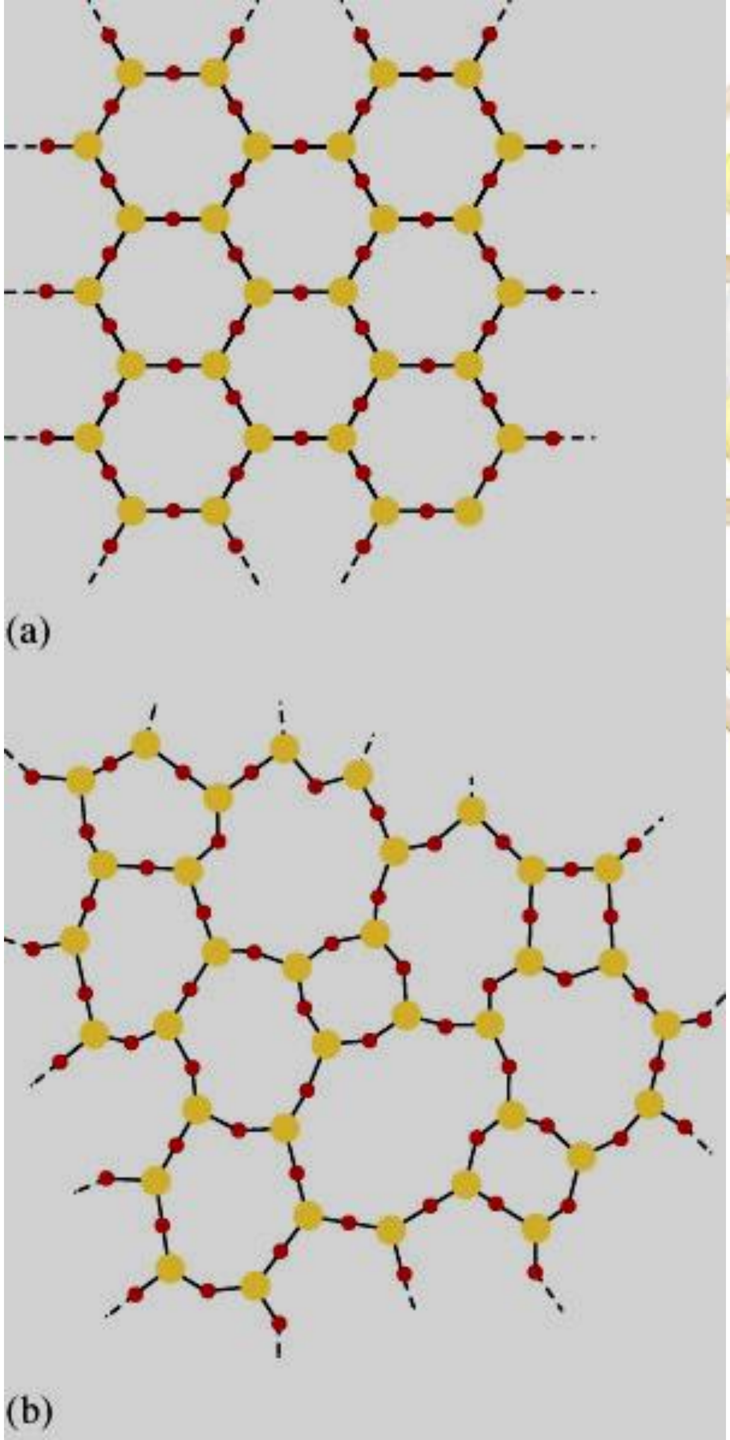
The p Orbitals



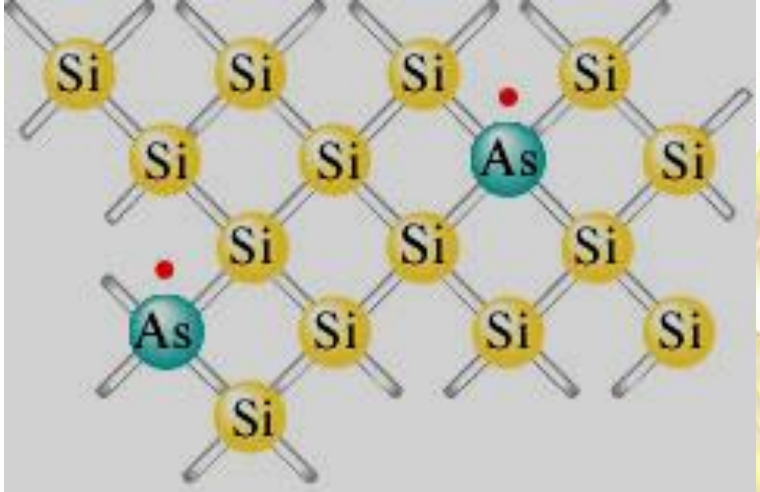
The Structure of Quartz



Two Dimensional Representations of (a) a Quartz Crystal and (b) a Quartz Glass

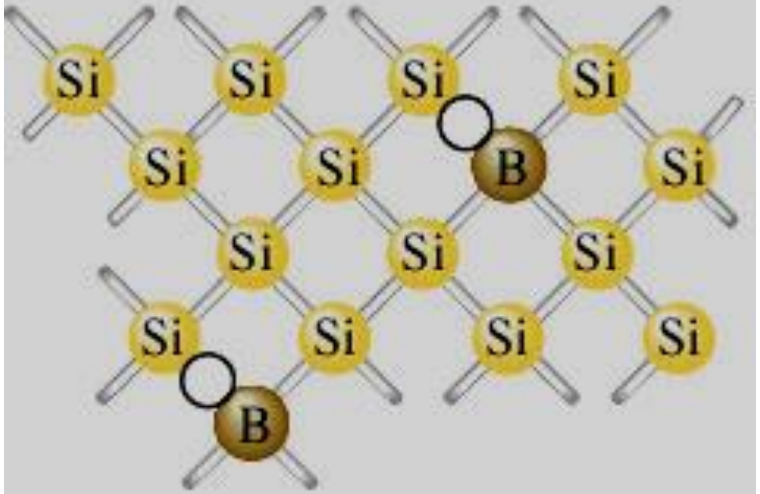


Silicon Crystal Doped with (a) Arsenic and (b) Boron



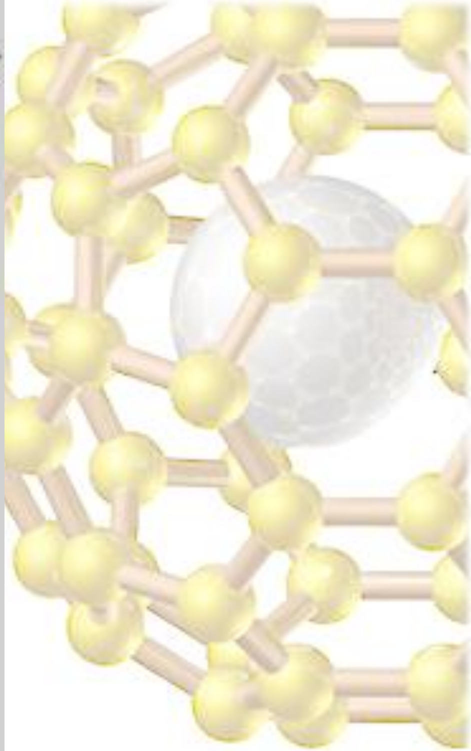
n-type semiconductor

(a)

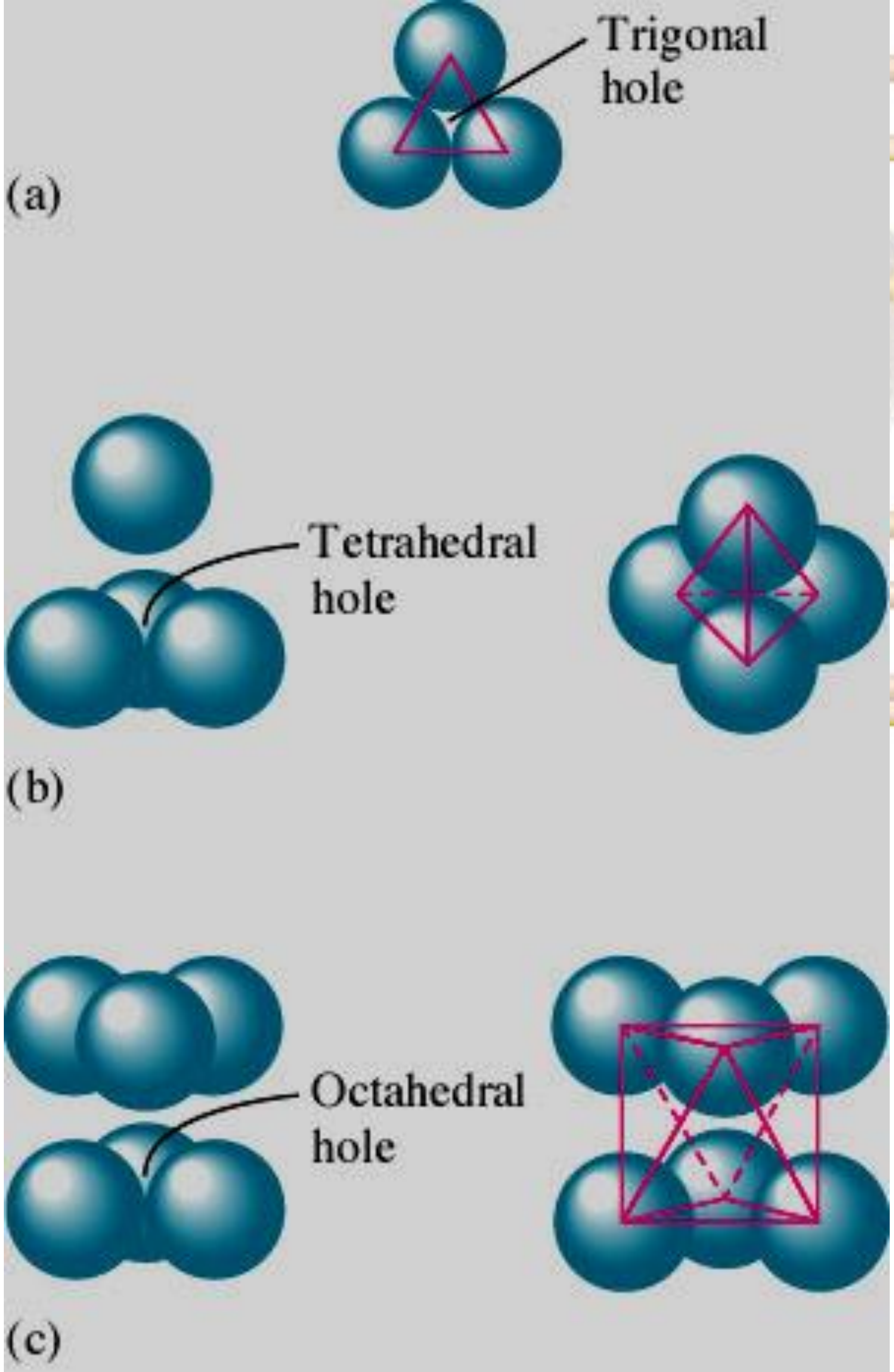


p-type semiconductor

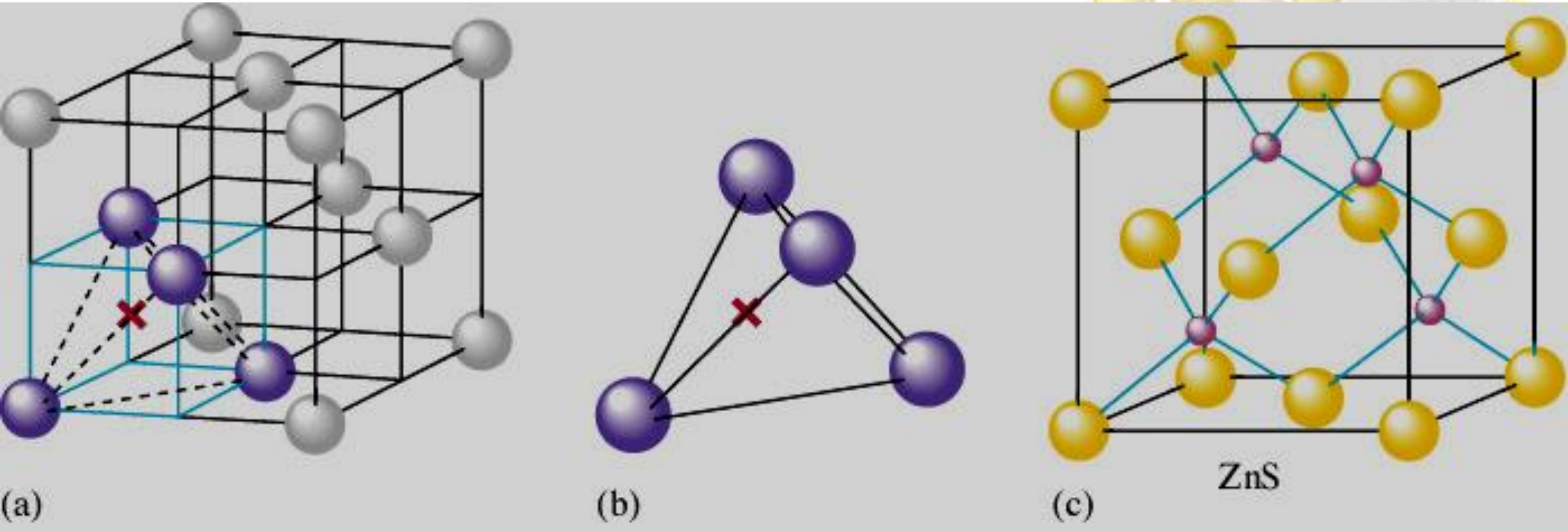
(b)



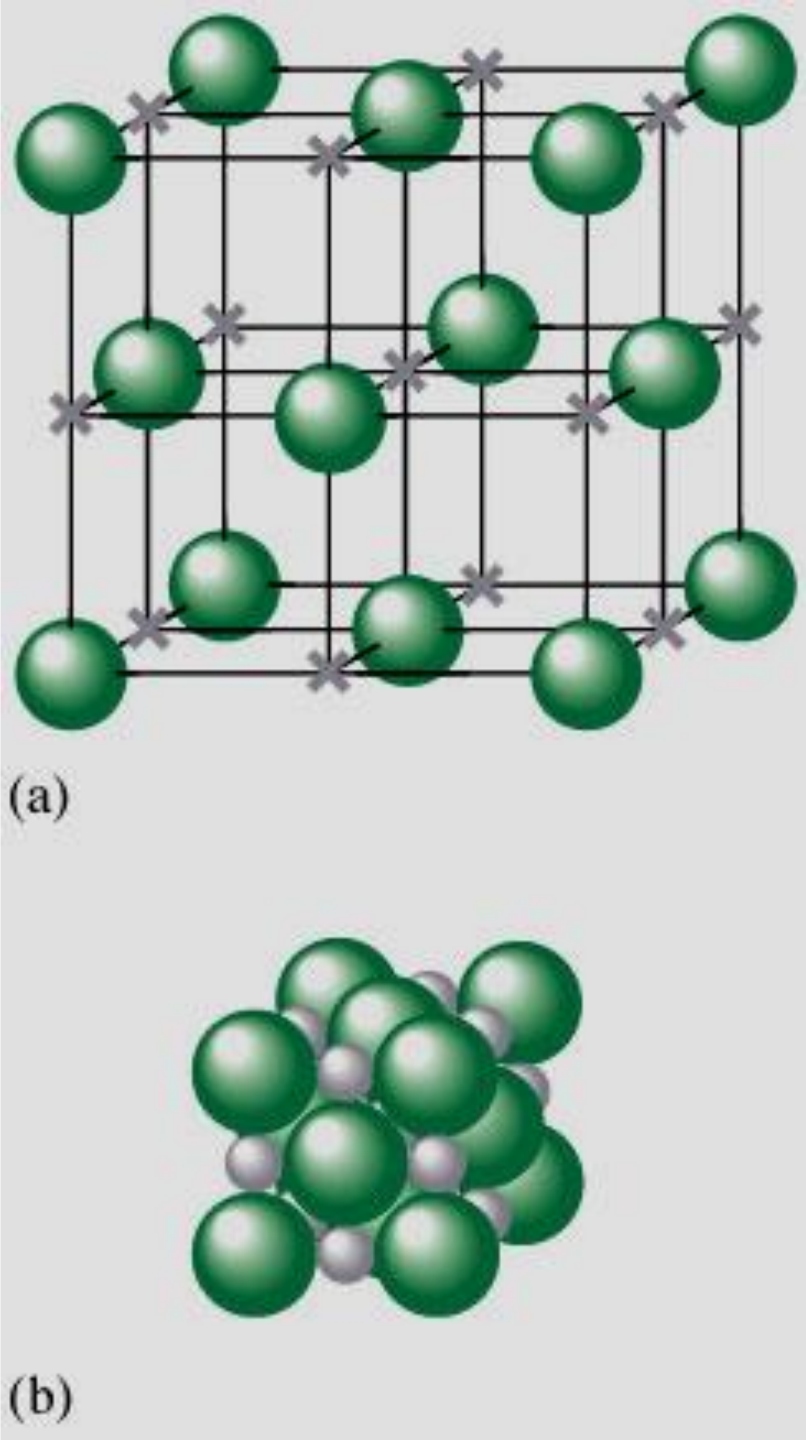
The Holes that Exist Among Closest Packed Uniform Spheres

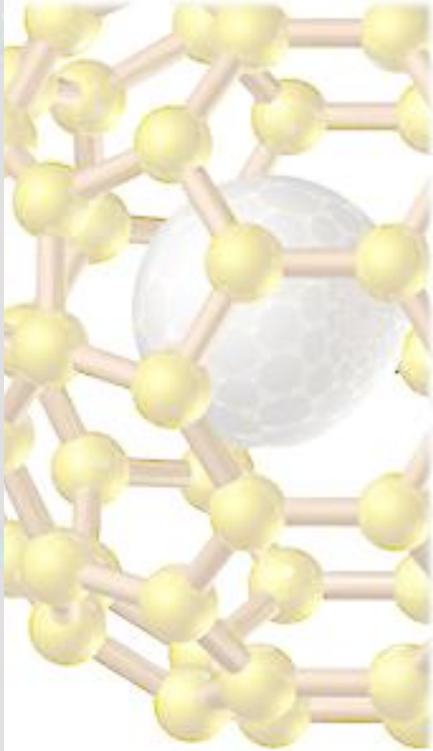


The Position of Tetrahedral Holes in a Face-Centered Cubic Unit Cell

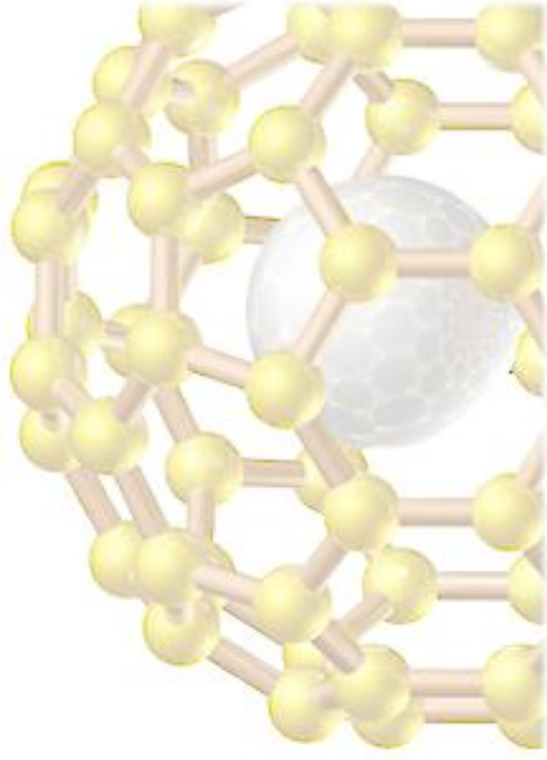


Cubic Closest Packing in NaCl





14.7 晶体的缺陷



14.7.1 晶体缺陷(crystal defect)

- 理想晶体(ideal crystal)
- 点缺陷
- 线缺陷
- 面缺陷
- 体缺陷

1. 肖特基缺陷
2. 弗仑克尔缺陷
3. 化学杂质缺陷
4. F-心缺陷

(a)点缺陷示例

(b)线缺陷示例

图 14.22　点缺陷、线缺陷示意图

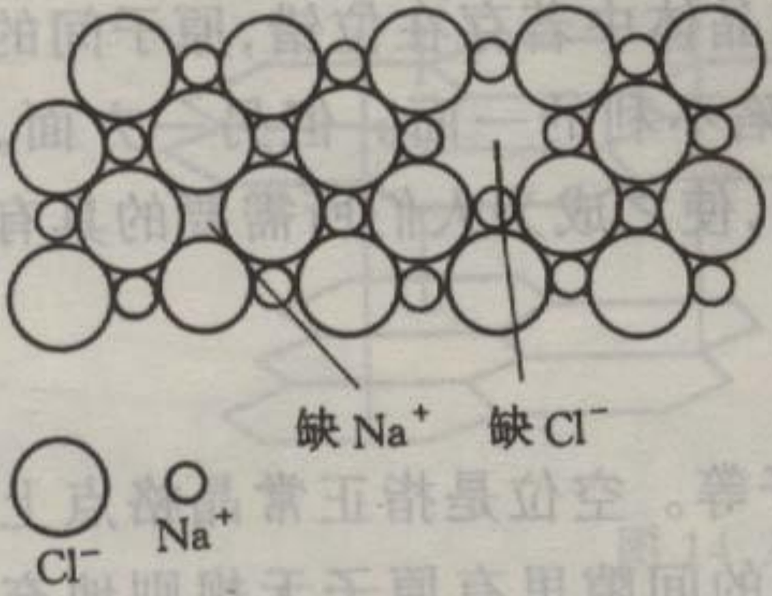


图 14.23 肖特基缺陷

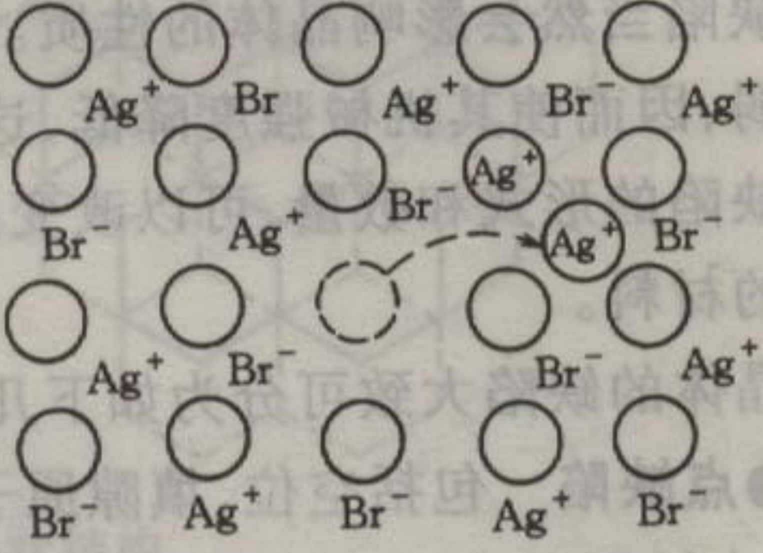
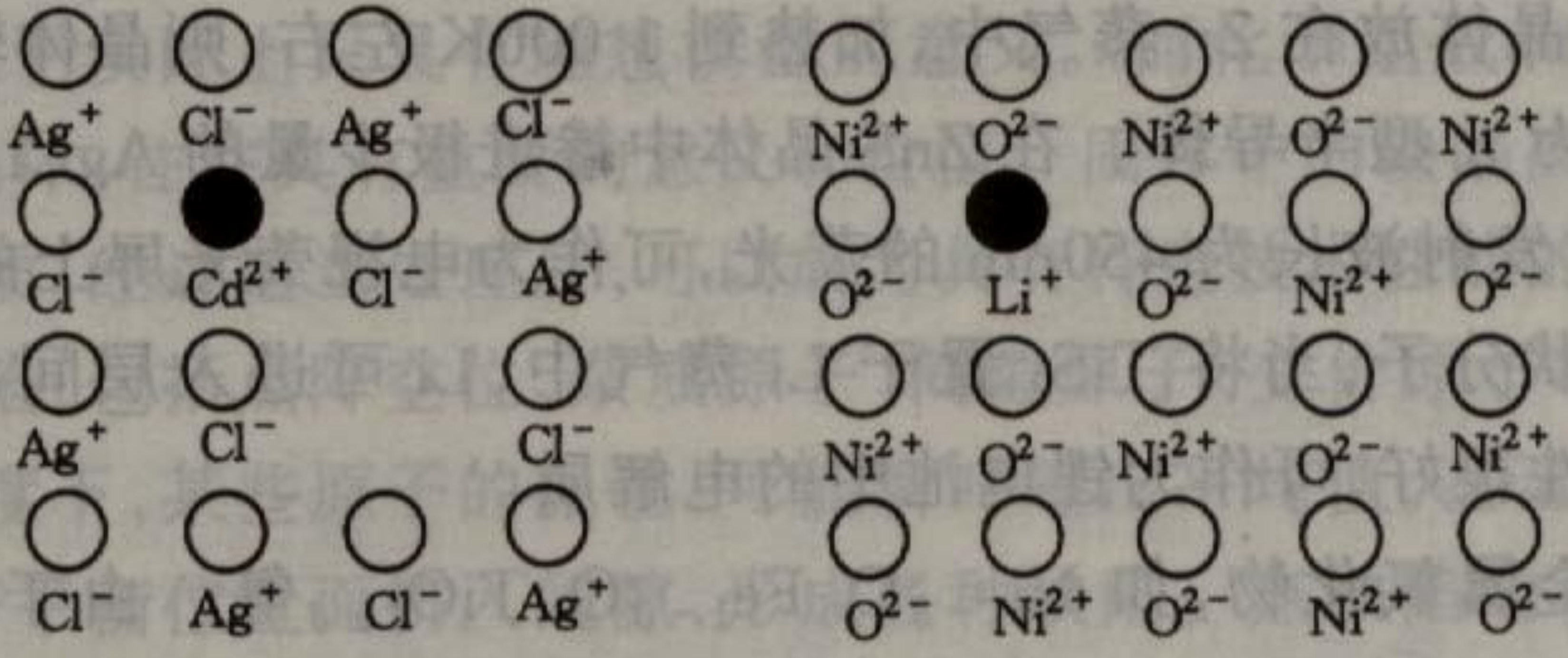


图 14.24 弗仑克尔缺陷



(a)　　(b)

图 14.25　化学杂质缺陷

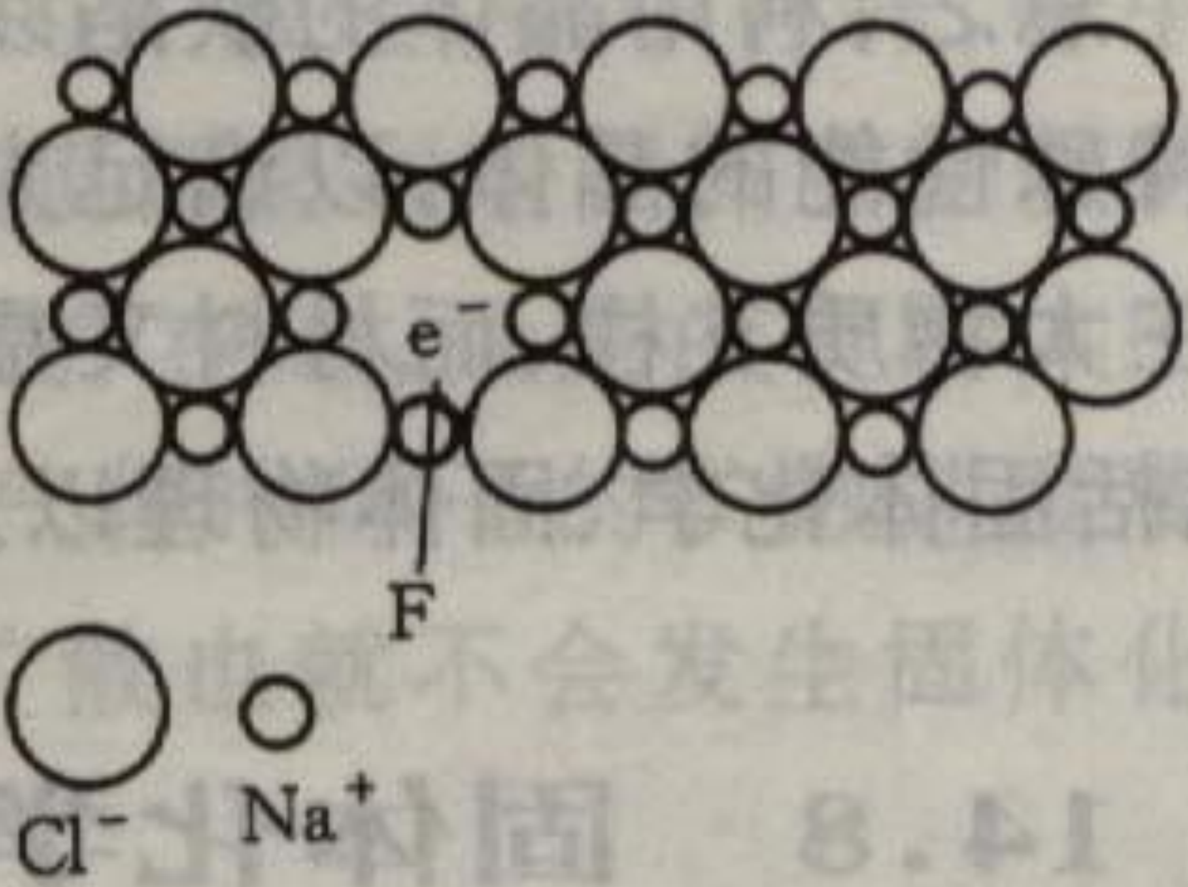
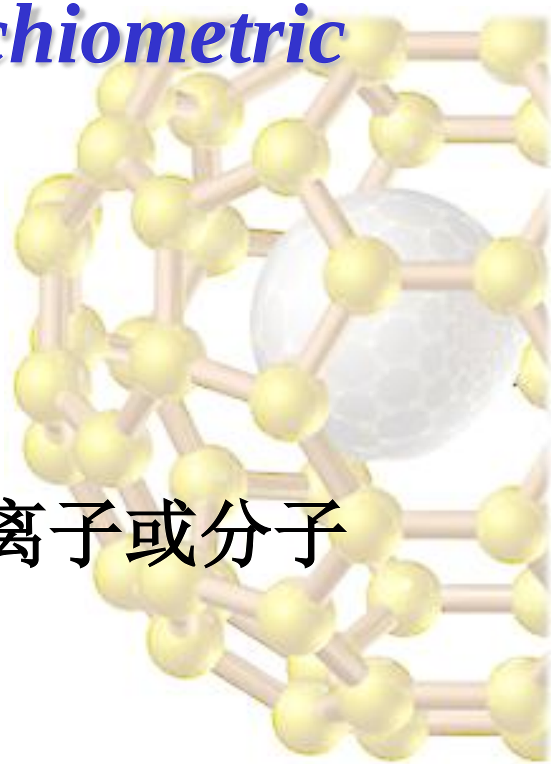


图 14.26　F－心缺陷

14.7.2 非整比化合物(non-stoichiometric compounds)

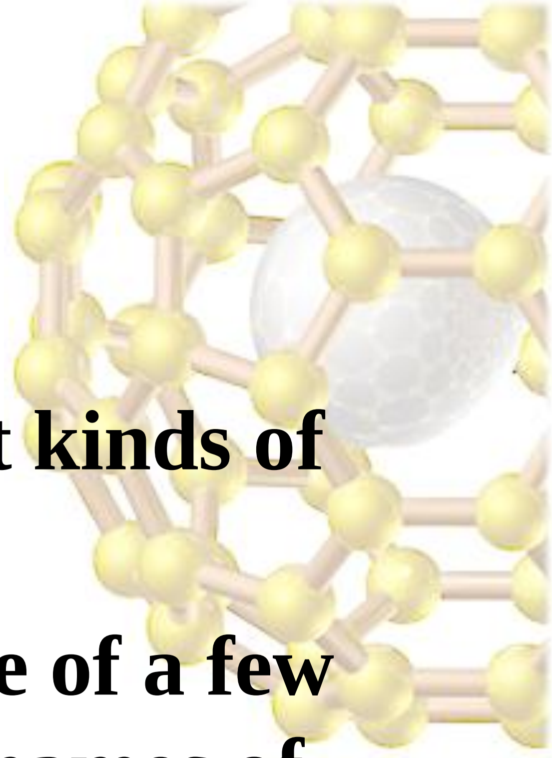


- 非计量化合物生成的原因

某一原子过多或短卸

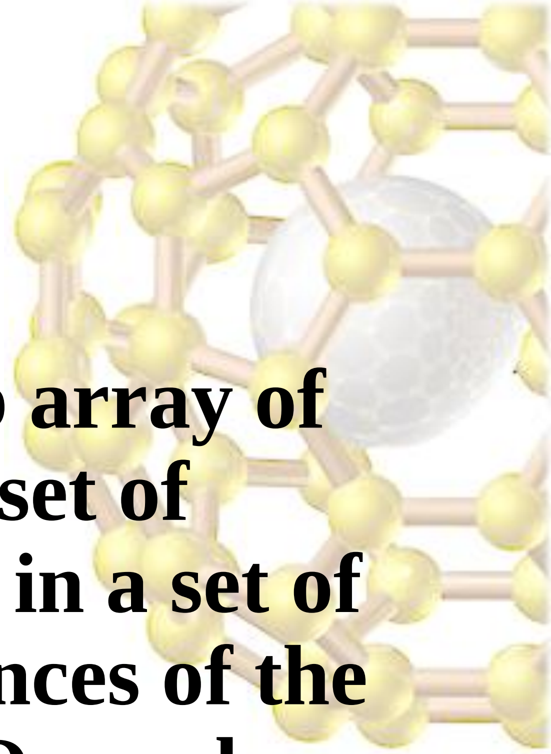
在层状结构中的层间嵌入某些原子、离子或分子

Mixed-metal Oxide

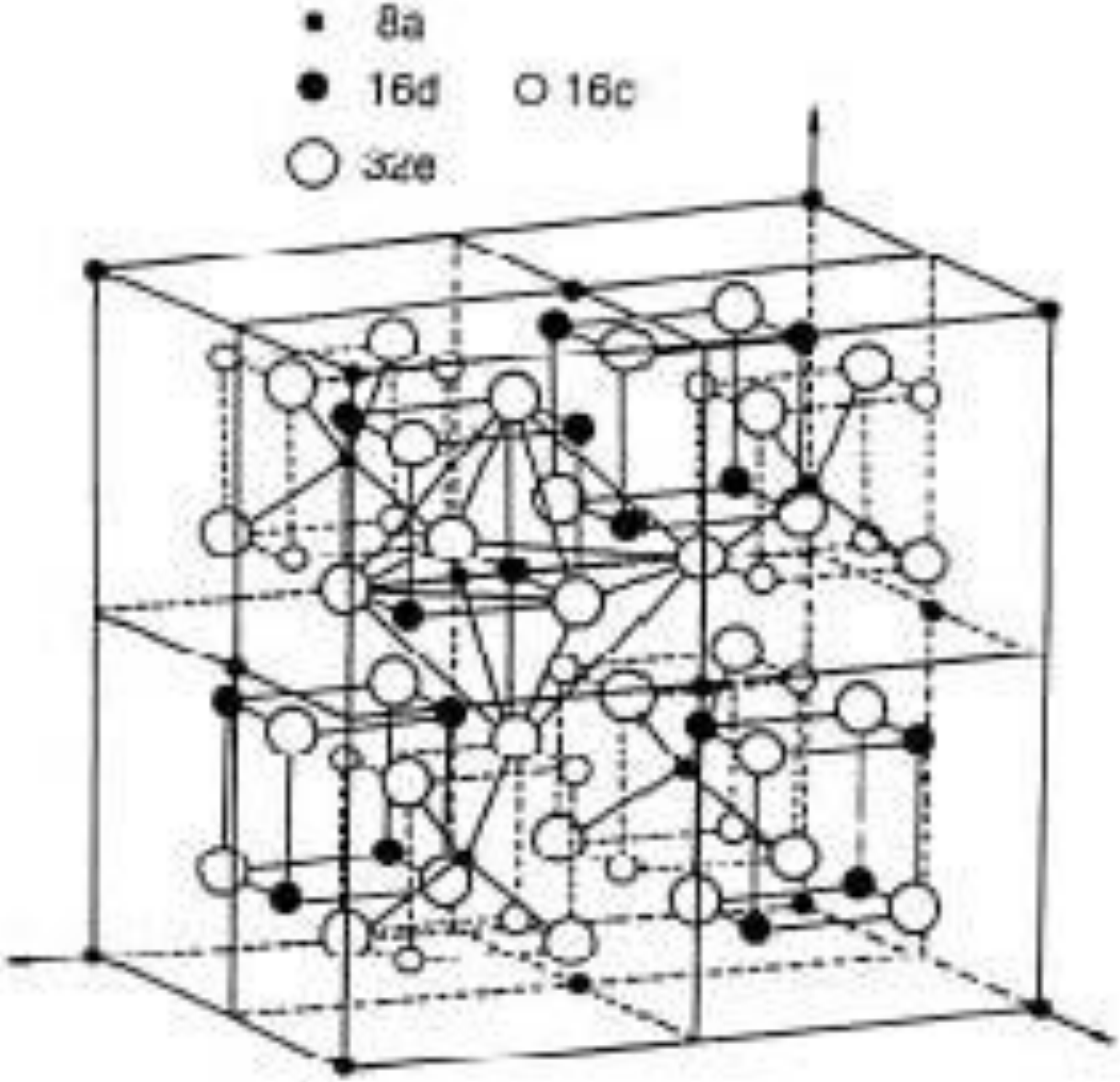


- **Contain two or more different kinds of metal ions.**
- **These oxides tend to adopt one of a few basic, general structures, the names of which are derived from the first compound (or an important one) found to have that structure.**

The spinel structure

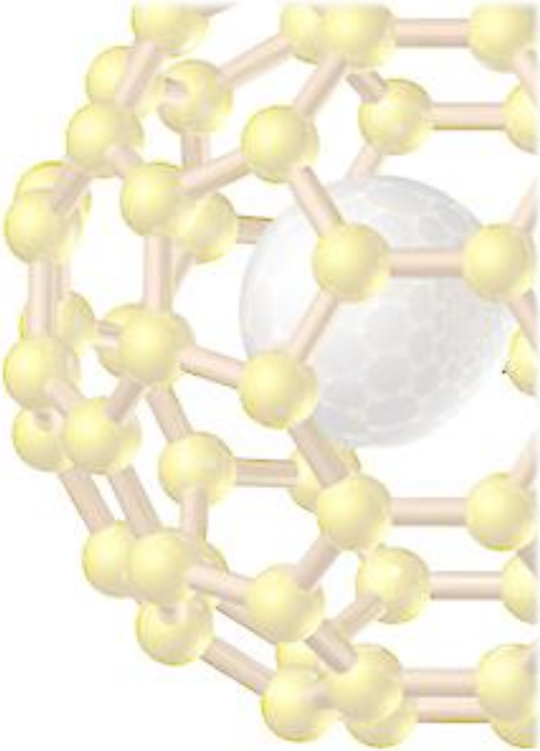


- **Spinel is a mineral ($MgAl_2O_4$).**
- **The structure is based on a ccp array of oxide ions, with Mg^{2+} ions in a set of tetrahedral holes and Al^{3+} ions in a set of octahedral holes. Many substances of the types $M^{2+}(M^{3+})_2O_4$, $M^{4+}(M^{2+})_2O_4$, and $M^{6+}(M^{+})_2O_4$ have this structure.**
- **$Li_2Mn_2O_4$**

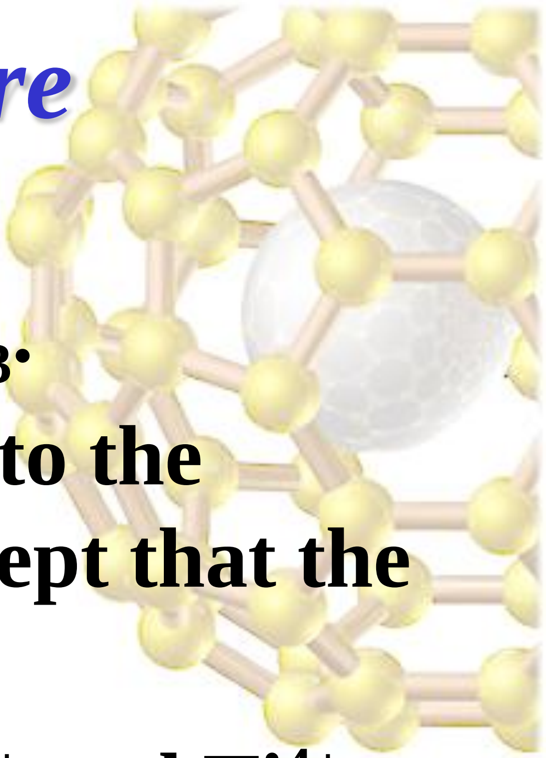


(a) lattice unit

$LiMn_2O_4$: $(Li)_{8a}[Mn_2]_{16d}O_4$

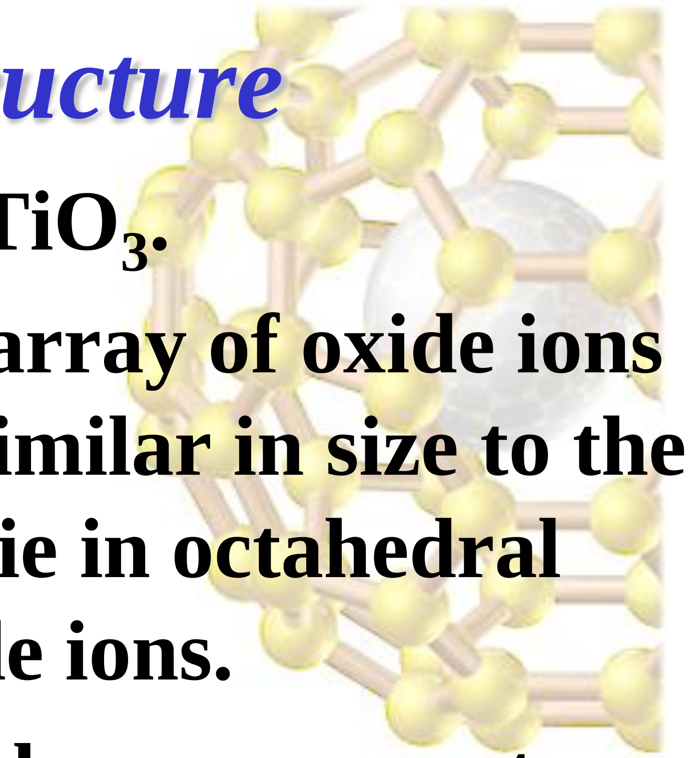


The ilmenite(钛铁矿) structure



- **Ilmenite is the mineral $FeTiO_3$.**
- **Its structure is closely related to the corundum(刚玉） structure except that the cations are of two kind.**
- **In ilmenite the cations are Fe^{2+} and Ti^{4+}, but many substances with the ilmenite structure have cations charges of (+1,+5) or (+3,+3).**

The perovskite(钙铁矿) structure



- **Perovskite is the mineral $CaTiO_3$.**
- **Its structure is based on ccp array of oxide ions together with large cations, similar in size to the oxide ion. The small cations lie in octahedral holes formed entirely by oxide ions.**
- **Again, the individual cation charges are not important so long as their sum in +6.**
- **The structure is adopted by many fluorides with cations of disparate sizes, such as $KZnF_3$.**

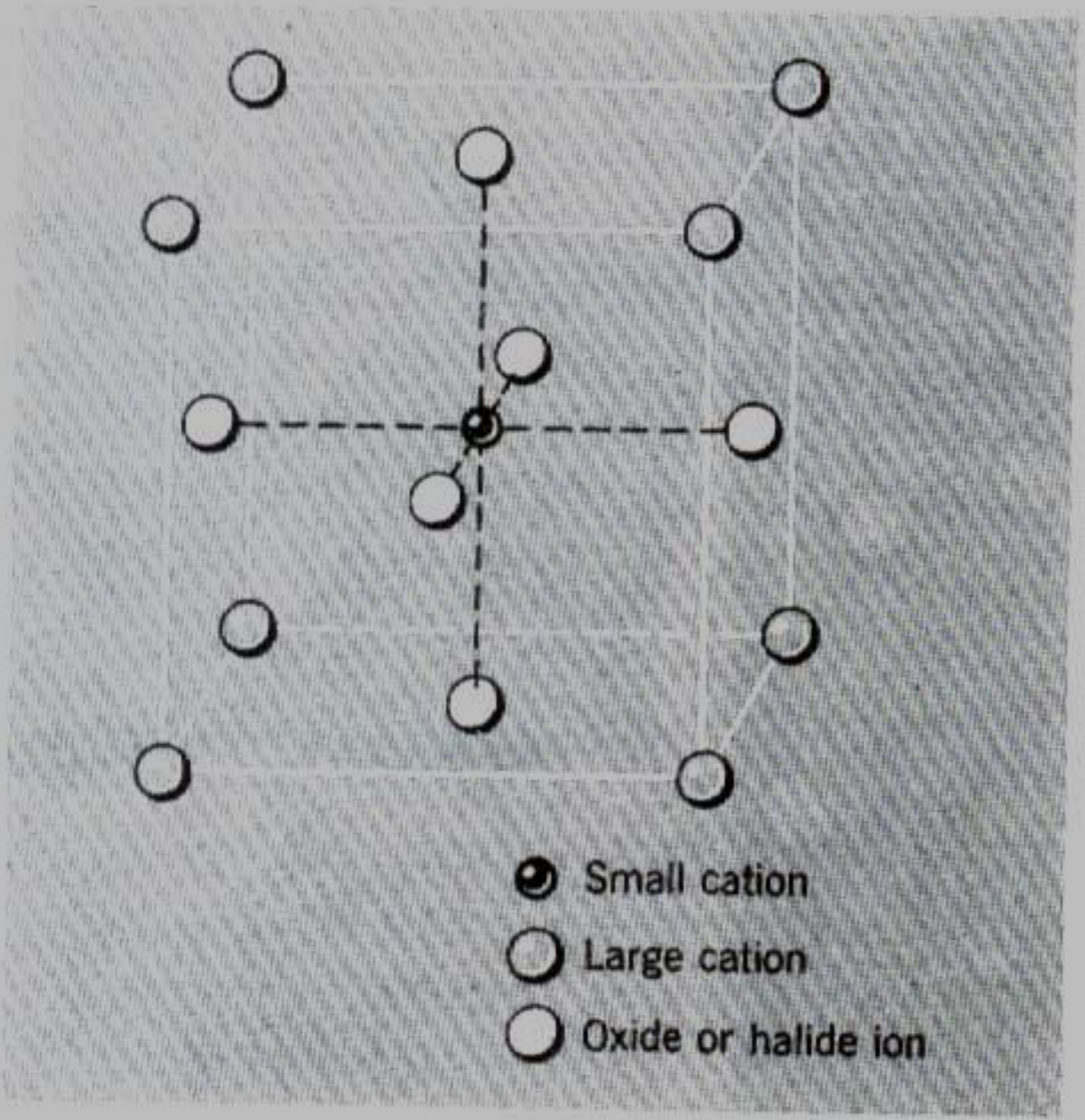
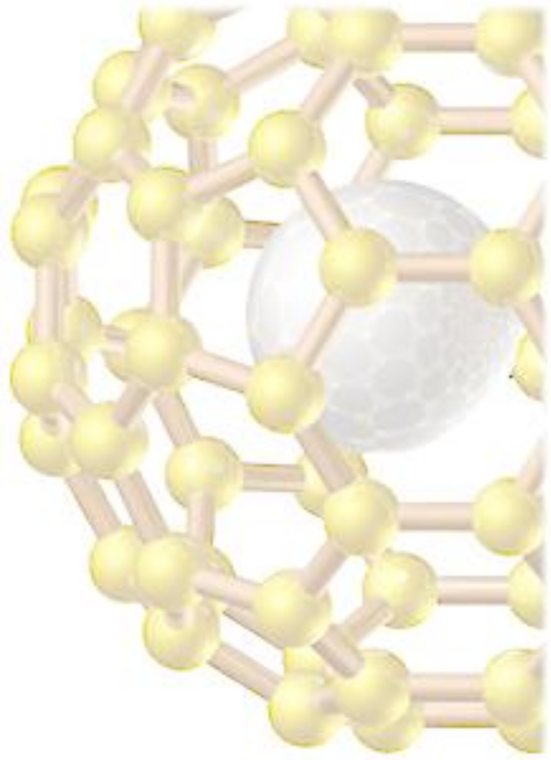


Figure 4-8 The perovskite structure.

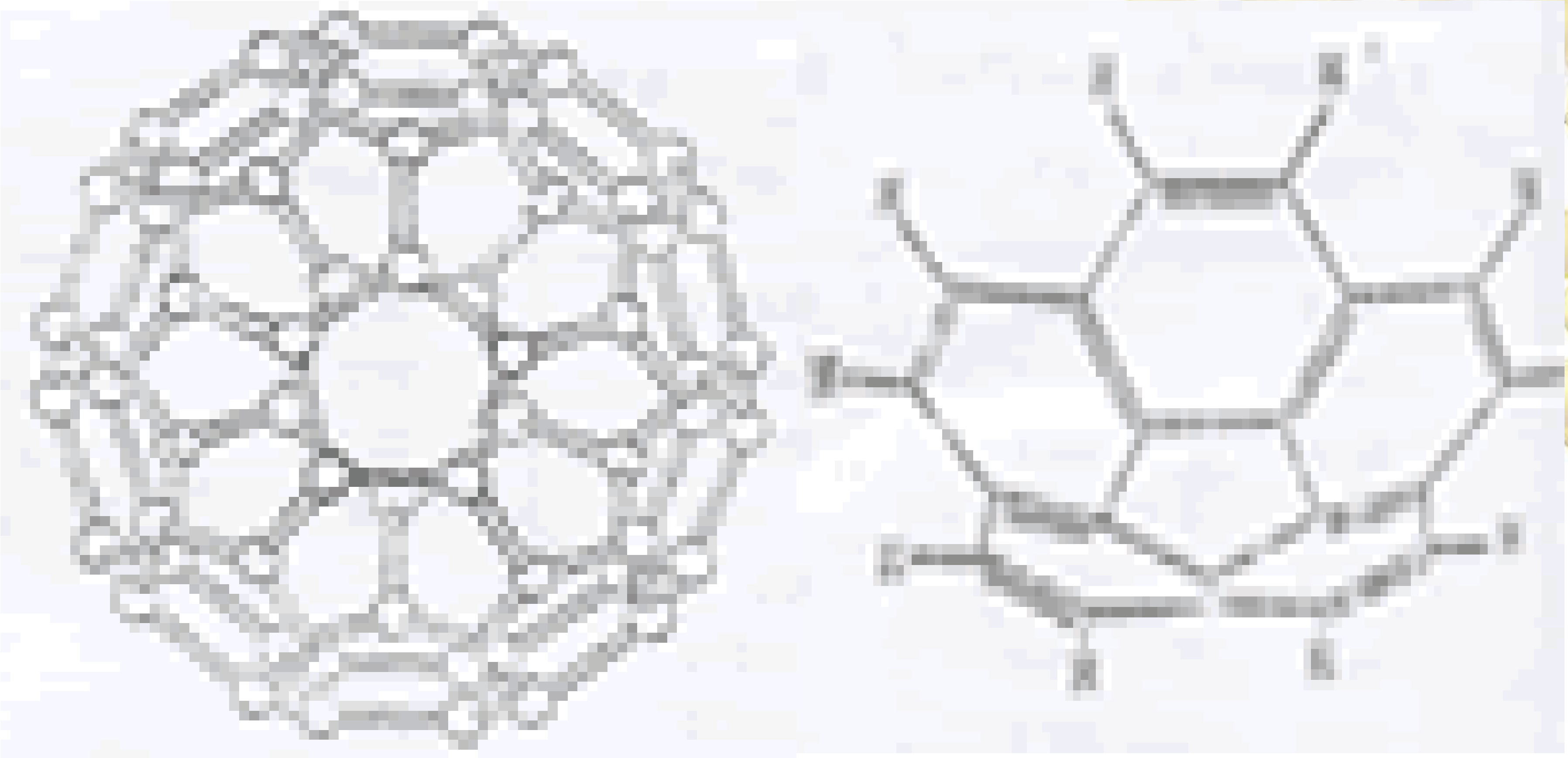
14.8 固体化学简介

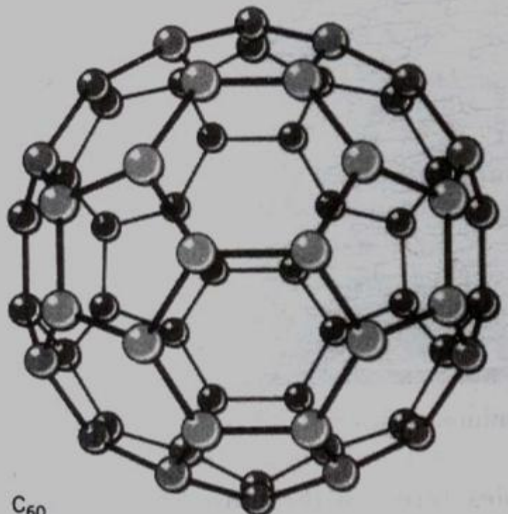


- 固体化学(solid chemistry)
- 固相化学反应
- 固相化学反应的规律

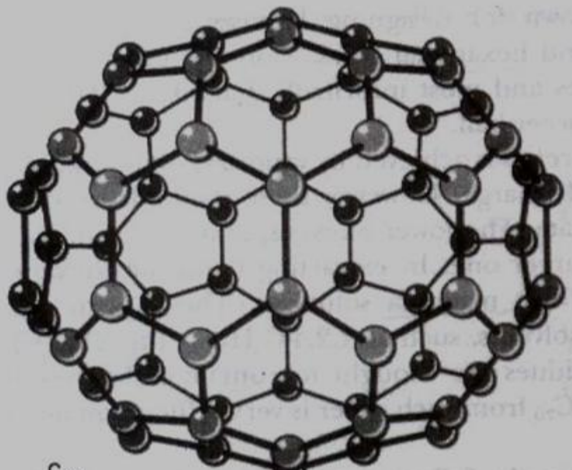
1. 反应有潜伏期
2. 反应不能建立平衡
3. 拓扑效应

14.9 固体碳的一种新形态----富勒烯

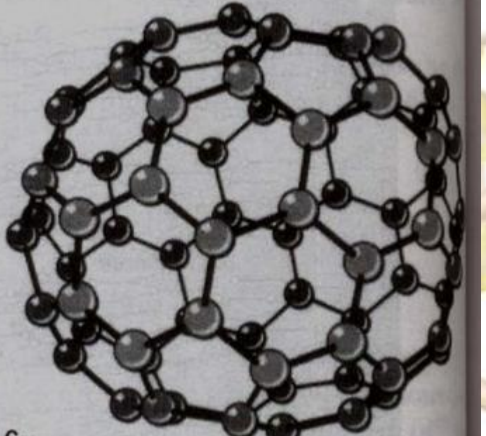




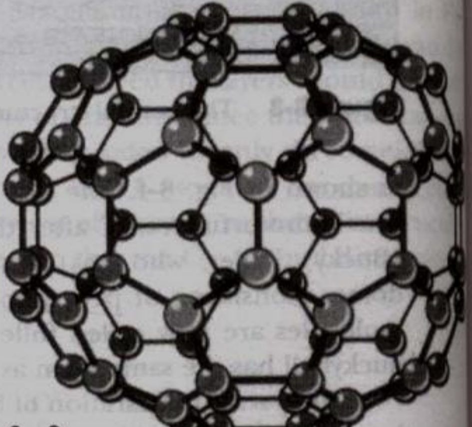
C_{60}



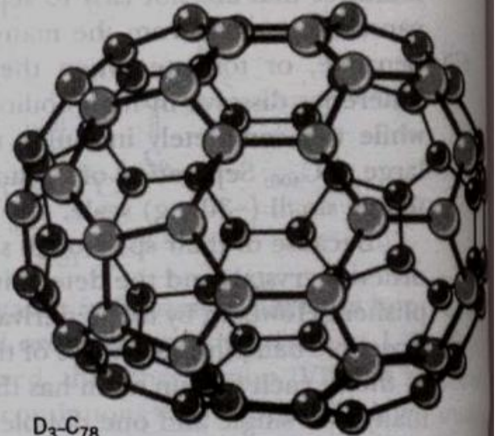
C_{70}



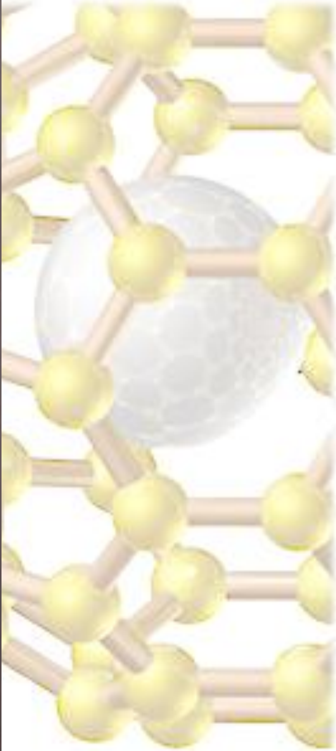
C_{76}



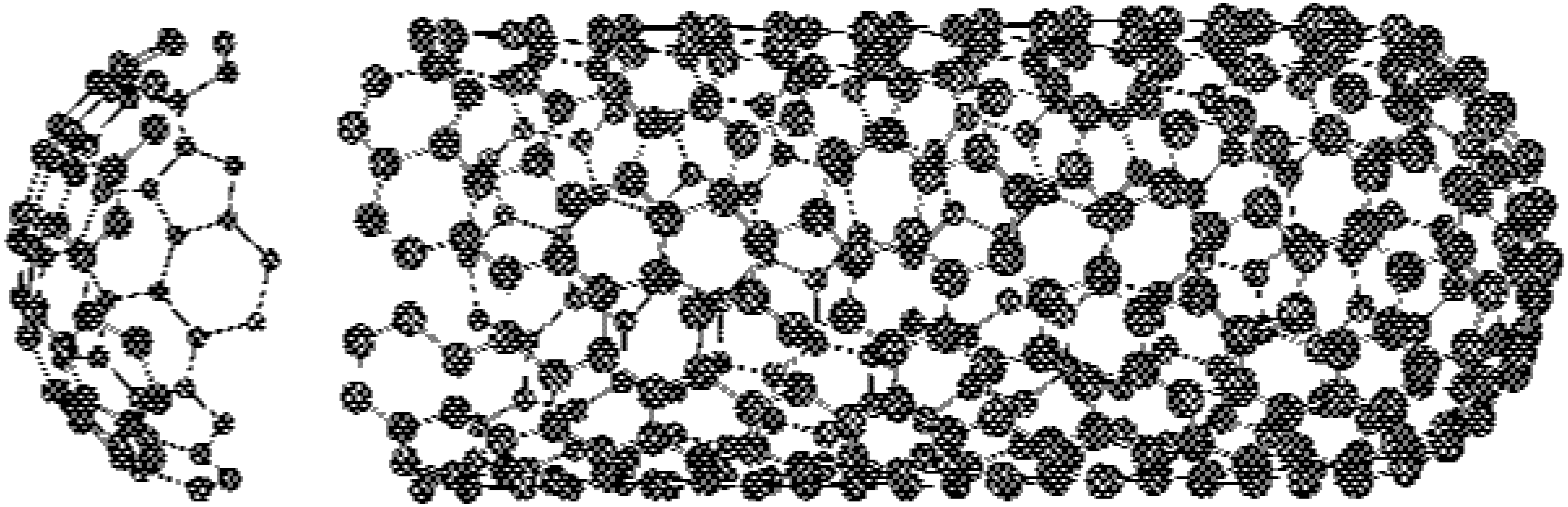
C_{2v}–C_{78}



D_3–C_{78}

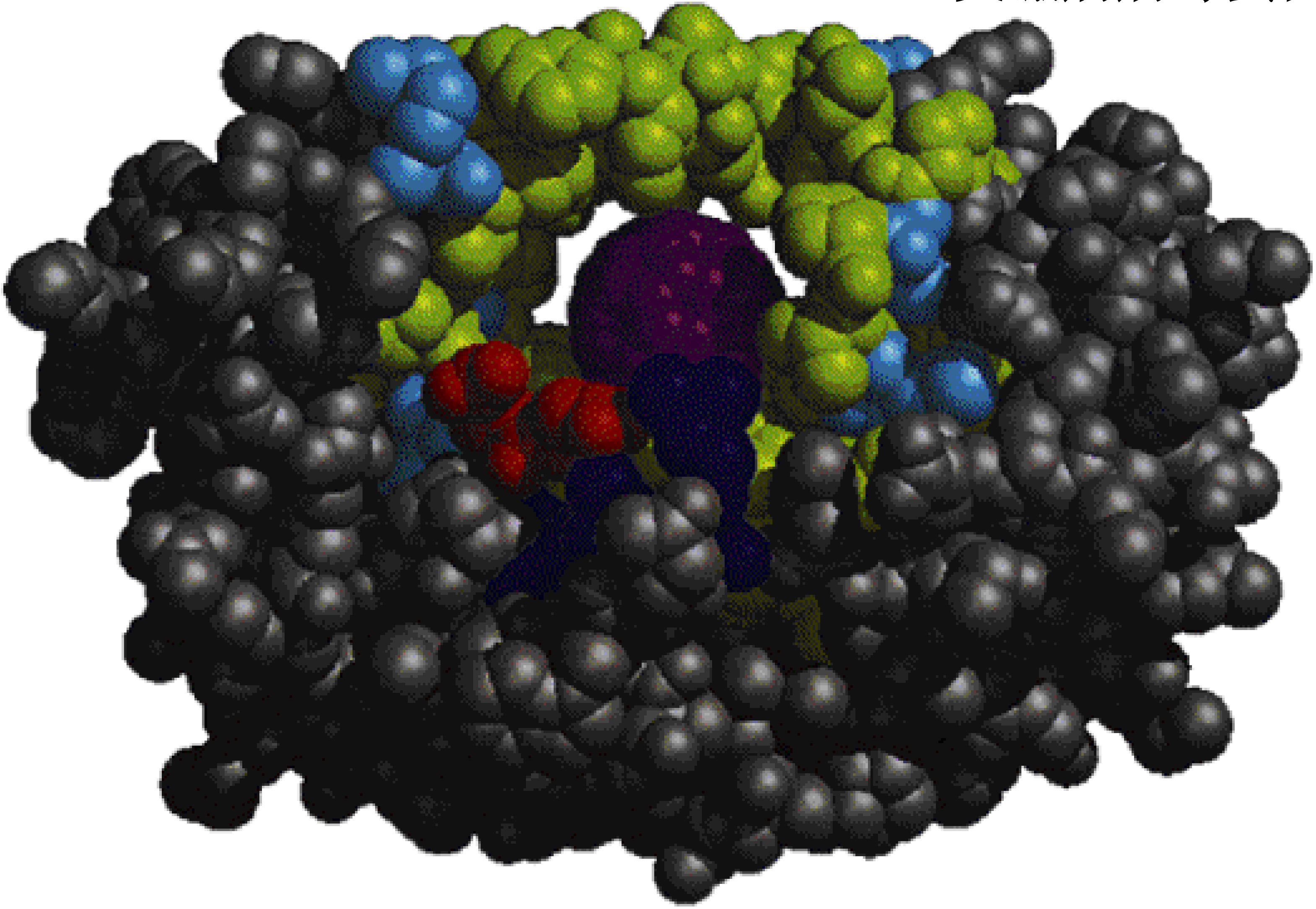


Structure of a Buckytube

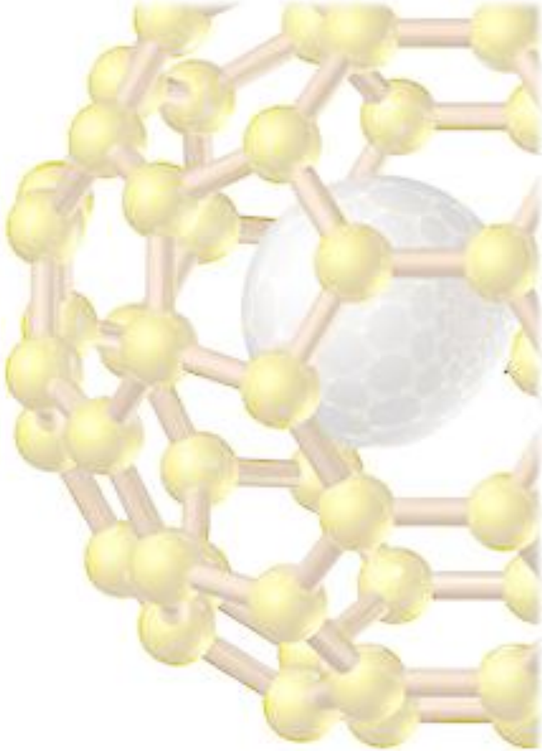


Binding of a Buckyball Derivative to the Site of HIV-Protease

艾滋病病毒蛋白酶

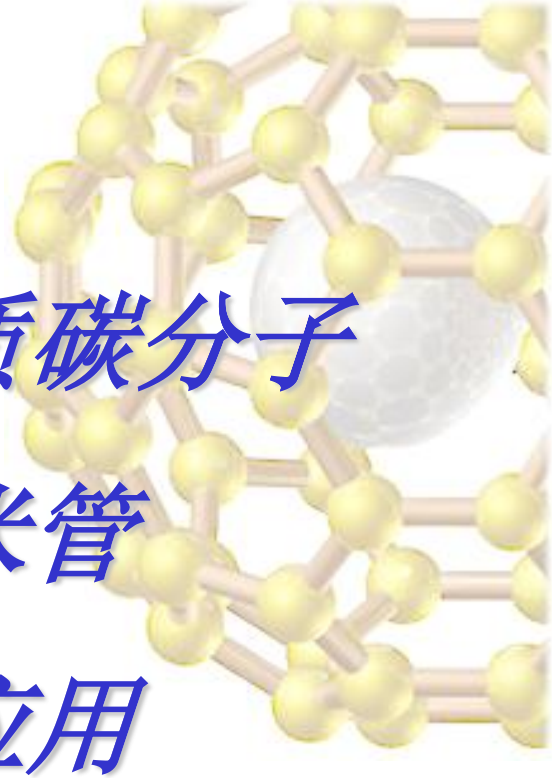


作业:



- P143
- 3、4、5、13

课外读物



足球烯——新发现的一种单质碳分子

固体碳的新形态——碳纳米管

固体无机化合物的制备及应用