

Arranjos Atômicos



Fotografia de vários cristais
de fluorita CaF_2

Conceito de Cristalinidade

Cristalinidade corresponde a forma de organização da estrutura em um modelo ordenado e repetitivo de longo alcance, também denominado de arranjo de longo alcance.
Ex.: metais e ligas

Quando o arranjo não tem longo alcance a estrutura se torna "amorfa", ou seja, não tem forma definida.
Ex.: maior parte dos polímeros e alguns cerâmicos

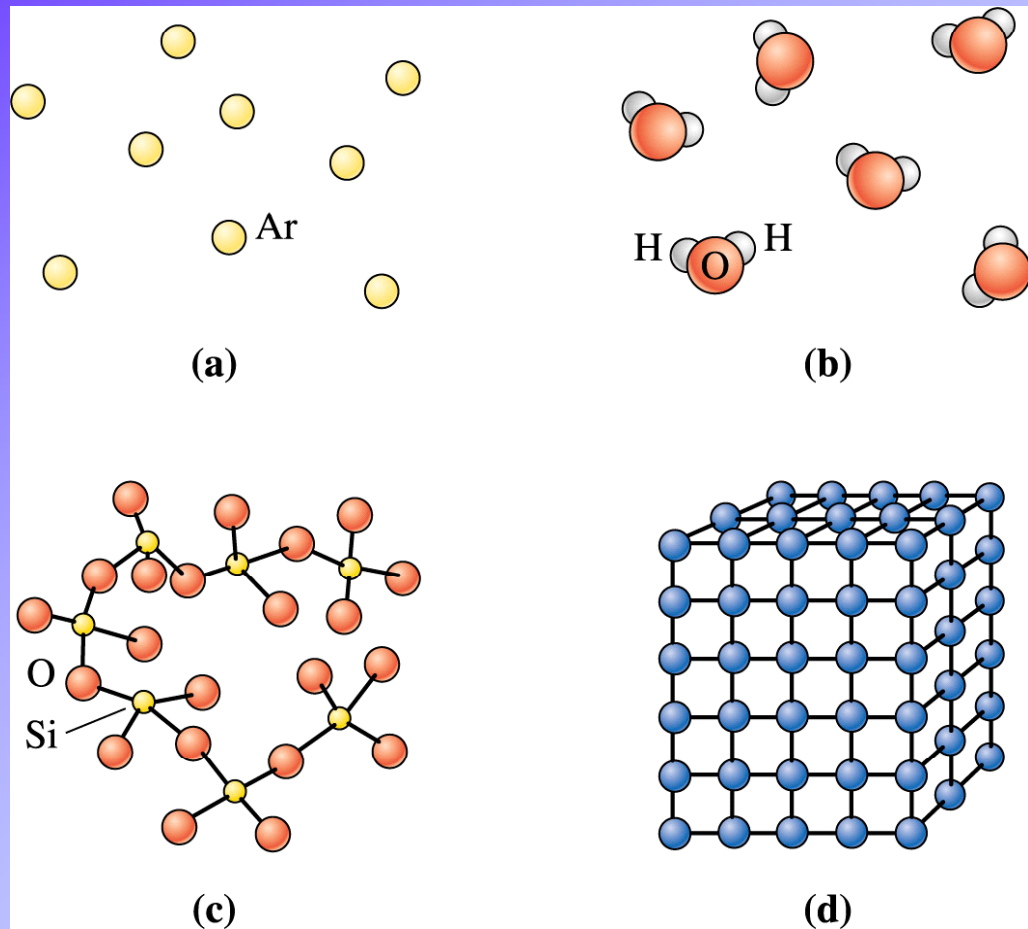


Fig. 3-1

Níveis de arranjos atômicos dos materiais:

(a) Gases inertes monoatômicos não possuem um arranjo regular dos átomos.

(b,c) Alguns materiais incluindo vapor d'água, nitrogênio gasoso, silício amorfo e vidros a base de sílica possuem arranjo de curto alcance.

(d) Metais, ligas metálicas, muitos cerâmicos e alguns polímeros possuem um arranjo ordenado de átomos/íons que se estende através de todo o material.

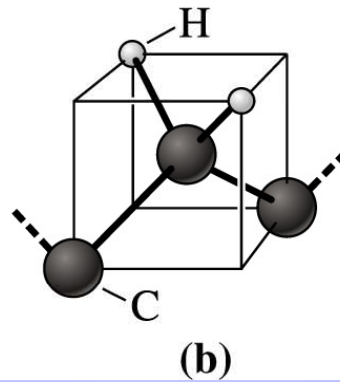
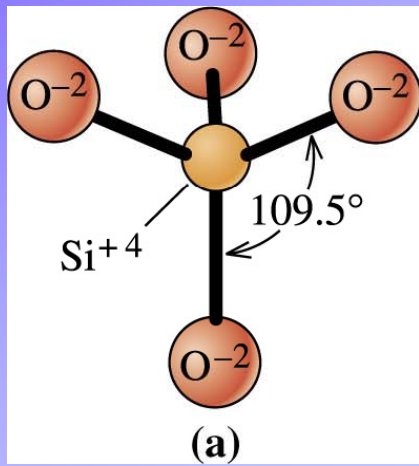


Fig. 3-2

(a) Tetraedro básico Si-O em vidros

(b) Arranjo Tetraédrico das ligações C-H no polietileno.

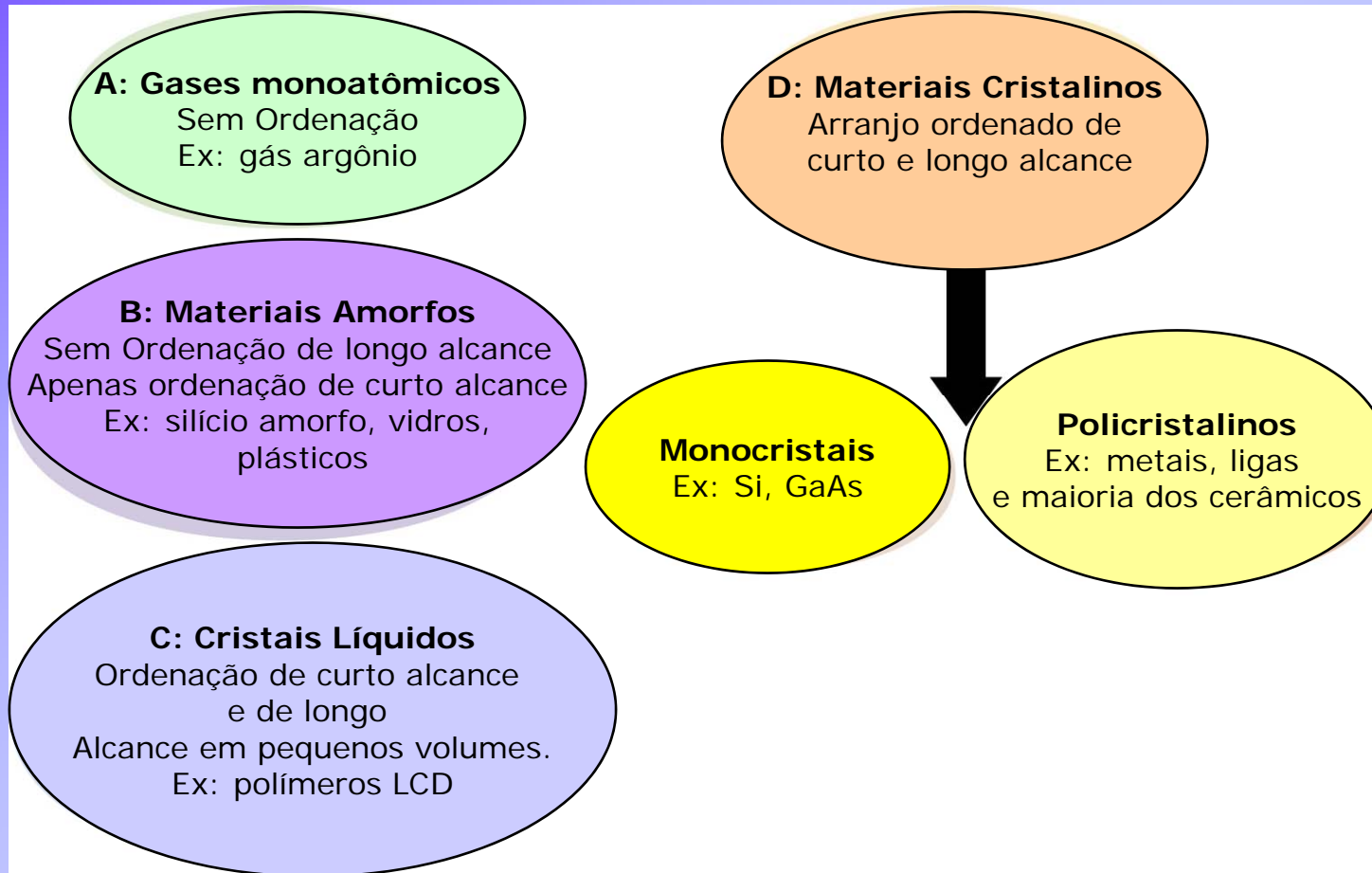
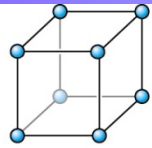
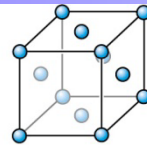


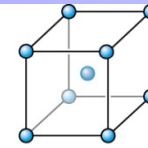
Fig.3-4 Classificação dos materiais com base no tipo de arranjo atômico.



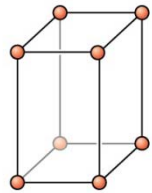
Cúbico simples



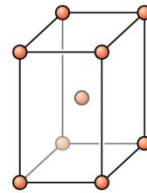
Cúbico de faces centradas



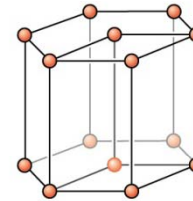
Cúbico de corpo centrado



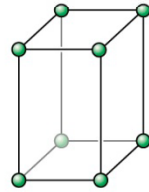
Tetragonal simples



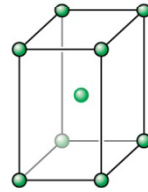
Tetragonal de corpo centrado



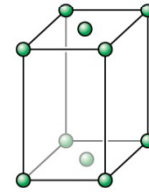
Hexagonal



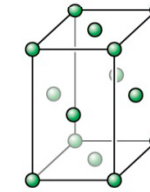
Ortorrômbo Simples



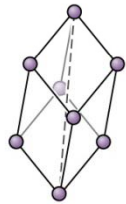
Ortorrômbo de corpo centrado



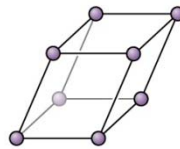
Ortorrômbo de base centrada



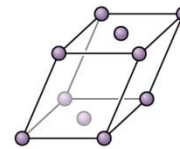
Ortorrômbo de face centrada



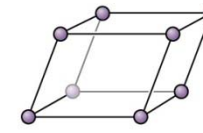
Romboédrico



Monoclínico simples

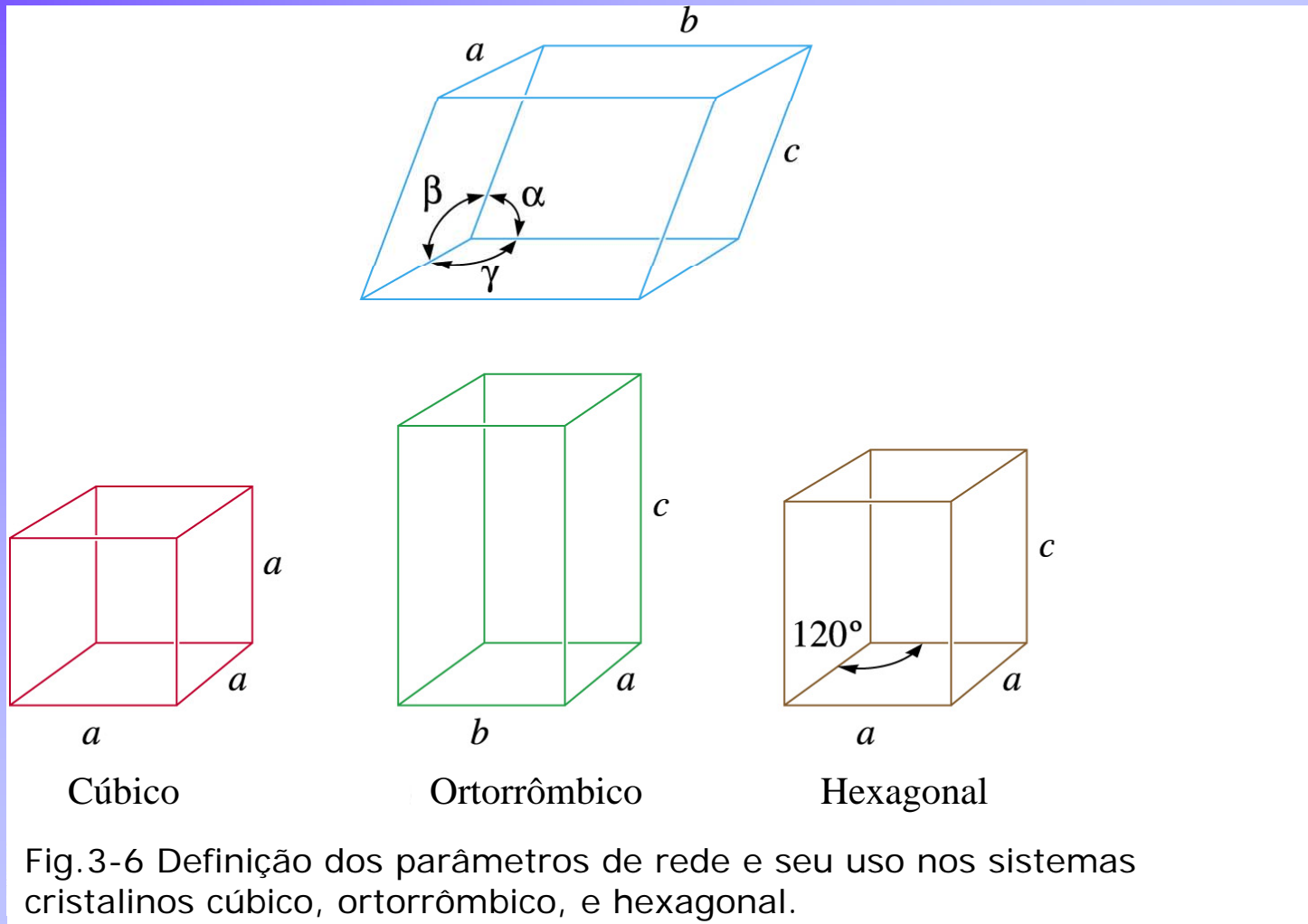


Monoclínico de base centrada



Triclínico

Fig. 3-5 – As 14 redes de Bravais, agrupadas em 7 sistemas cristalino.



Características dos sete sistemas cristalinos

Estrutura	Eixos	Ângulos entre eixos	Volume da Célula Unitária
Cúbica	$a=b=c$	Todos iguais a 90°	a^3
Tetragonal	$a=b \neq c$	Todos iguais a 90°	a^2c
Ortorrômbico	$a \neq b \neq c$	Todos iguais a 90°	abc
Hexagonal	$a=b \neq c$	dois iguais a 90° e um igual a 120°	$0,866a^2c$
Romboédrico	$a=b=c$	Todos os ângulos iguais e nenhum igual a 90°	$a^3 \sqrt{1 - 3 \cos^2 \alpha + 2 \cos^3 \alpha}$
Monoclínico	$a \neq b \neq c$	Dois ângulos iguais a 90° . Um ângulo (β) diferente de 90°	$abc \cdot \text{sen} \beta$
Triclínico	$a \neq b \neq c$	Todos os ângulos são diferentes e nenhum igual a 90°	$abc \sqrt{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cdot \cos \beta \cdot \cos \gamma}$

Caracterização das células unitárias

- número de átomos na célula
- parâmetro de rede (a)
- número de coordenação ou coordenação atômica
- fator de empacotamento atômico (FEA)

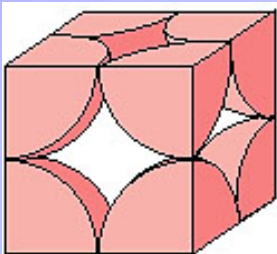
$$FEA = \frac{\textit{volume de átomos dentro da célula}}{\textit{volume da célula}}$$

Célula cúbica simples (CS)

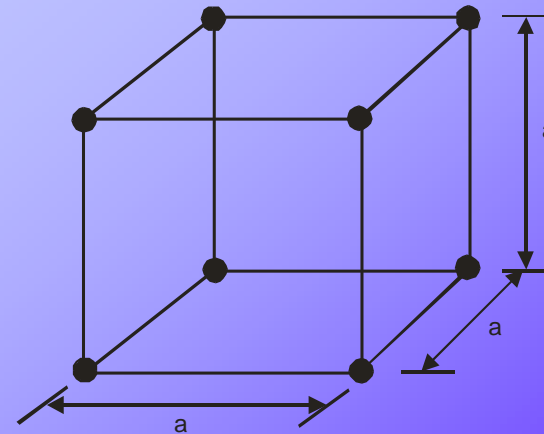
- número de átomos na célula = 1
- 1 átomo em cada canto (1/8 do volume dentro da célula)
- parâmetro de rede (a) $\Rightarrow a=2r$
- fator de empacotamento atômico (FEA)

$$FEA = \frac{\frac{4}{3} \pi r^3}{a^3} = \frac{\frac{4}{3} \pi r^3}{(2r)^3} = 0,52$$

Significa que do volume total da célula apenas 52% são ocupados.
Número de coordenação = 6



Representação do modelo de esferas rígidas na célula CS.



Representação reduzida da célula CS

Célula cúbica de corpo centrado (CCC)

- número de átomos na célula = 2
- 1 átomo em cada canto e 1 no centro da célula ($8 \times 1/8 + 1$)
- Determinação do parâmetro de rede a :

$$\text{Diagonal principal } (D) = 4r = a\sqrt{3} \therefore a = \frac{4r}{\sqrt{3}}$$

Fator de empacotamento atômico (FEA)

$$FEA = \frac{2 \times \frac{4}{3} \pi r^3}{a^3} = \frac{2 \times \frac{4}{3} \pi r^3}{\left(\frac{4r}{\sqrt{3}}\right)^3} = 0,68$$

Significa que do volume total da célula apenas 68% são ocupados.

Número de coordenação = 8

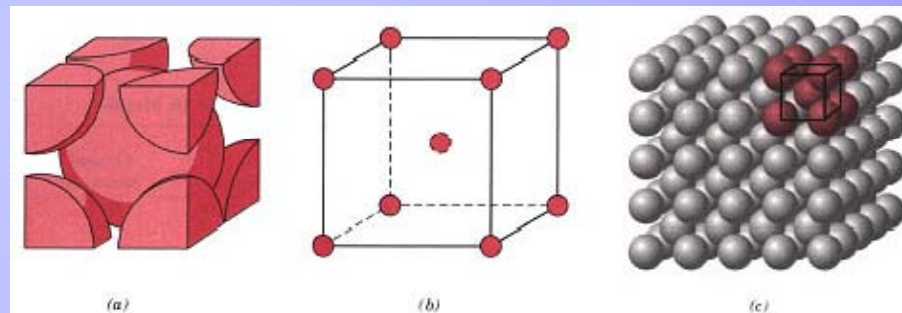


FIGURE 3.2 For the body-centered cubic crystal structure, (a) a hard sphere unit cell representation, (b) a reduced-sphere unit cell, and (c) an aggregate of many atoms. (Figure (c) from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*, p. 51. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

Célula cúbica de faces centradas (CFC)

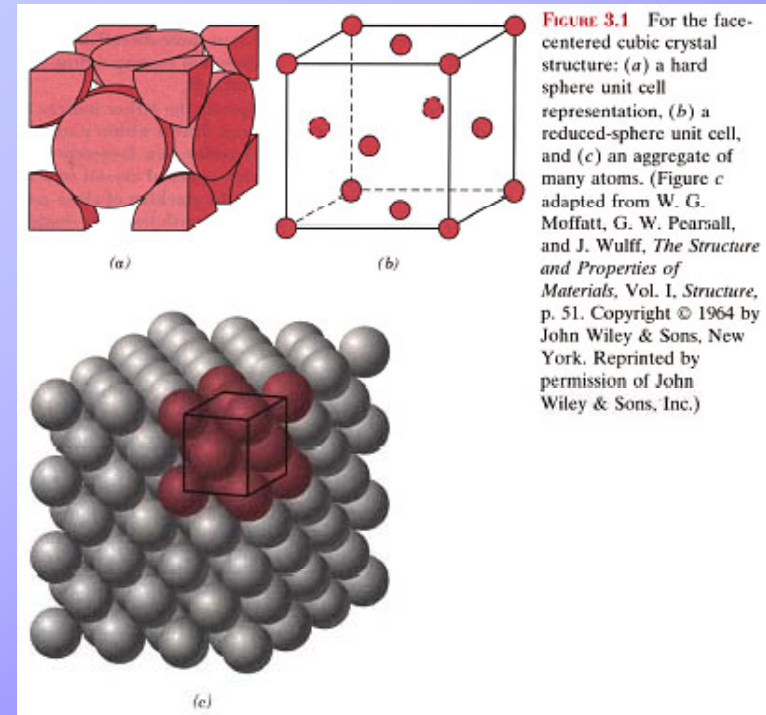
- número de átomos na célula = 4
- 1 átomo em cada canto e $\frac{1}{2}$ em cada uma das 6 faces
($8 \times \frac{1}{8} + 6 \times \frac{1}{2}$)
- Determinação do parâmetro de rede a :

$$\text{Diagonal principal } (D) = 4r = a\sqrt{2} \therefore a = \frac{4r}{\sqrt{2}}$$

Fator de empacotamento atômico (FEA)

$$FEA = \frac{4 \times \frac{4}{3} \pi r^3}{a^3} = \frac{4 \times \frac{4}{3} \pi r^3}{\left(\frac{4r}{\sqrt{2}}\right)^3} = 0,74$$

Significa que do volume total da célula apenas 74% são ocupados.
Número de coordenação = 12



Célula hexagonal simples (HS)

• número de átomos na célula = 3

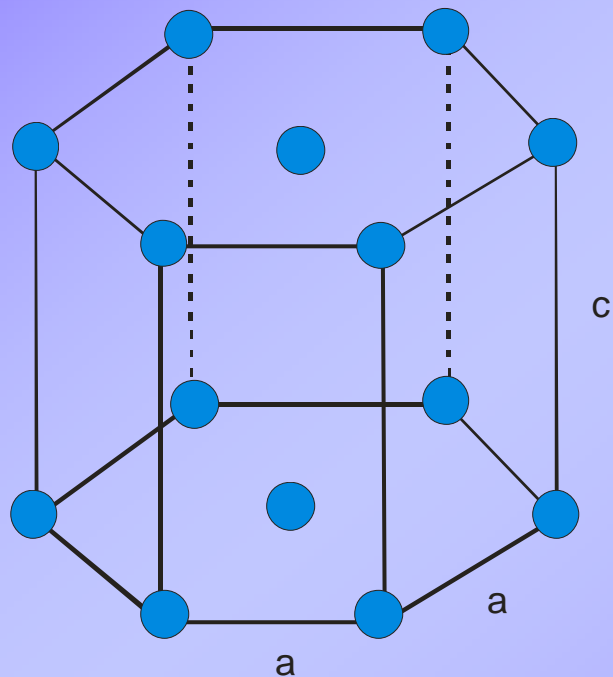
1 átomo em cada canto contribui com $1/6$

1 átomo em cada base contribui com $1/2$

$12 \times 1/6 + 2 \times 1/2 = 3$ átomos

Fator de empacotamento atômico (FEA) = 0,52

Número de coordenação = 8



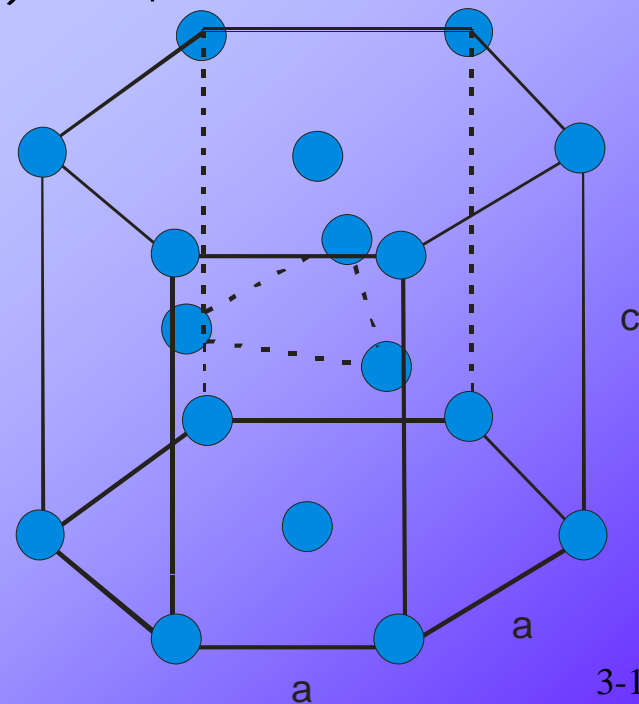
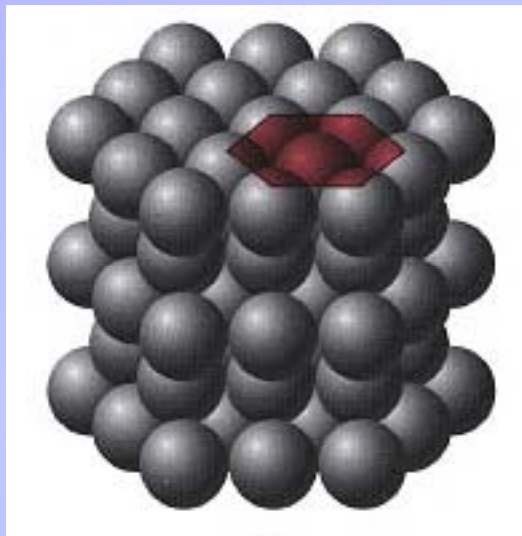
Célula hexagonal compacta (HCP)

Neste sistema cada átomo está localizado no interstício formado por três outros átomos de modo que cada átomo fica em contato com 6 outros átomos em seu próprio plano, 3 no plano superior e 3 no plano inferior.

- número de átomos na célula = 6
 - 1 átomo em cada canto contribui com $1/6$
 - 1 átomo em cada base contribui com $1/2$
 - 3 átomos entre as bases
 - $12 \times 1/6 + 2 \times 1/2 + 3 = 6$ átomos

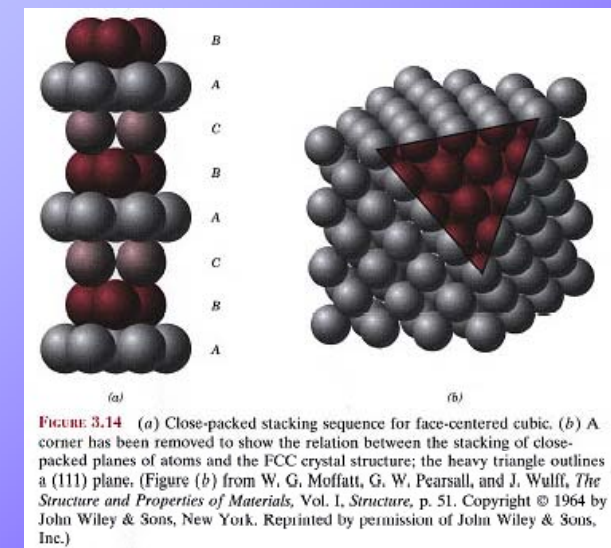
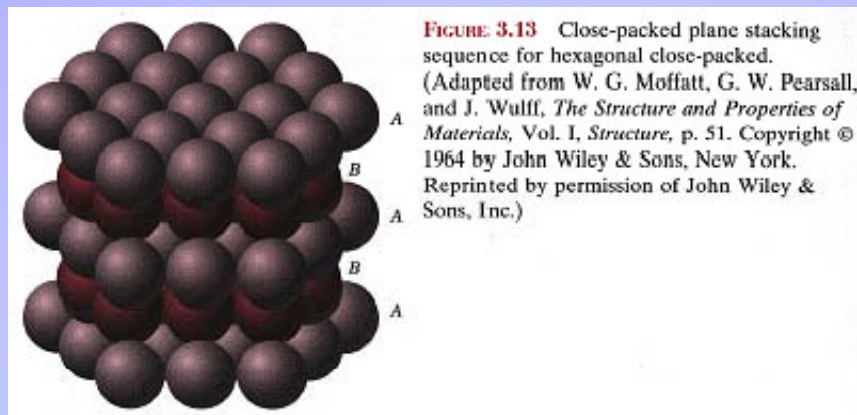
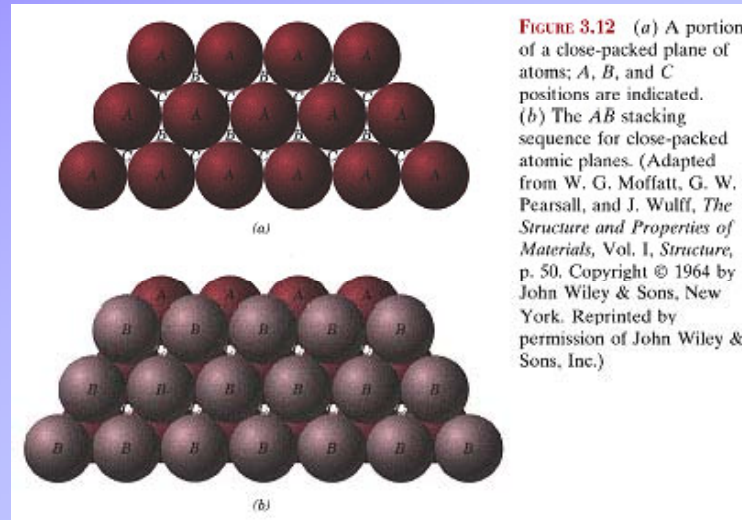
Fator de empacotamento atômico (FEA) = 0,74

Número de coordenação = 12



Sequência de Empilhamento

Os sistemas CFC e HC diferem pela sequência de empilhamento a qual corresponde a ordem de formação das camadas atômicas.



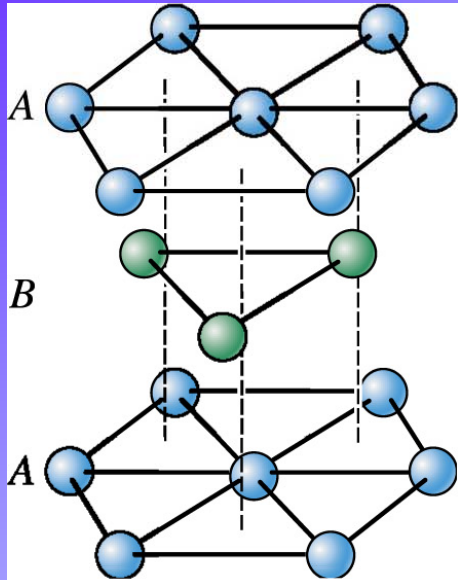


Figure 3-20

The *ABABAB* stacking sequence of close-packed planes produces the HCP structure.

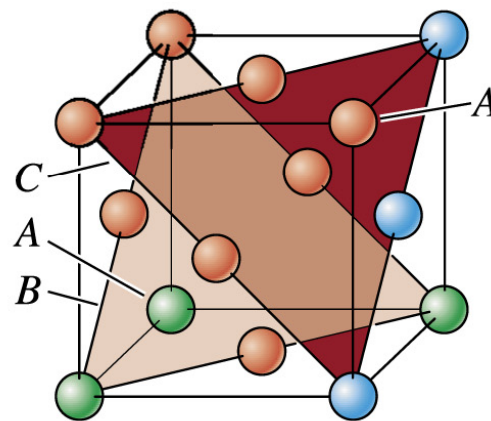
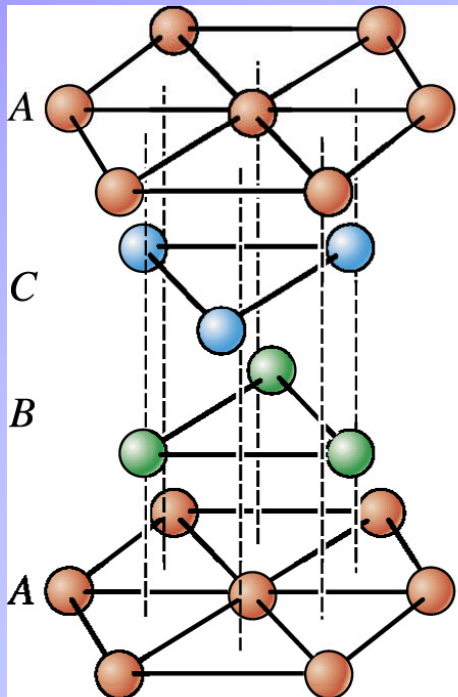
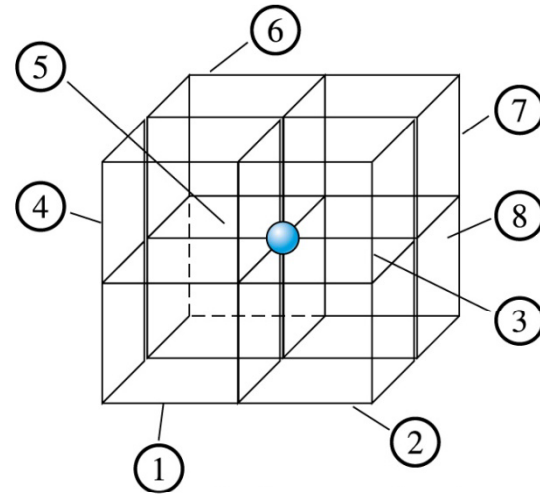
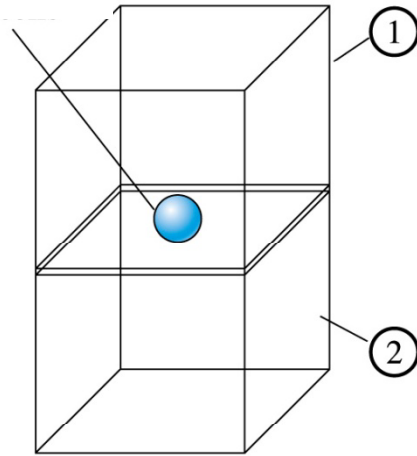


Figure 3-21

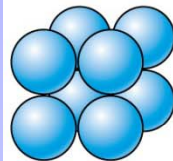
The *ABCABCABC* stacking sequence of close-packed planes produces the FCC structure.

No CFC, o átomo da face é compartilhado por duas células unitárias

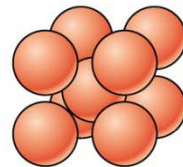


Cada átomo do canto é compartilhado por 8 células unitárias

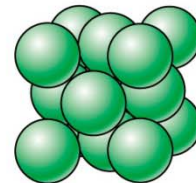
(a)



Cúbico simples



Cúbico de corpo centrado



Cúbico de face centrada

(b)

Fig. 3-7 (a) Ilustração mostrando o compartilhamento de átomos da face e do canto. (b) Modelos de arranjos: CS, CCC e CFC.

Alotropia ou Polimorfismo

Uma mesma espécie química pode apresentar diferentes estruturas cristalinas.

Ex.: Carbono Grafite e Carbono Diamante

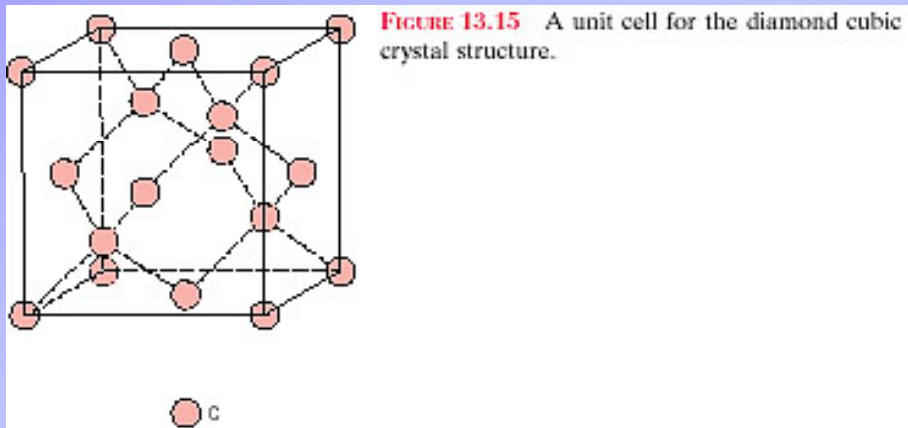
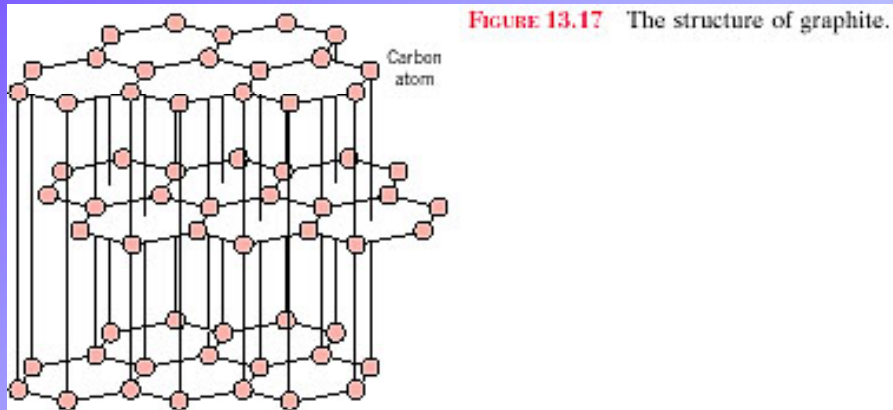
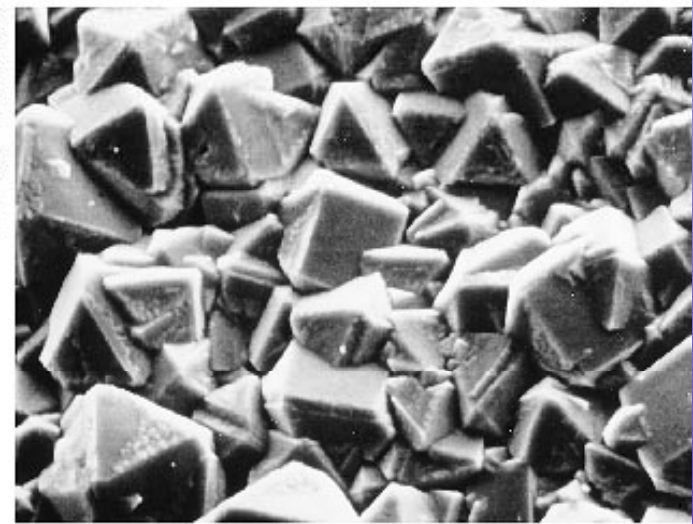


FIGURE 13.16 Scanning electron micrograph of a diamond thin film in which is shown numerous multifaceted microcrystals. 1000 \times . (Photograph courtesy of the Norton Company.)



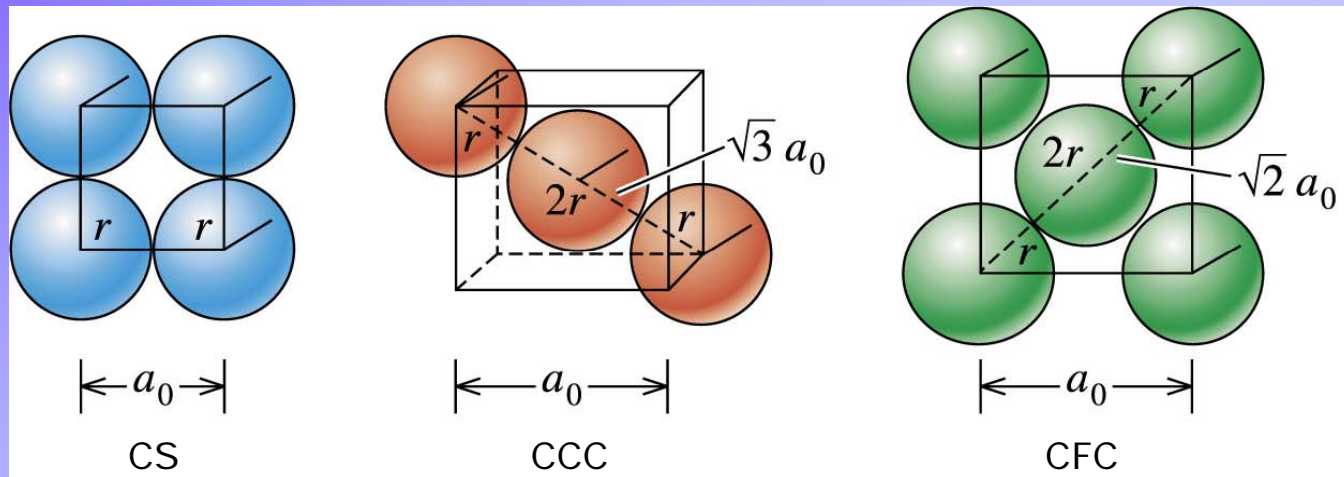
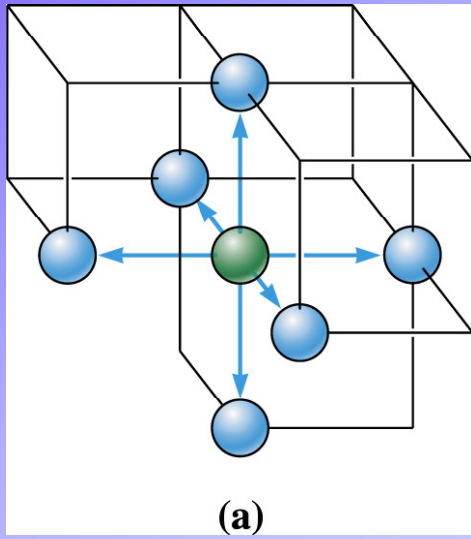
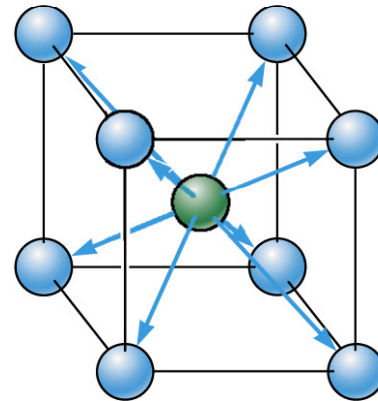


Fig.3-8 Relações entre o raio atômico e o parâmetro de rede no sistema cúbico.



(a)

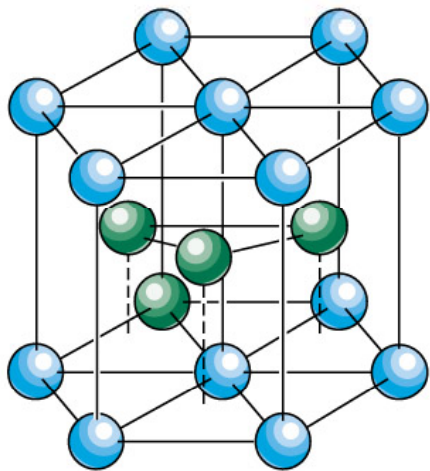


(b)

Fig.3-9

Ilustração de coordenação atômica

- (a) CS – cada átomo está ligado a seis outros átomos
- (b) CCC - cada átomo está ligado a oito outros átomos.



$$Volume = a_0^2 \cdot c_0 \cdot \cos 30^\circ$$

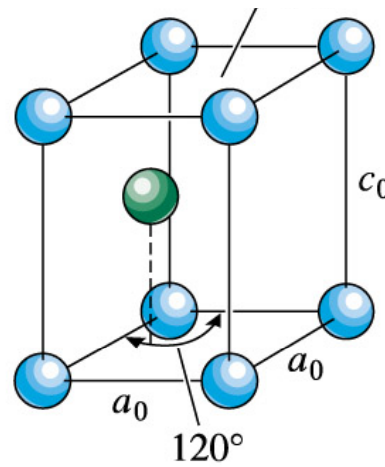


Fig.3-10

Estrutura hexagonal compacta (HCP) a esquerda e sua célula unitária.

TABLE 3-2 ■ *Crystal structure characteristics of some metals*

Structure	a_0 versus r	Atoms per Cell	Coordination Number	Packing Factor	Examples
Simple cubic (SC)	$a_0 = 2r$	1	6	0.52	Polonium (Po), α -Mn
Body-centered cubic (BCC)	$a_0 = 4r/\sqrt{3}$	2	8	0.68	Fe, Ti, W, Mo, Nb, Ta, K, Na, V, Zr, Cr
Face-centered cubic (FCC)	$a_0 = 4r/\sqrt{2}$	4	12	0.74	Fe, Cu, Au, Pt, Ag, Pb, Ni
Hexagonal close-packed (HCP)	$a_0 = 2r$ $c_0 \approx 1.633a_0$	2	12	0.74	Ti, Mg, Zn, Be, Co, Zr, Cd

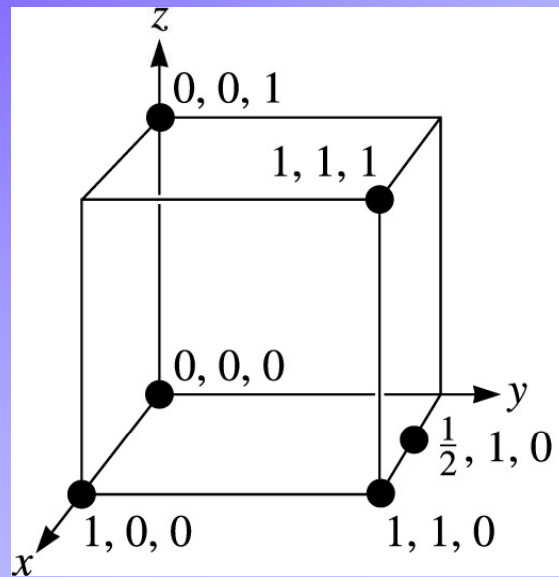


Fig. 3-11

Coordenadas de pontos selecionados na célula unitária. O número se refere a distância a partir da origem em termos de parâmetros de rede.

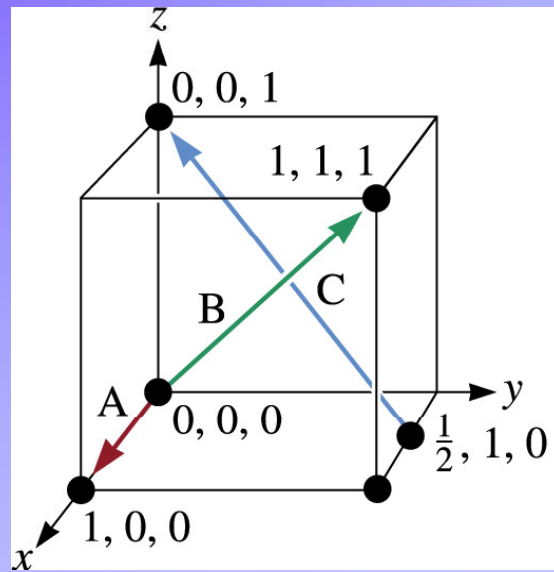


Fig. 3-12

Direções cristalográficas e suas coordenadas.

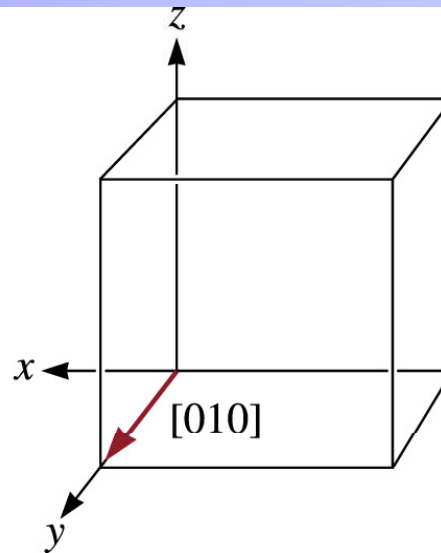
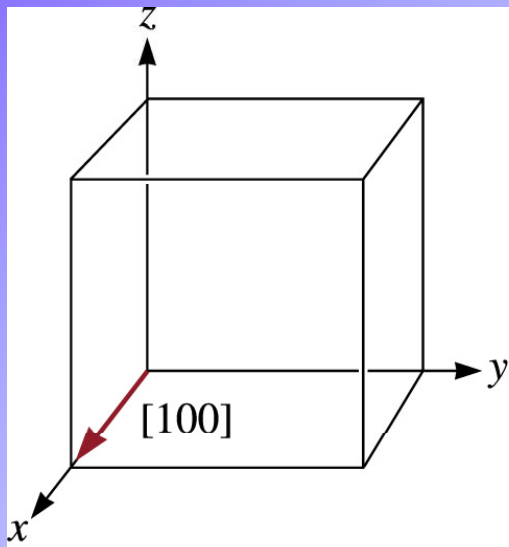


Fig. 3-13

Equivalência de uma família de direções cristalográficas nos sistemas cúbicos.

Tab. 3-3 *Direções da família <110> no sistema cúbico*

$$\langle 110 \rangle = \left\{ \begin{array}{ll} [110] & [\bar{1}\bar{1}0] \\ [101] & [\bar{1}0\bar{1}] \\ [011] & [0\bar{1}\bar{1}] \\ [1\bar{1}0] & [\bar{1}10] \\ [10\bar{1}] & [\bar{1}01] \\ [01\bar{1}] & [0\bar{1}1] \end{array} \right.$$

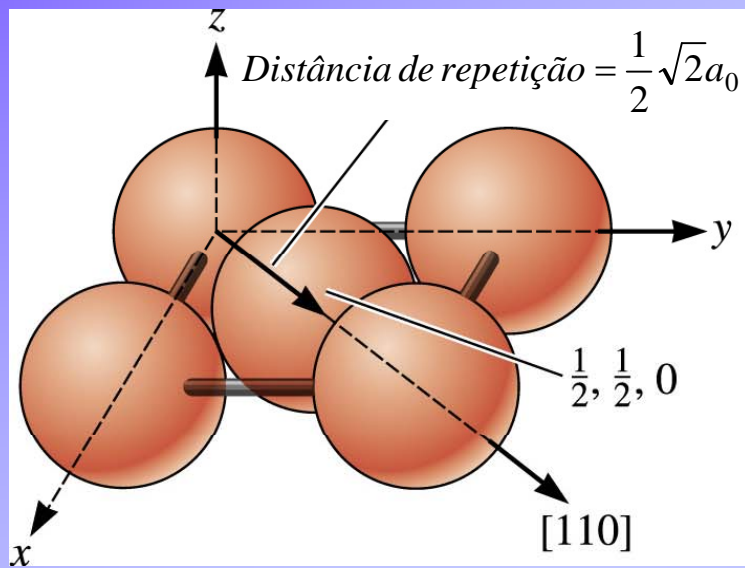


Fig.3-14

Determinando a distância de repetição, densidade linear e fração de empacotamento para a direção $[110]$ no cobre CFC.

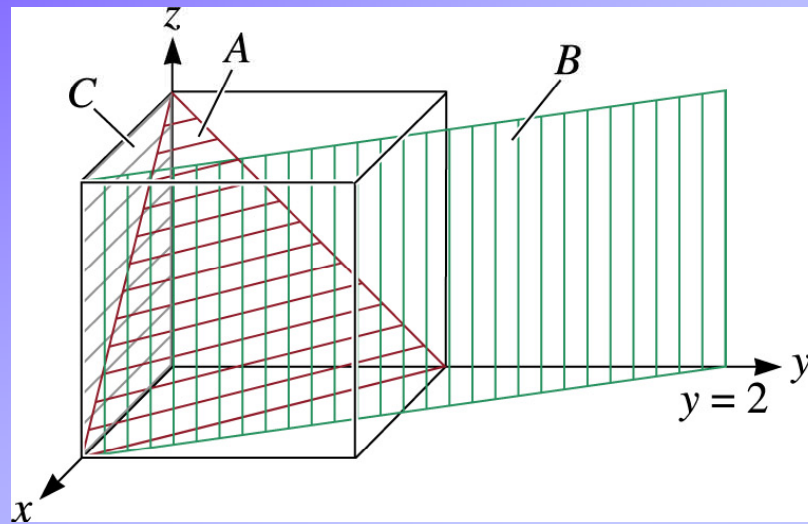


Fig. 3-15

Planos cristalográficos e interseções.

Tab. 3-4 Planos da família {110} no sistema cúbico

$$\{110\} \left\{ \begin{array}{l} (110) \\ (101) \\ (011) \\ (1\bar{1}0) \\ (10\bar{1}) \\ (01\bar{1}) \end{array} \right.$$

Nota: O negativo dos planos não são planos únicos

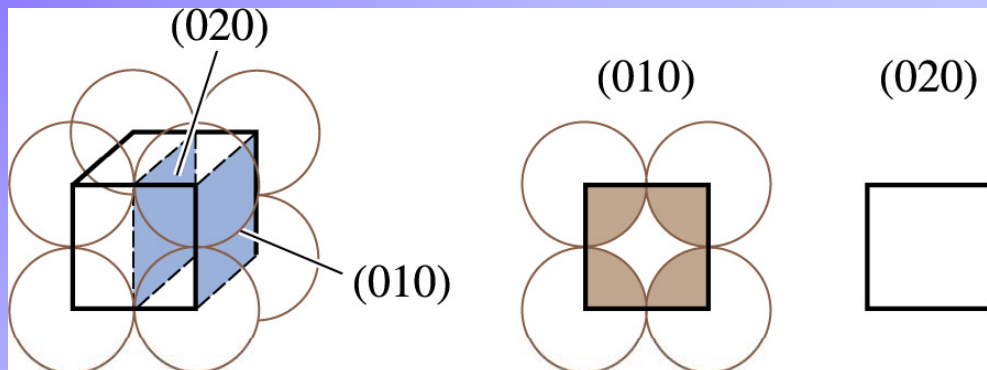


Fig.3-16

A densidade planar dos planos (010) e (020) em uma célula CS.

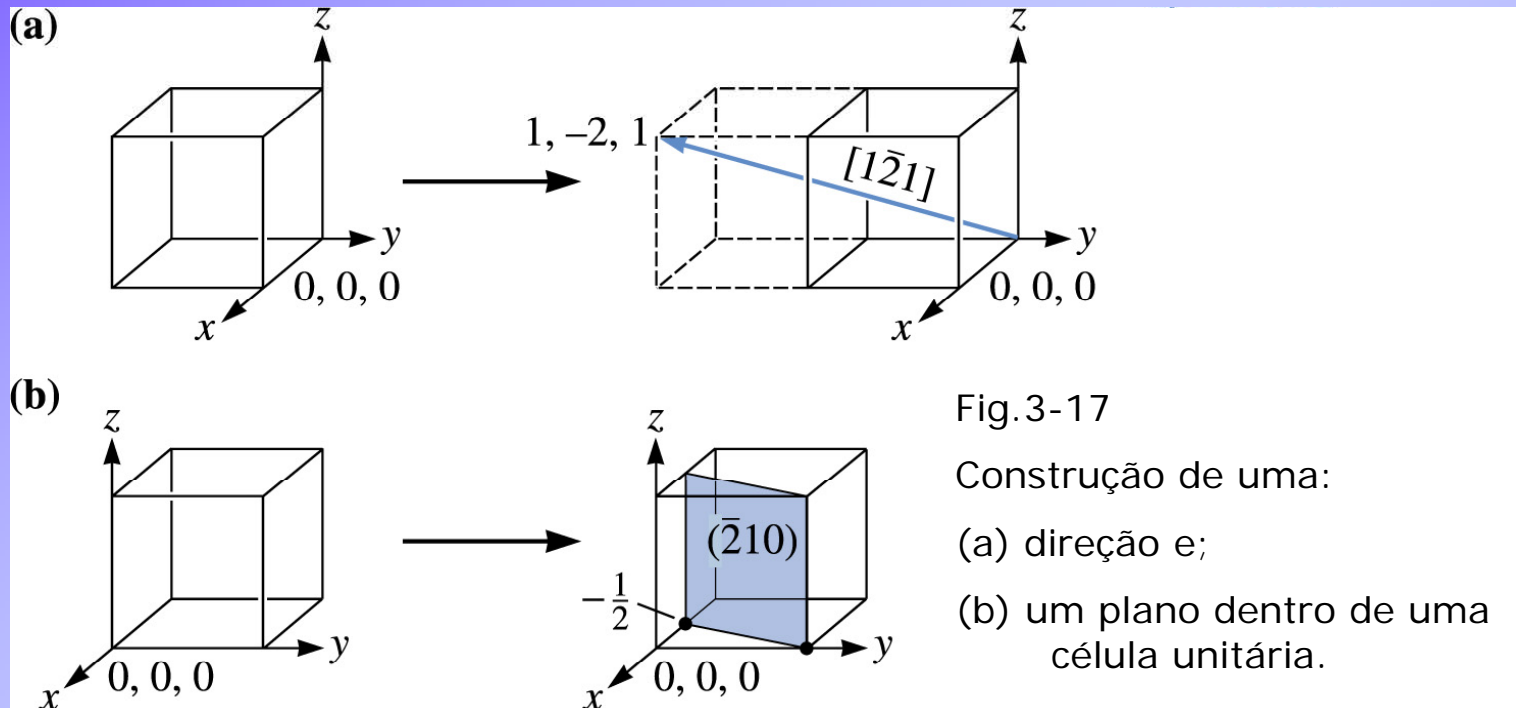


Fig.3-17

Construção de uma:

(a) direção e;

(b) um plano dentro de uma célula unitária.

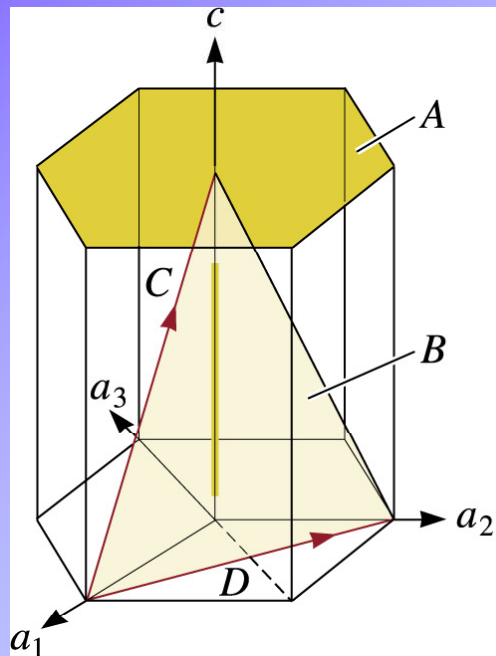


Fig.3-18

Índices do plano A:

1. $a_1 = a_2 = a_3 = \infty, c = 1$
2. $\frac{1}{a_1} = \frac{1}{a_2} = \frac{1}{a_3} = 0, \frac{1}{c} = 1$
3. (0001)

Índices do plano B:

1. $a_1 = 1, a_2 = 1, a_3 = -\frac{1}{2}, c = 1$
2. $\frac{1}{a_1} = 1, \frac{1}{a_2} = 1, \frac{1}{a_3} = -2, \frac{1}{c} = 1$
3. $(11\bar{2}1)$

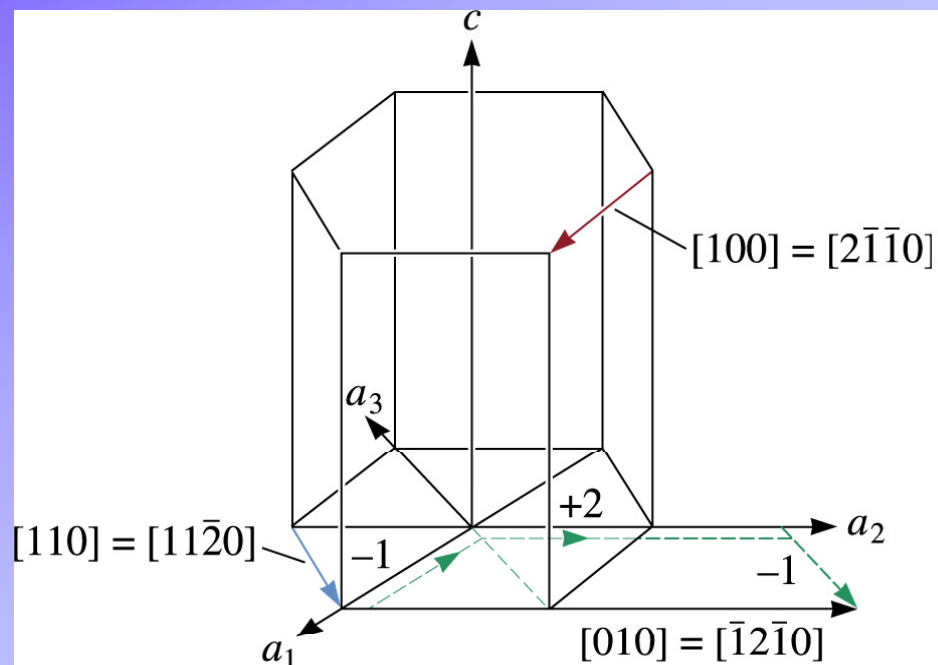


Figure 3-19

Typical directions in the HCP unit cell, using both three- and four-axis systems. The dashed lines show that the $[\bar{1}2\bar{1}0]$ direction is equivalent to a $[010]$ direction.

TABLE 3-5 ■ *Close-packed planes and directions*

Structure	Directions	Planes
SC	$\langle 100 \rangle$	None
BCC	$\langle 111 \rangle$	None
FCC	$\langle 110 \rangle$	$\{111\}$
HCP	$\langle 100 \rangle, \langle 110 \rangle$ or $\langle 11\bar{2}0 \rangle$	(0001), (0002)

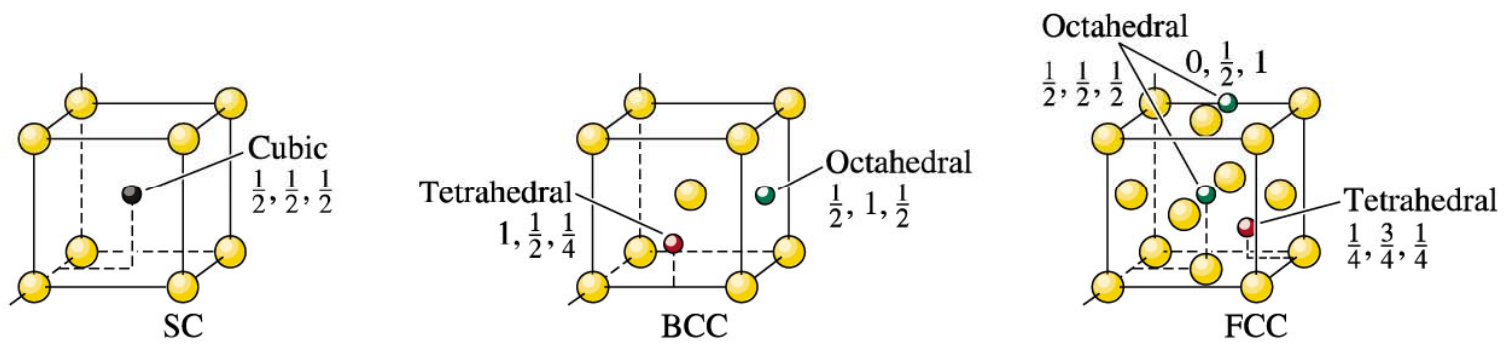
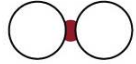
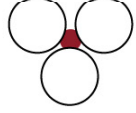
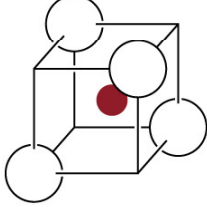

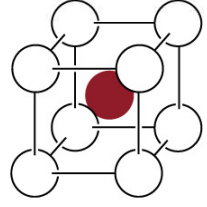


Figure 3-22 The location of the interstitial sites in cubic unit cells. Only representative sites are shown.

TABLE 3-6 ■ *The coordination number and the radius ratio*

Coordination Number	Location of Interstitial	Radius Ratio	Representation
2	Linear	0–0.155	
3	Center of triangle	0.155–0.225	
4	Center of tetrahedron	0.225–0.414	
6	Center of octahedron	0.414–0.732	
8	Center of cube	0.732–1.000	

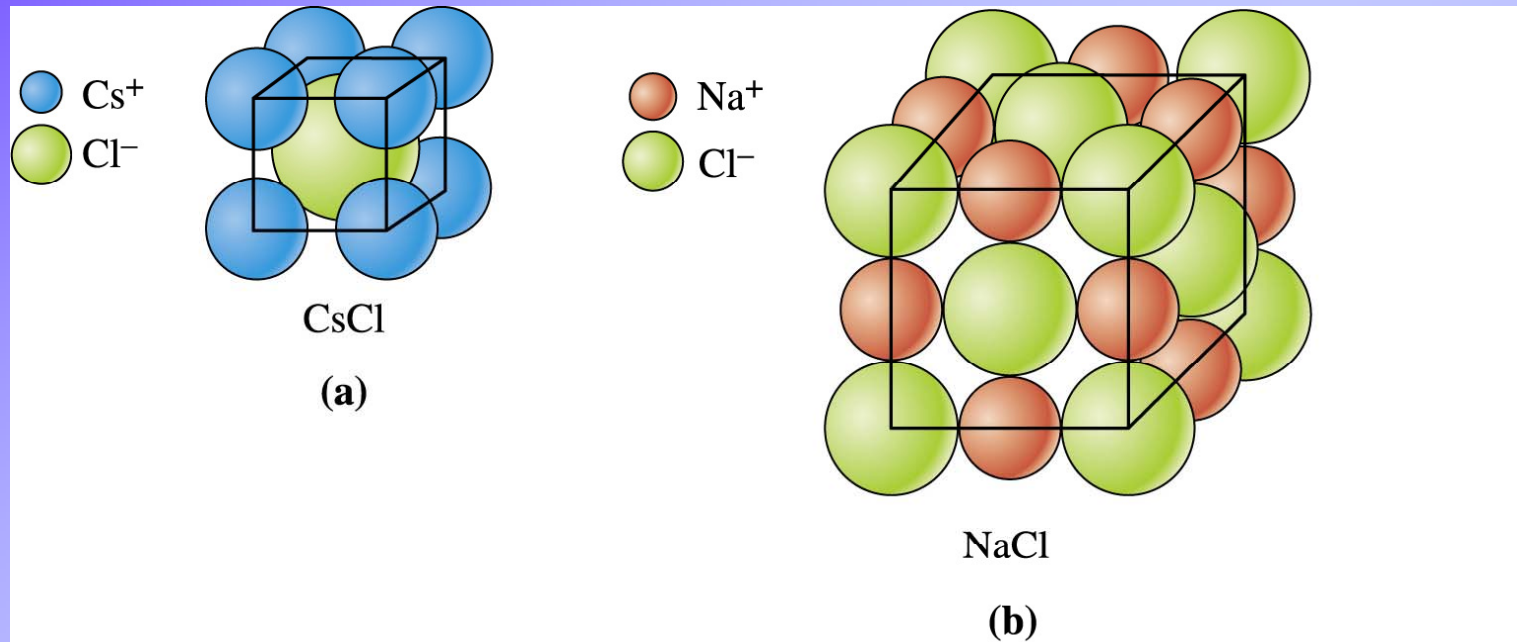


Figure 3-23 (a) The cesium chloride structure, a SC unit cell with two ions (Cs^+ and Cl^-) per lattice point. (b) The sodium chloride structure, a FCC unit cell with two ions (Na^+ and Cl^-) per lattice point. *Note:* Ion sizes not to scale.

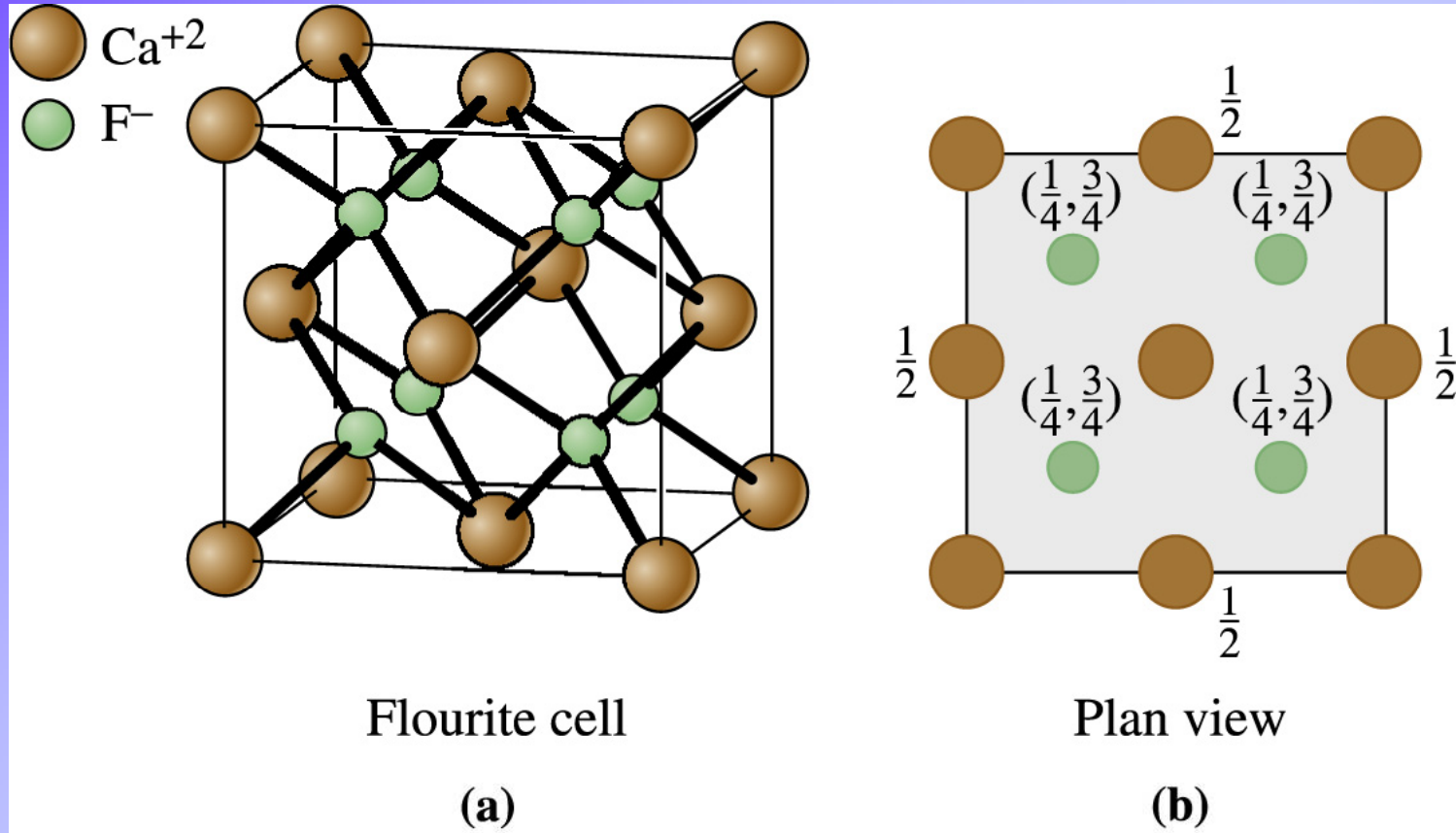


Figure 3-25 (a) Fluorite unit cell, (b) plan view.

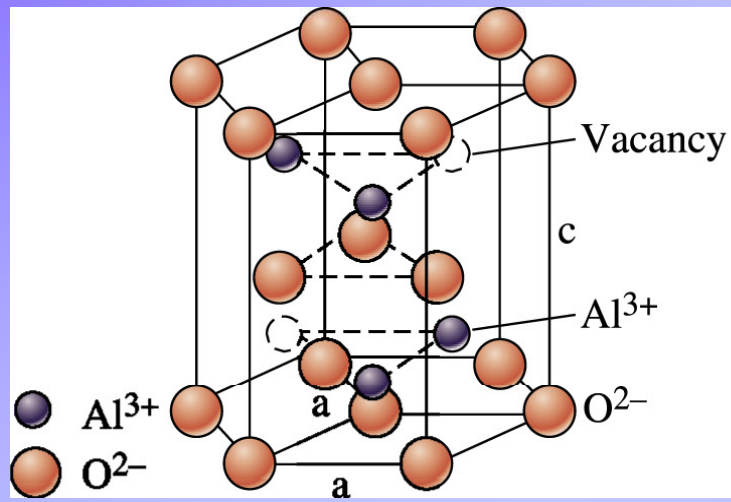
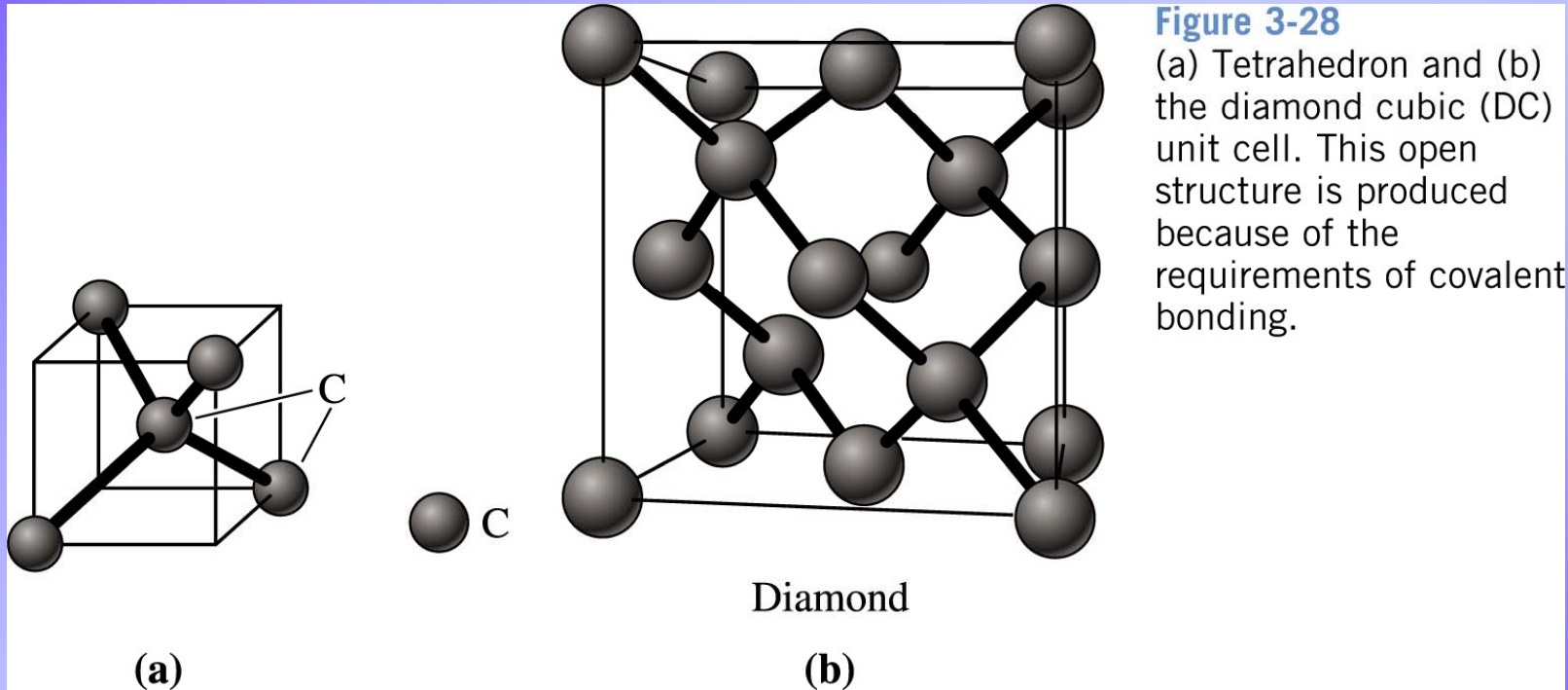


Figure 3-27
Corundum structure of alpha-alumina ($\alpha\text{-Al}_2\text{O}_3$).



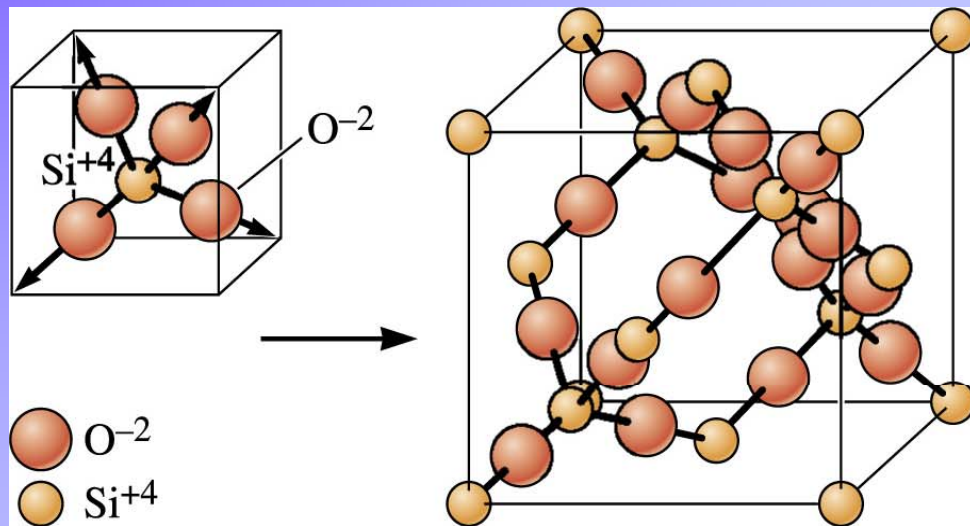
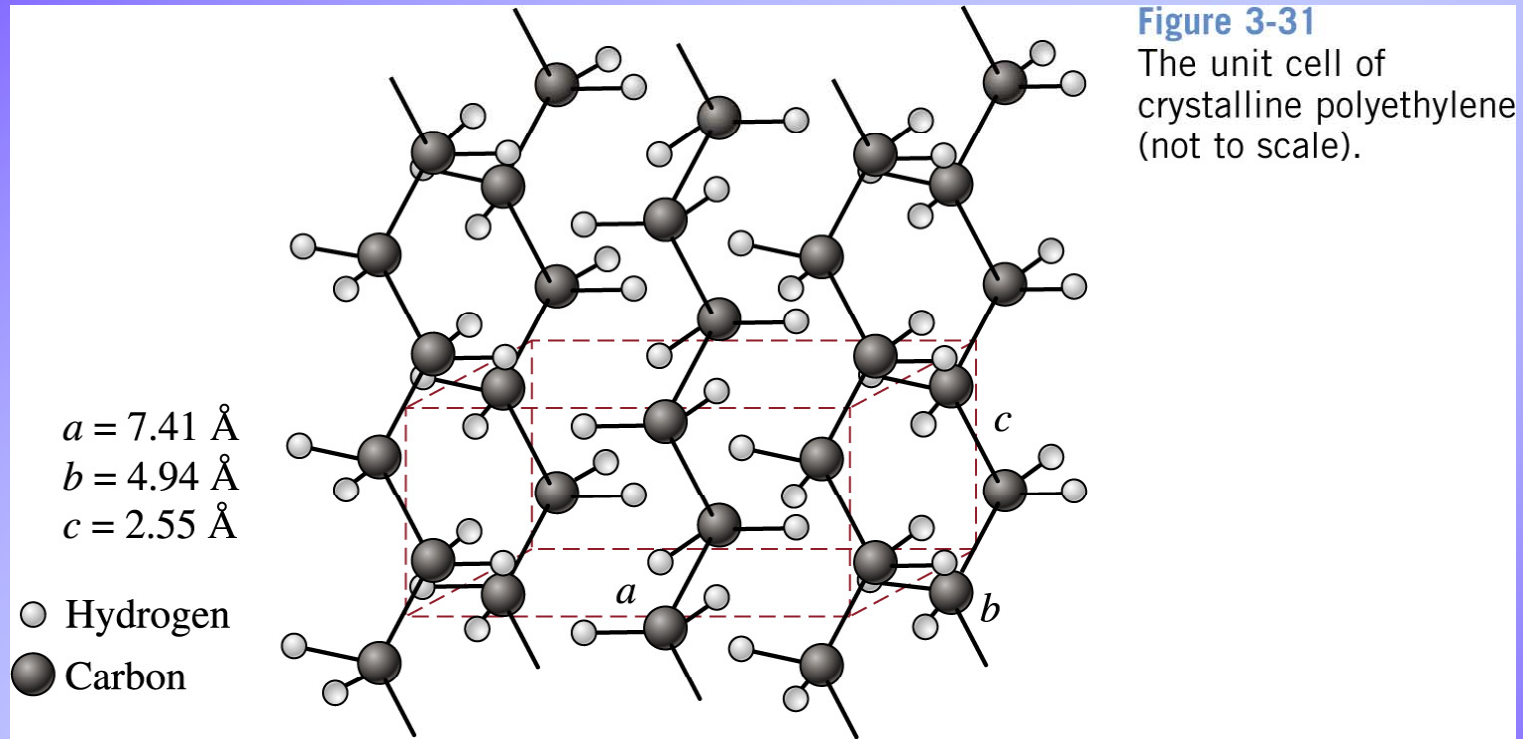
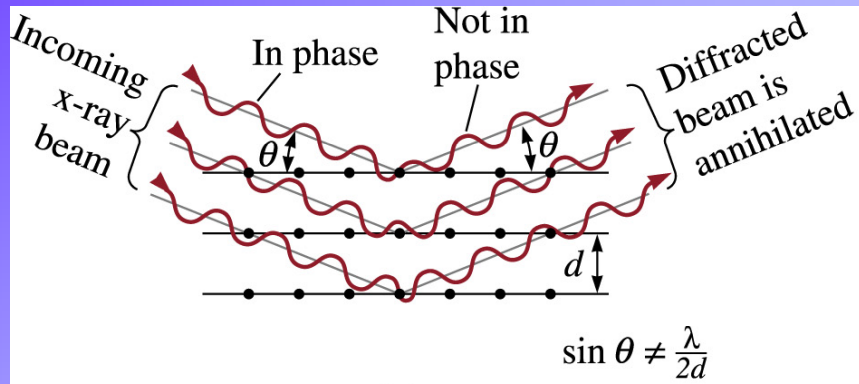
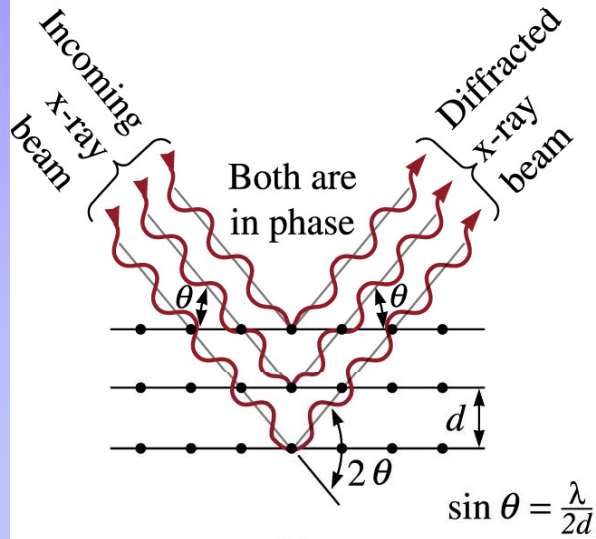


Figure 3-30
The silicon-oxygen tetrahedron and the resultant β -cristobalite form of silica.





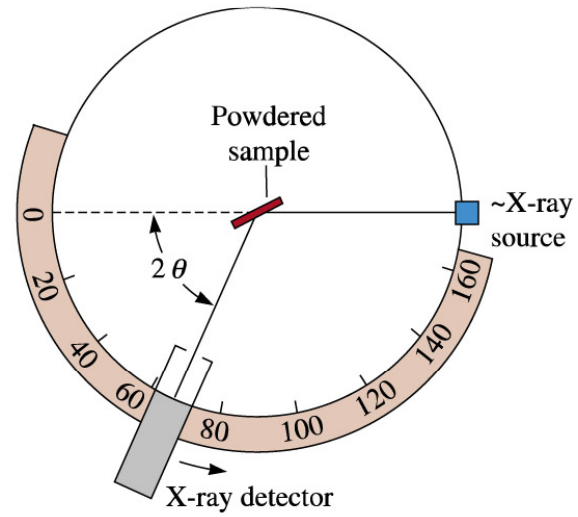
(a)



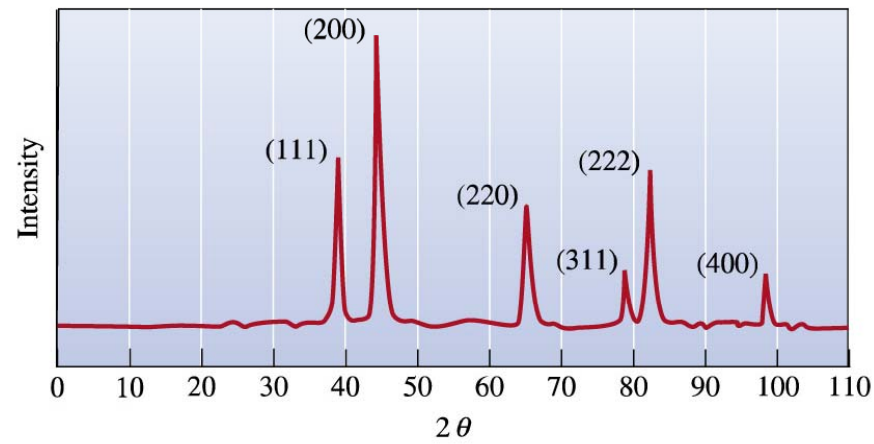
(b)

Figure 3-32

(a) Destructive and (b) reinforcing interactions between x-rays and the crystalline material. Reinforcement occurs at angles that satisfy Bragg's law.



(a)



(b)

Figure 3-33 (a) Diagram of a diffractometer, showing powder sample, incident and diffracted beams. (b) The diffraction pattern obtained from a sample of gold powder.