Lecture Note #5

Atomic structure of solid surfaces

Reading: Somorjai, ch. 2, Shaw, ch. 5,
Atkins, Phys. Chem.

Key words

Lattice,14 Bravis lattice (3D)
fcc, bcc, hcp structures
Miller index

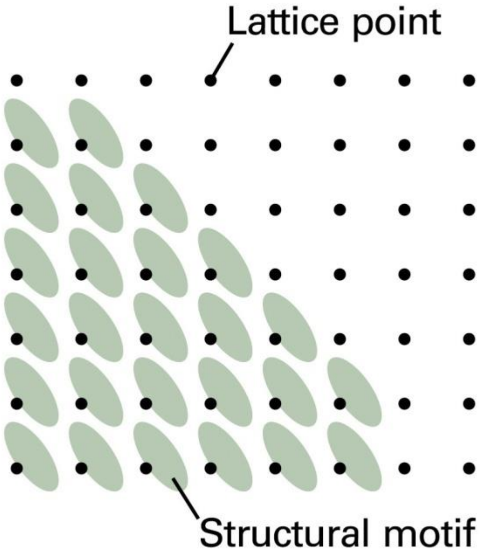
Kinematic theory of x-ray diffraction
Reciprocal lattice
Bragg reflection

5 Bravis lattice (2D)
Low energy electron diffraction
De Broglie wavelength
LEED pattern
I-V curve

Overlayer structure
Stepped surface
Domain structure
Debye-Waller factor: T-depencence
Instrumentation

Lattices

Crystal structure = lattice + basis
Unit cell, primitive unit cell



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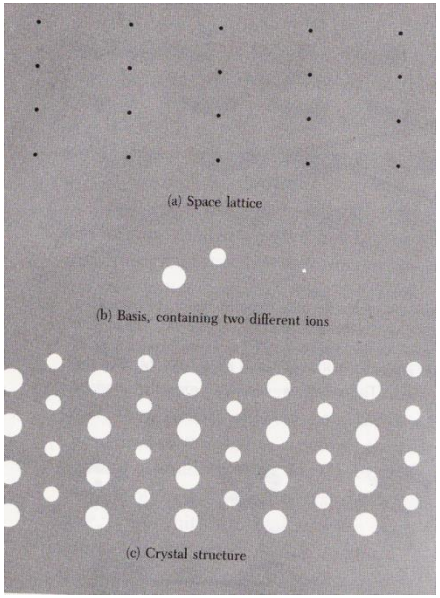
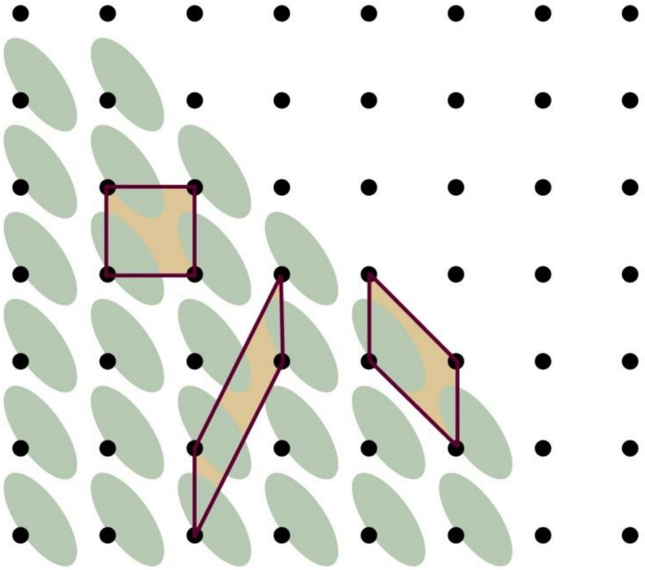


Unit cell, primitive unit cell



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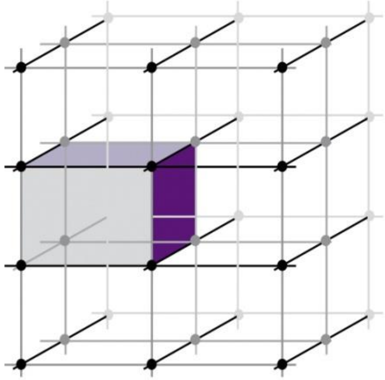

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Translation symmetry
Primitive translation vector $\vec{a}_1$, $\vec{a}_2$, $\vec{a}_3$
Translation T = l $\vec{a}_1$ +m $\vec{a}_2$, +n $\vec{a}_3$
(l,m,n are integers)

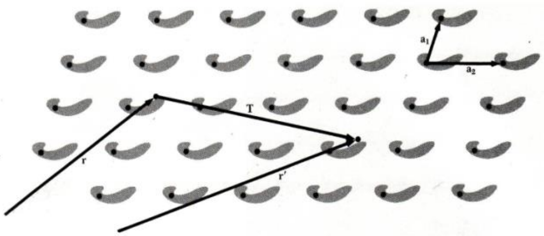


Figure 2 Portion of a crystal of an imaginary protein molecule, in a two-dimensional world. (We picked a protein molecule because it is not likely to have a special symmetry of its own.) The atomic arrangement in the crystal looks exactly the same to an observer at $\mathbf{r}'$ as to an observer at $\mathbf{r}$, provided that the vector $\mathbf{T}$ which connects $\mathbf{r}'$ and $\mathbf{r}$ may be expressed as an integral multiple of the vectors $\mathbf{a}_1$ and $\mathbf{a}_2$. In this illustration, $\mathbf{T} = -\mathbf{a}_1 + 3\mathbf{a}_2$. The vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ are primitive translation vectors of the two-dimensional lattice.

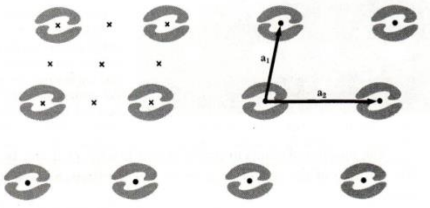


Figure 3 Similar to Fig. 2, but with protein molecules associated in pairs. The crystal translation vectors are $\mathbf{a}_1$ and $\mathbf{a}_2$. A rotation of π radians about any point marked × will carry the crystal into itself. This occurs also for equivalent points in other cells, but we have marked the points × only within one cell.

14 Bravais lattice: 3D

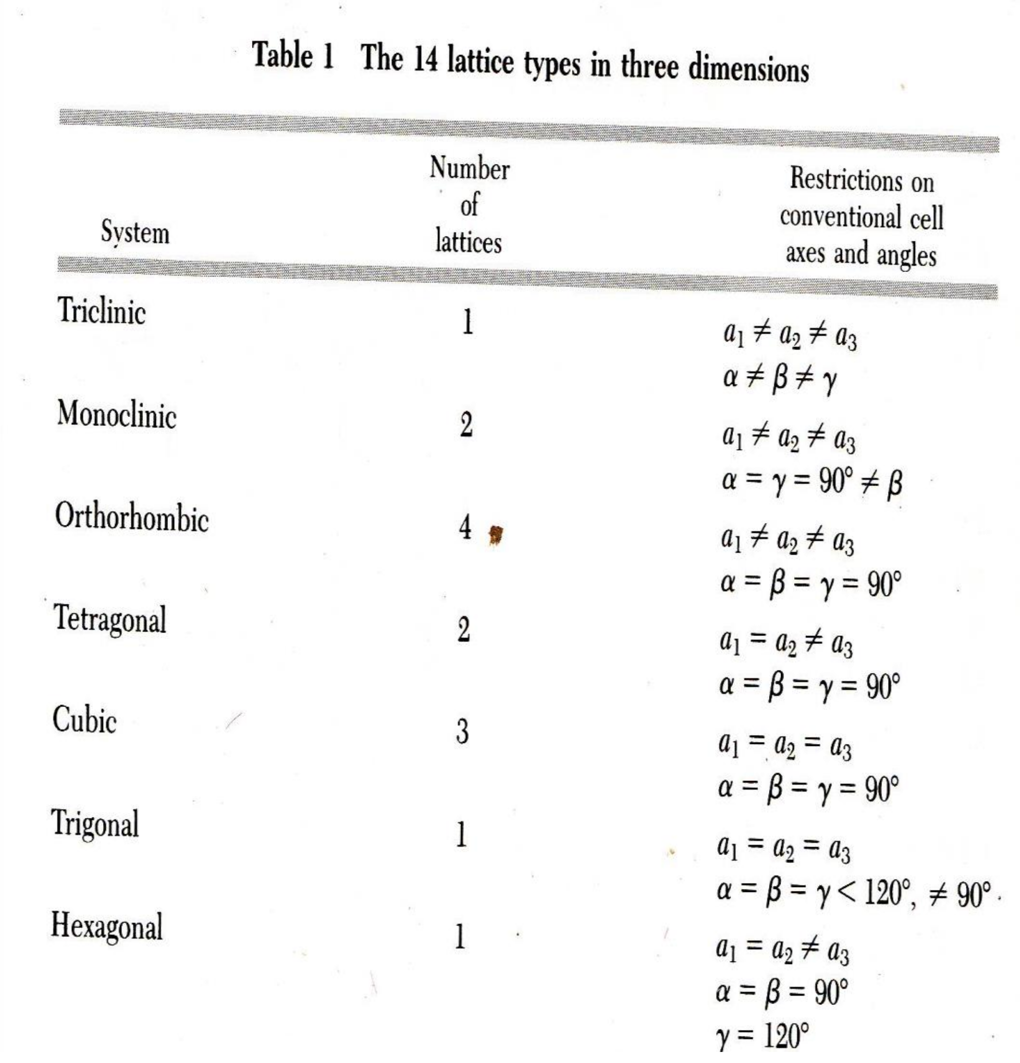
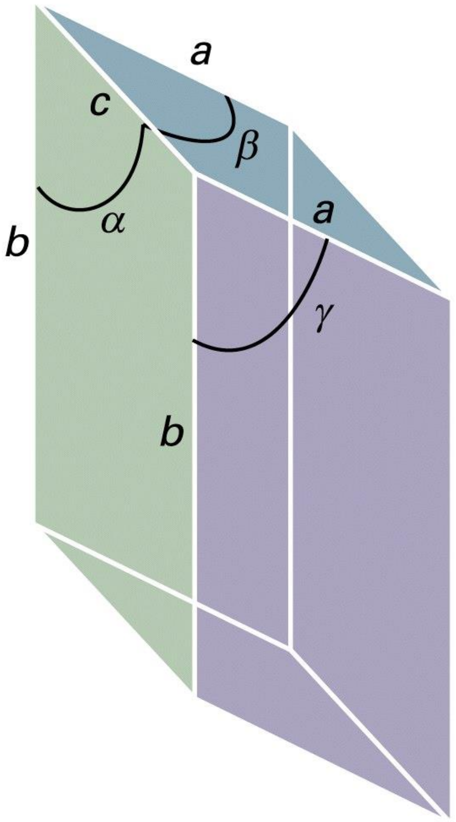


Table 1 The 14 lattice types in three dimensions

System	Number of lattices	Restrictions on conventional cell axes and angles
Triclinic	1	$a_1 \neq a_2 \neq a_3$ $\alpha \neq \beta \neq \gamma$
Monoclinic	2	$a_1 \neq a_2 \neq a_3$ $\alpha = \gamma = 90° \neq \beta$
Orthorhombic	4	$a_1 \neq a_2 \neq a_3$ $\alpha = \beta = \gamma = 90°$
Tetragonal	2	$a_1 = a_2 \neq a_3$ $\alpha = \beta = \gamma = 90°$
Cubic	3	$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma = 90°$
Trigonal	1	$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma < 120°, \neq 90°$
Hexagonal	1	$a_1 = a_2 \neq a_3$ $\alpha = \beta = 90°$ $\gamma = 120°$



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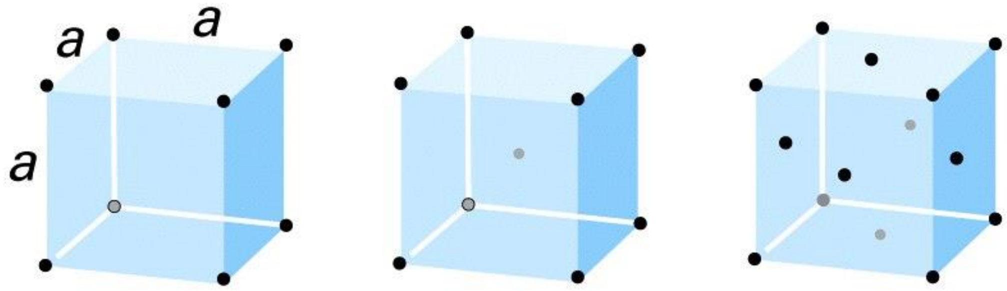
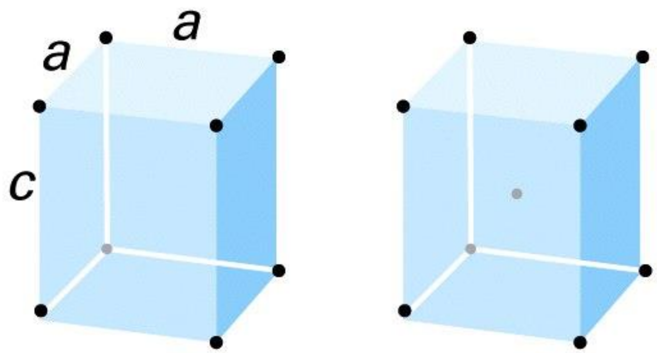
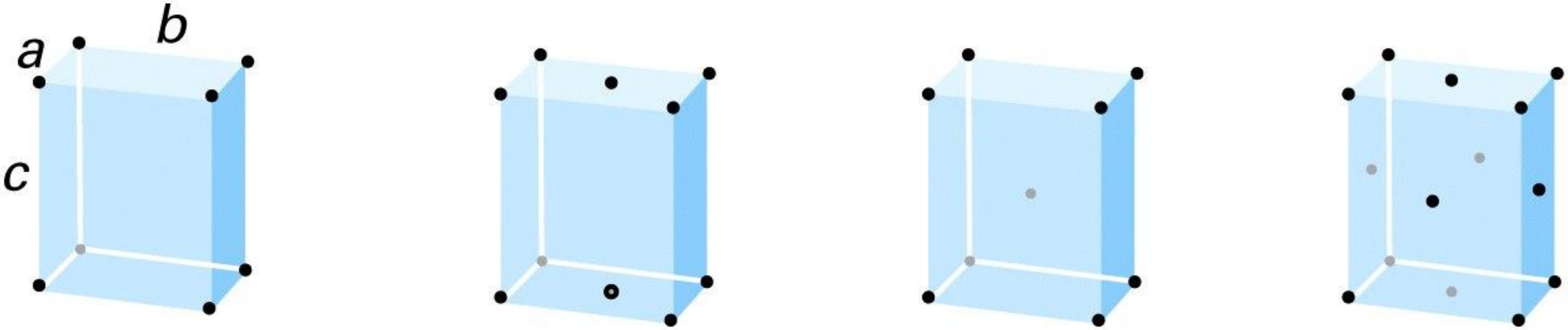


Cubic P Cubic I Cubic F



Tetragonal P Tetragonal I



Orthorhombic P Orthorhombic C Orthorhombic I Orthorhombic F

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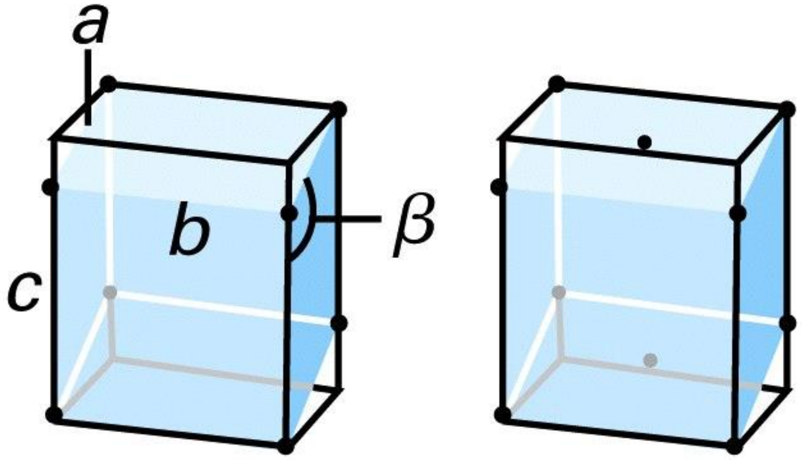
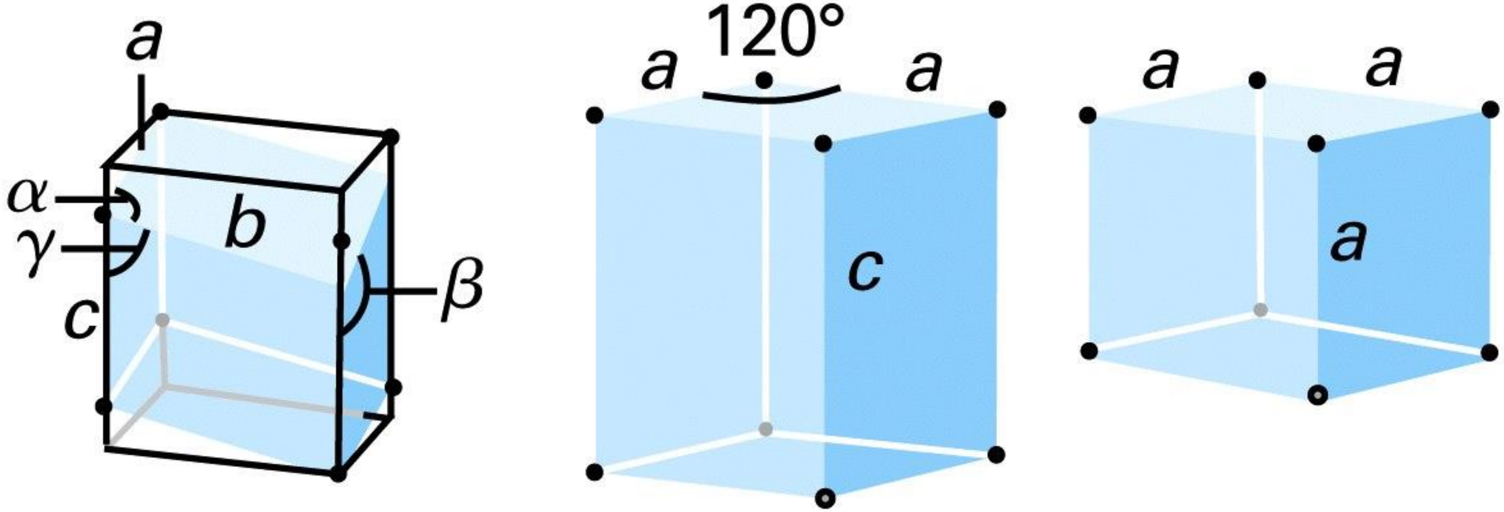


Monoclinic P Monoclinic C



Triclinic Hexagonal Trigonal R

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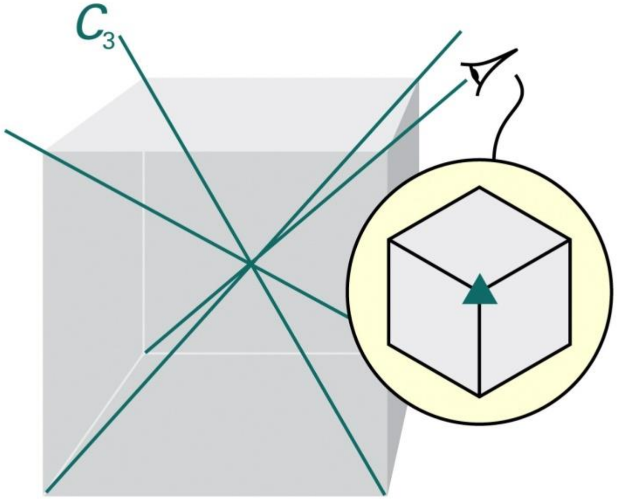
Rotational symmetry



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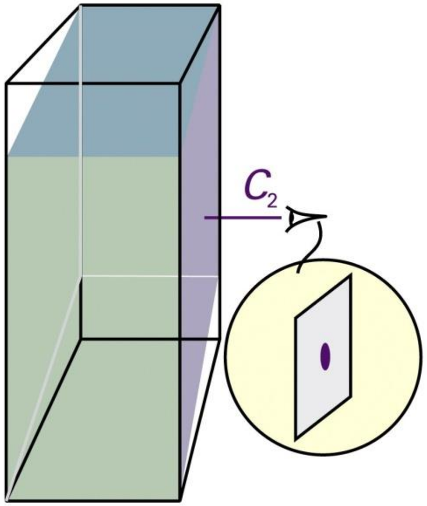

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triclinic

No rotational symmetry

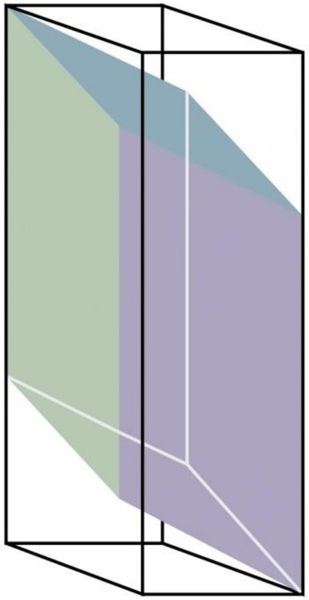

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Table 20.1 The seven crystal systems

System	Essential symmetries
Triclinic	None
Monoclinic	One C_2 axis
Orthorhombic	Three perpendicular C_2 axes
Rhombohedral	One C_3 axis
Tetragonal	One C_4 axis
Hexagonal	One C_6 axis
Cubic	Four C_3 axes in a tetrahedral arrangement

Table 20-1
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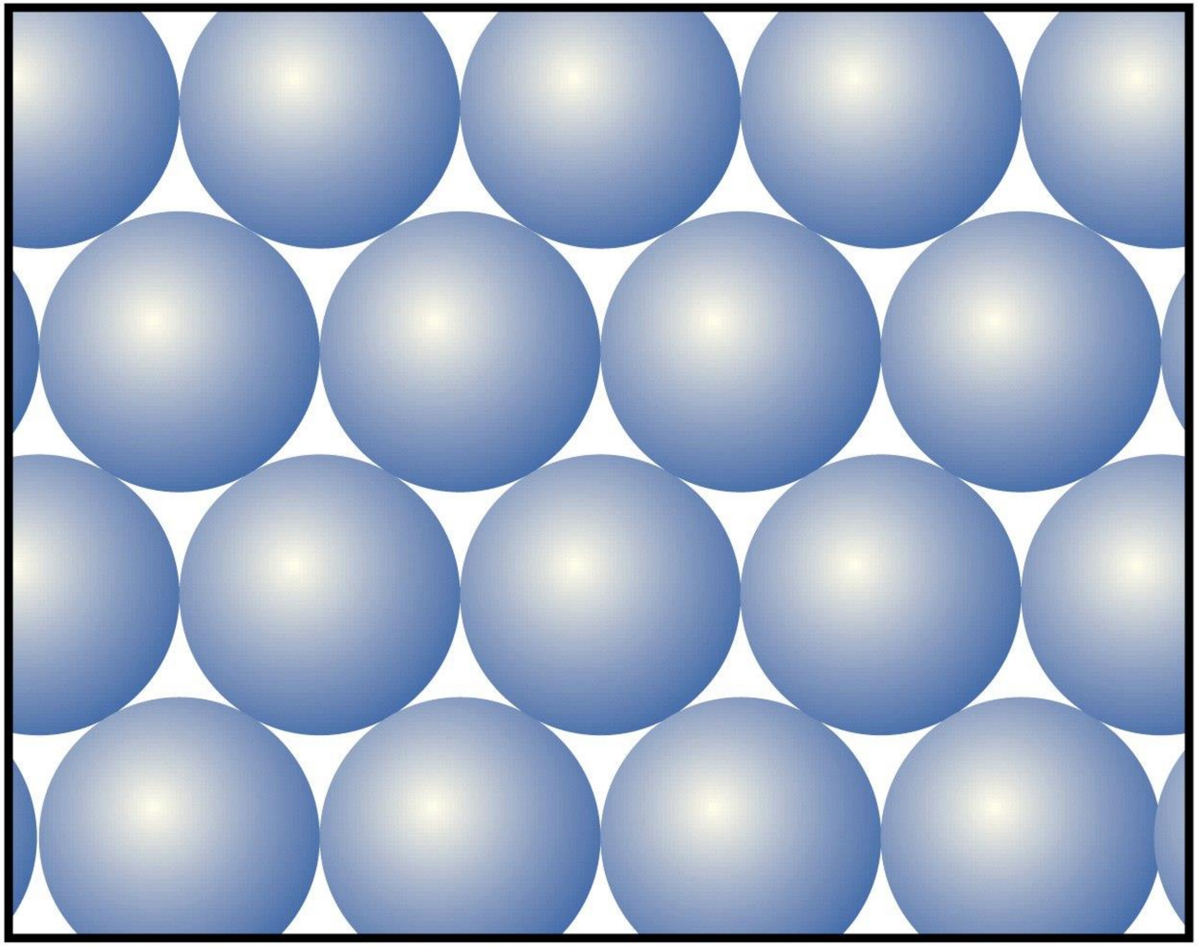

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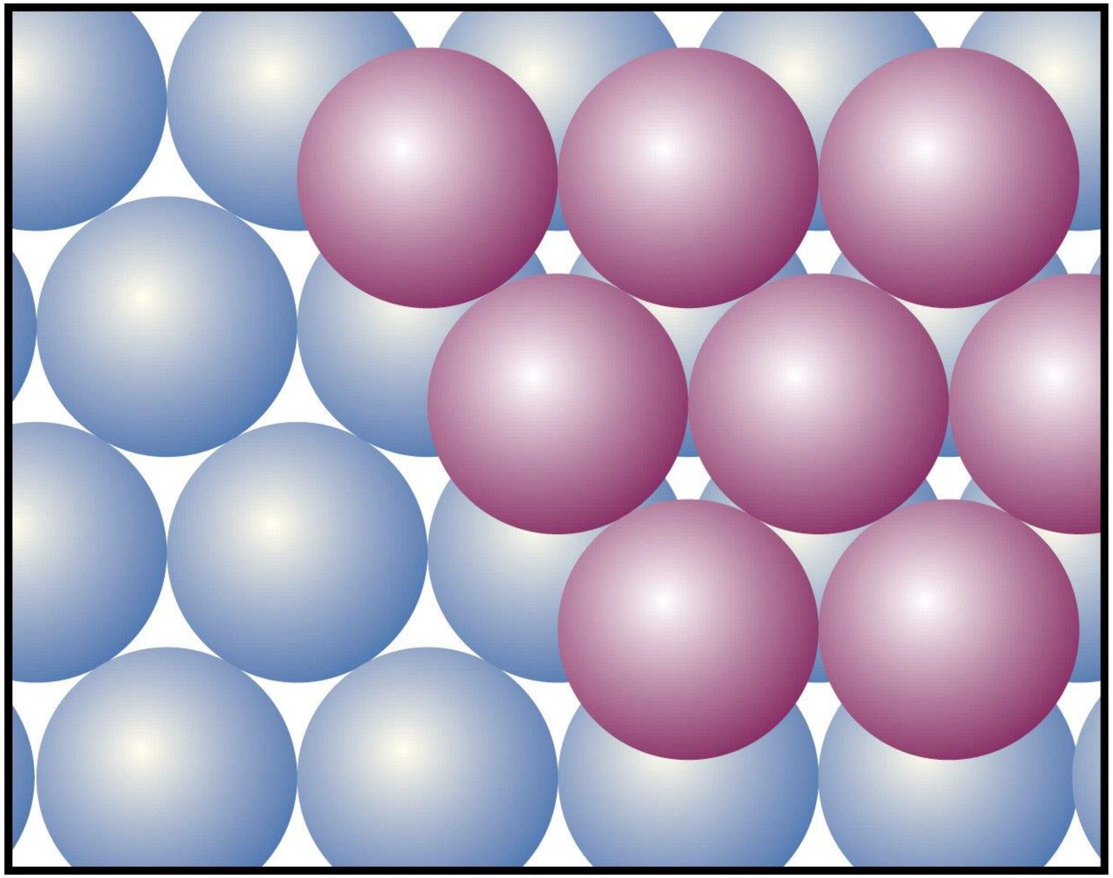

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hcp fcc

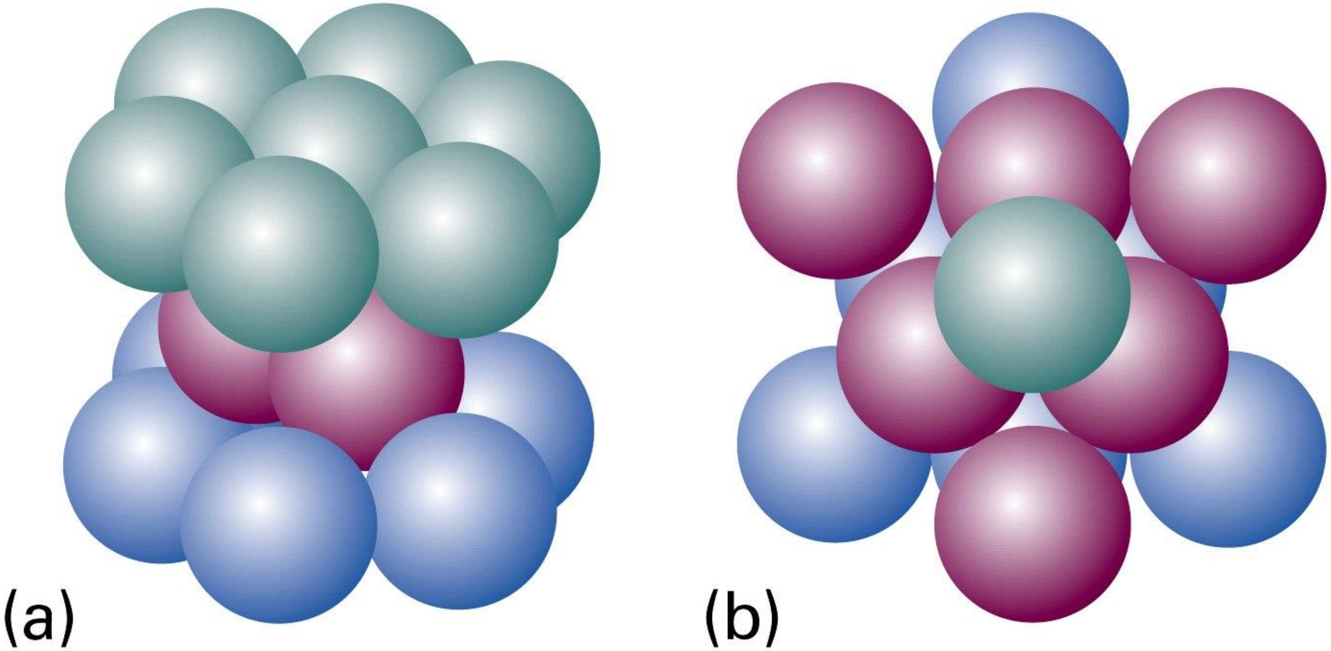

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Table 20.2 The crystal structures of some elements

Structure	Element
hcp*	Be, Cd, Co, He, Mg, Sc, Ti, Zn
fcc* (ccp, cubic F)	Ag, Al, Ar, Au, Ca, Cu, Kr, Ne, Ni, Pd, Pb, Pt, Rh, Rn, Sr, Xe
bcc (cubic I)	Ba, Cs, Cr, Fe, K, Li, Mn, Mo, Rb, Na, Ta, W, V
cubic P	Po

* Close-packed structures.

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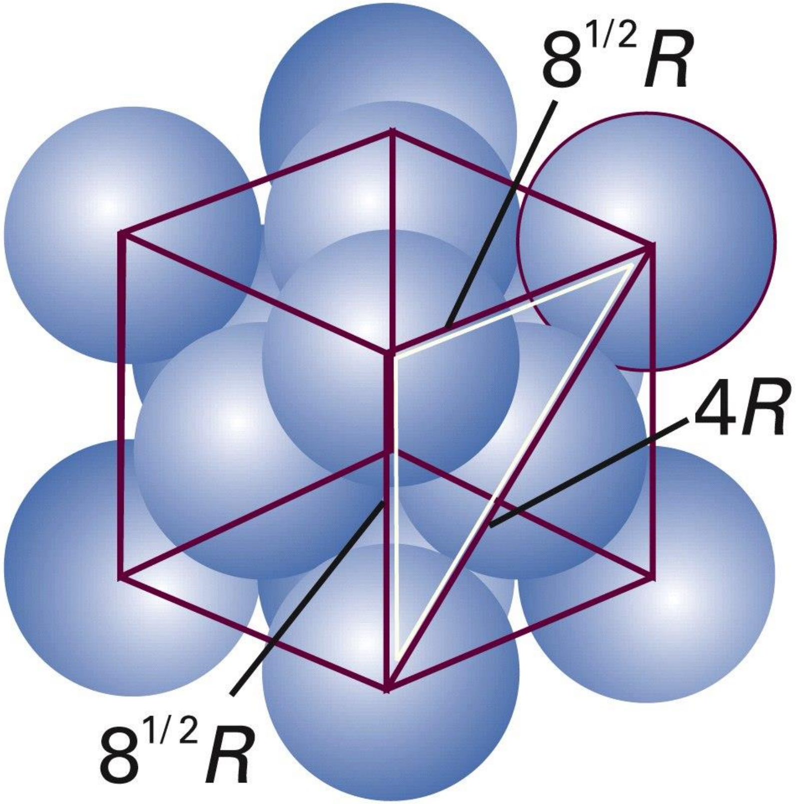

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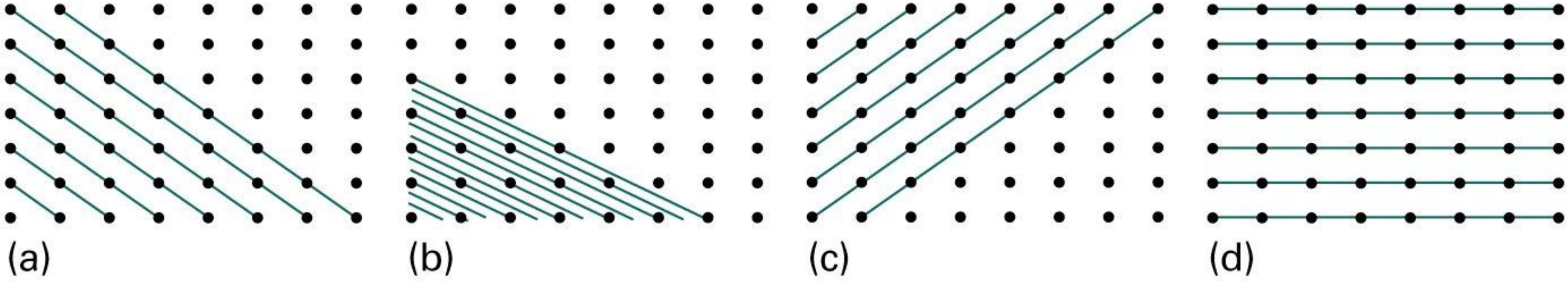
Crystal planes
Miller index



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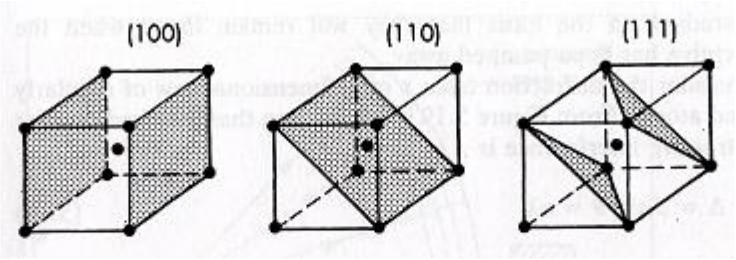

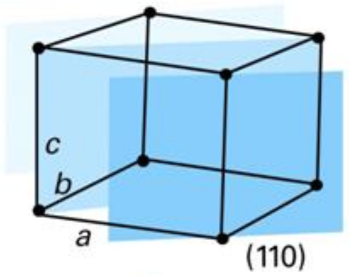

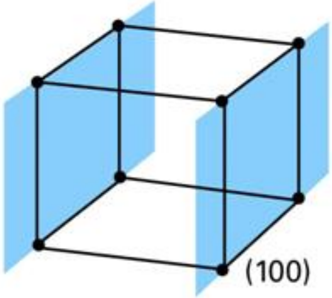

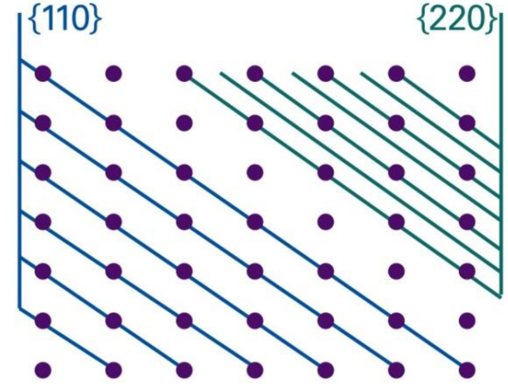

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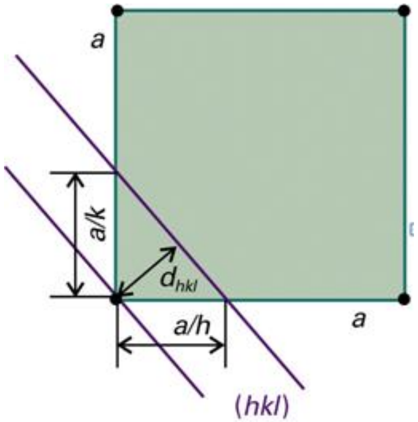
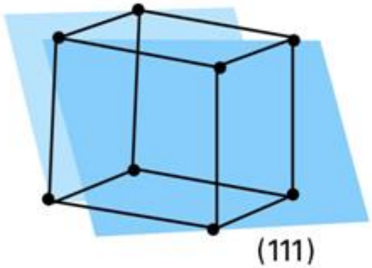
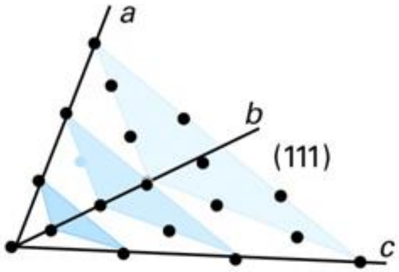




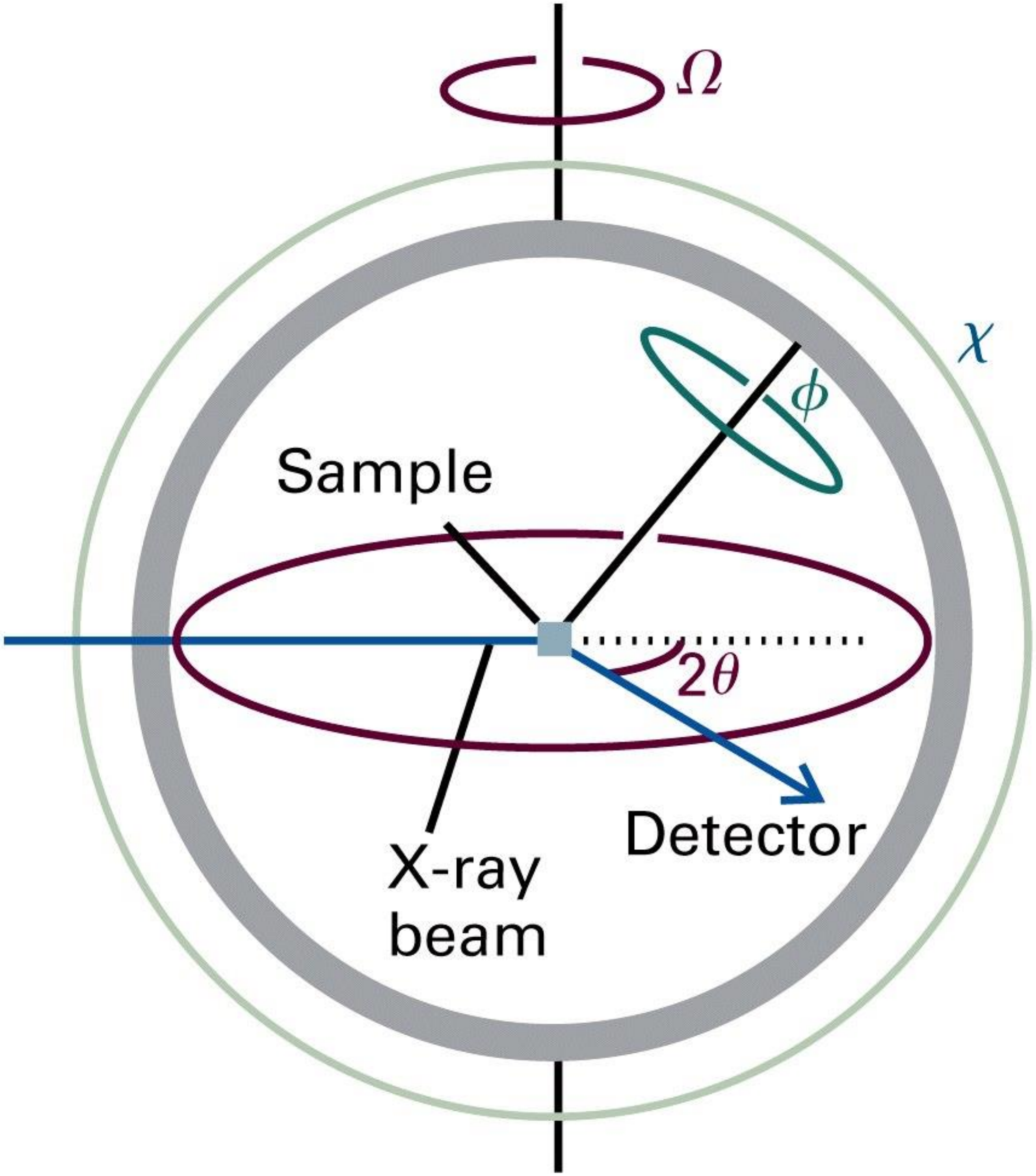


$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2} \quad \text{or} \quad d_{hkl} = \frac{a}{(h^2 + k^2 + l^2)^{1/2}}$$

; cubic

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

; orthorhombic



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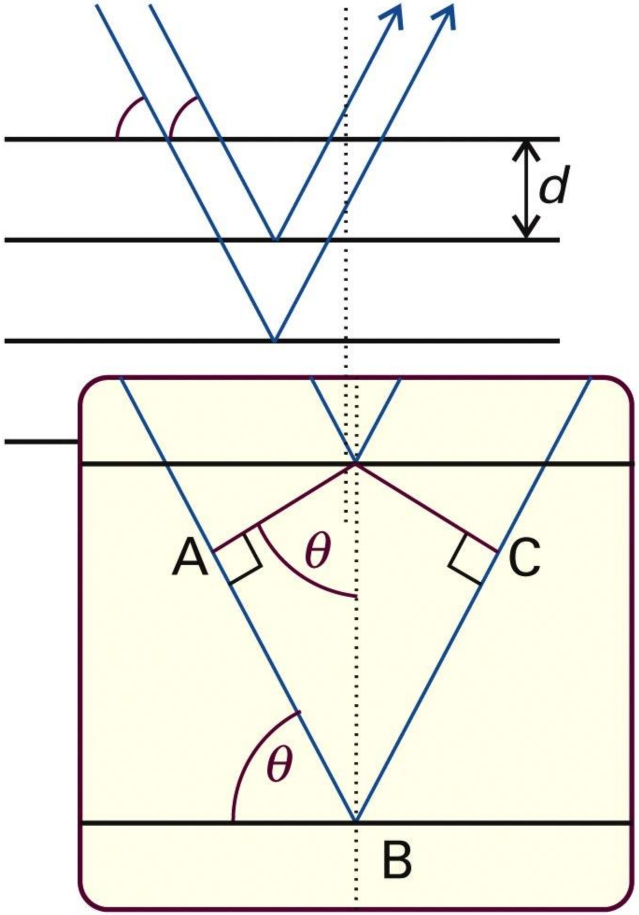
Bragg reflection



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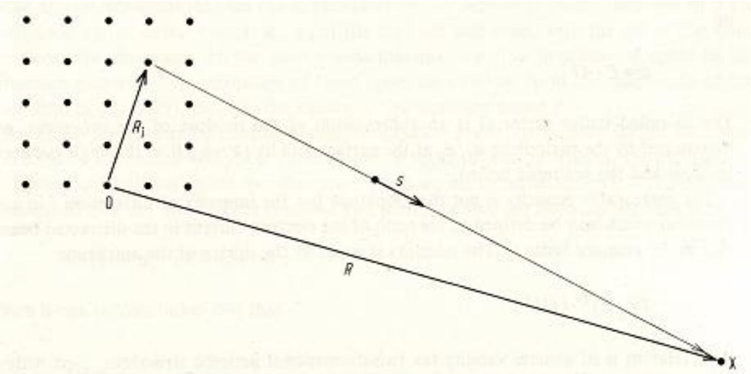
Kinematic theory of x-ray diffraction



.21. Scattering at the points of a lattice. X = point of observation.

- Incident wave ψ_0 is a plane wave with
  $\mathbf{k_0} = \lambda / 2\pi\, \mathbf{u_0}$
- Take one lattice point as the origin O.
- In diffraction the relative phase difference matters
- Incident wave at O is ψ_0
- Incident wave at $\boldsymbol{R_j}$)
- is $\psi_0 \exp(\mathbf{k_0} \cdot \boldsymbol{R_j})$
- Scattered wave from j-th lattice point at the detector is

$\boldsymbol{R_j} = l\, \boldsymbol{a_1} + m\, \boldsymbol{a_2}, + n\, \boldsymbol{a_3}$
(l,m,n are integers)

$$\psi_j = \left(\psi_0 \cdot \frac{e^{i\boldsymbol{k}\cdot\boldsymbol{R}}}{R}\right) \cdot f_j(\boldsymbol{k}_0, \boldsymbol{k})\, e^{i(\boldsymbol{k}-\boldsymbol{k}_0)\cdot\boldsymbol{R}_j}$$

where $f_j(\mathbf{k_0}, \mathbf{k})$ = atomic scattering factor

- Scattered waves from all the lattice points at the detector are $\psi = \Sigma_j\, \psi_j$ and the detected intensity is $I = |\psi|^2$.

- Diffraction occurs when the scattered waves from all the lattice points are in phase, i.e., $\Delta\mathbf{k} \cdot \boldsymbol{R_j} = \mathbf{0}$. This condition is satisfied when
- $\Delta\mathbf{k} = \boldsymbol{G} = l'\, \boldsymbol{b_1} + m'\, \boldsymbol{b_2}, + n'\, \boldsymbol{b_3}$, where l',m',n' are integers, and
  $\boldsymbol{b_1} = 2\pi\, \boldsymbol{a_2} \times \boldsymbol{a_3} / \boldsymbol{a_1} \cdot (\boldsymbol{a_2} \times \boldsymbol{a_3})$,
  $\boldsymbol{b_2} = 2\pi\, \boldsymbol{a_3} \times \boldsymbol{a_1} / \boldsymbol{a_2} \cdot (\boldsymbol{a_3} \times \boldsymbol{a_1})$, and
  $\boldsymbol{b_3} = 2\pi\, \boldsymbol{a_1} \times \boldsymbol{a_2} / \boldsymbol{a_3} \cdot (\boldsymbol{a_1} \times \boldsymbol{a_2})$.
- $\boldsymbol{b_1}$, $\boldsymbol{b_2}$, and $\boldsymbol{b_3}$,defines another lattice called reciprocal lattice of the real lattice.

Reciprocal Lattice Vectors

To proceed further with the Fourier analysis of the electron concentration we must find the vectors **G** of the Fourier sum $\Sigma n_{\mathbf{G}} \exp(i\mathbf{G} \cdot \mathbf{r})$ as in (9). There is a powerful, somewhat abstract procedure for doing this. The procedure forms the theoretical basis for much of solid state physics, where Fourier analysis is the order of the day.

We construct the axis vectors $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$ of the reciprocal lattice:

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3} \; ; \quad \mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3} \; ; \quad \mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3} \; . \tag{13}$$

The factors 2π are not used by crystallographers but are convenient in solid state physics.

If $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ are primitive vectors of the crystal lattice, then $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$ are primitive vectors of the reciprocal lattice. Each vector defined by (13) is orthogonal to two axis vectors of the crystal lattice. Thus $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$ have the property

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij} \; , \tag{14}$$

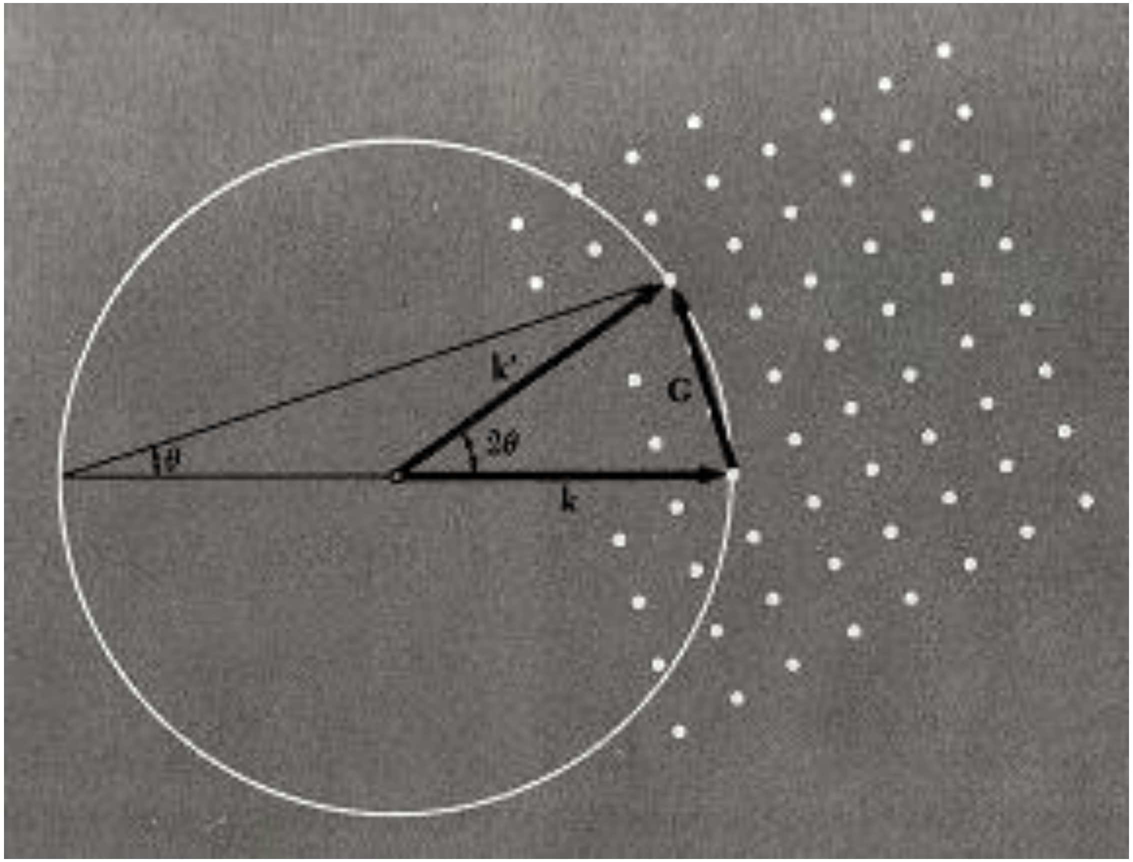
where $\delta_{ij} = 1$ if $i = j$ and $\delta_{ij} = 0$ if $i \neq j$.

Points in the reciprocal lattice are mapped by the set of vectors

$$\mathbf{G} = v_1\mathbf{b}_1 + v_2\mathbf{b}_2 + v_3\mathbf{b}_3 \; , \tag{15}$$

where v_1, v_2, v_3 are integers. A vector **G** of this form is a **reciprocal lattice vector**.

Ewald construction



- Reciprocal lattice of fcc crystal
- Brillouin zone in k-space

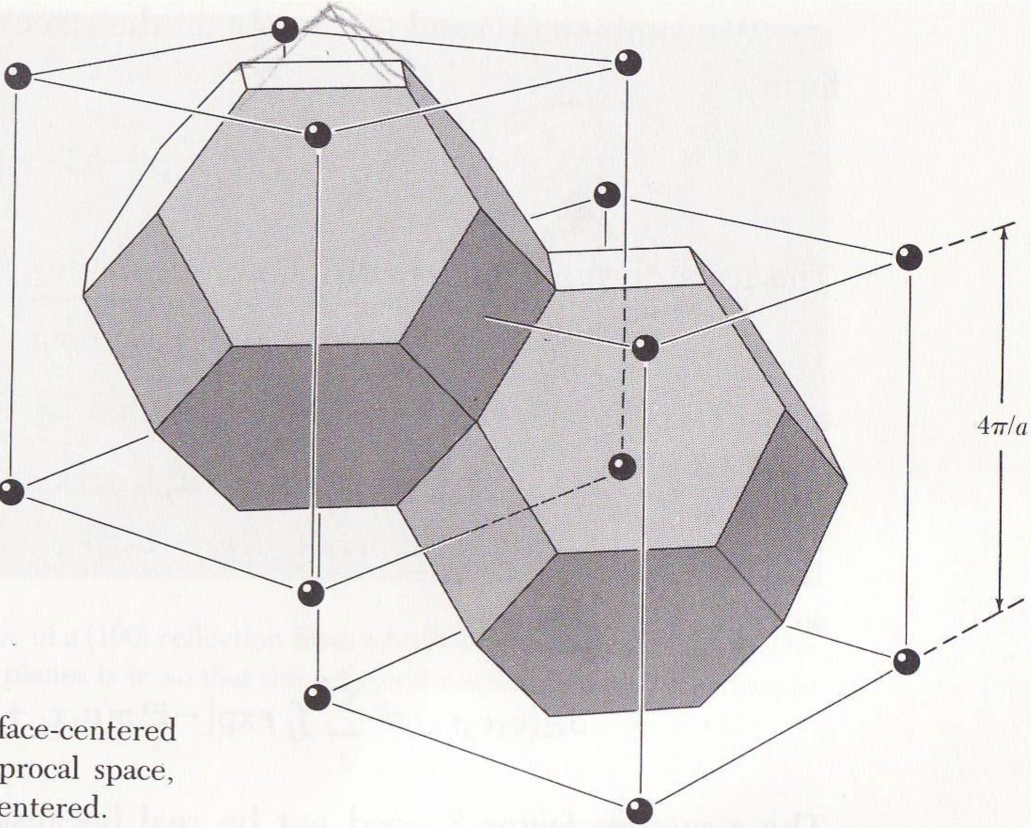


Figure 15 Brillouin zones of the face-centered cubic lattice. The cells are in reciprocal space, and the reciprocal lattice is body centered.

Five 2D Bravais lattice

Cubic
Rectangular
Centered rectangular
Hexagonal
Oblique

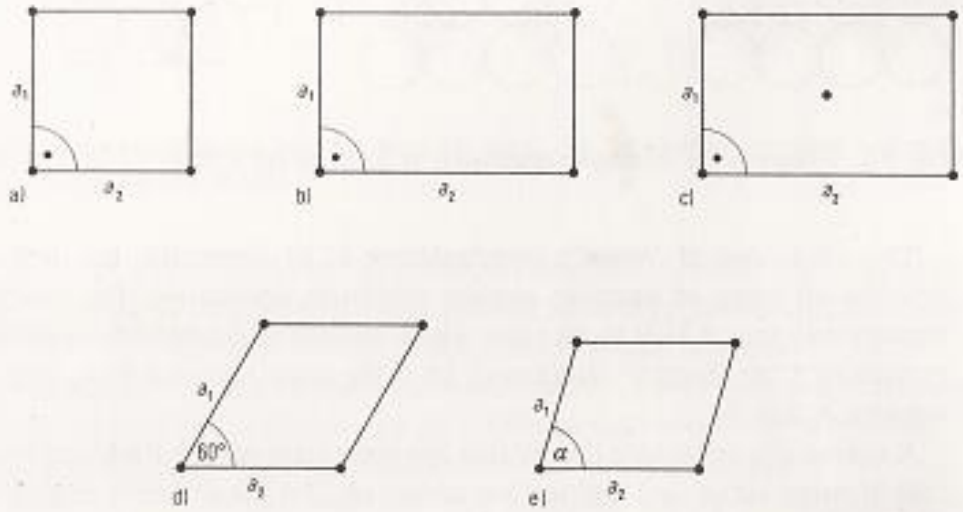
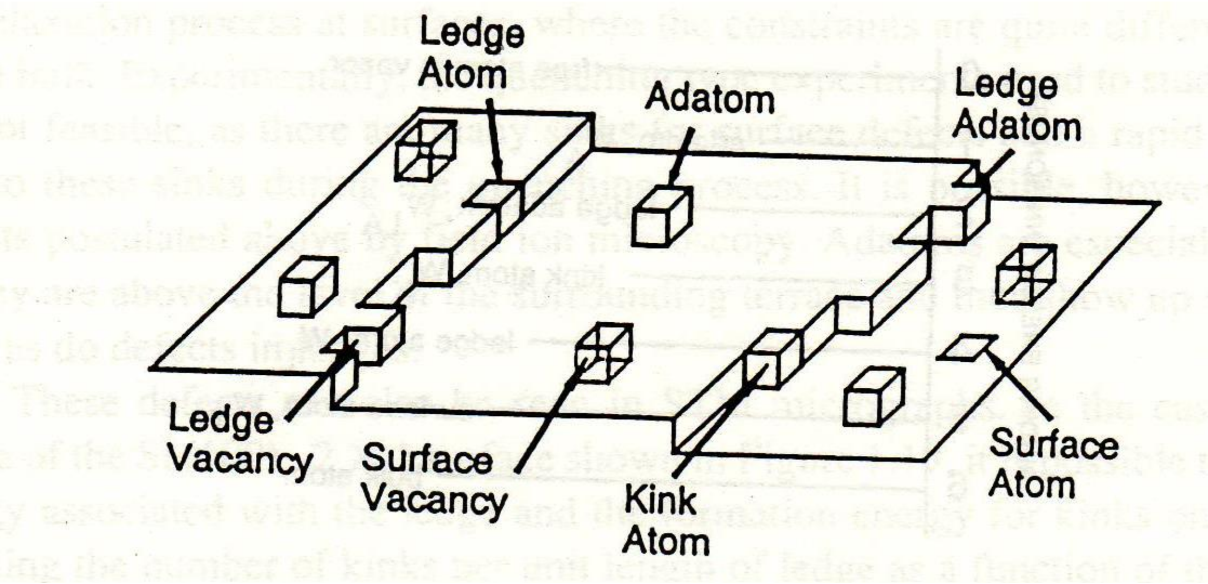


Fig. 9.1. The five types of two-dimensional Bravais lattices. a) square, $a_1 = a_2$, $\alpha = 90°$. b) primitive rectangular, $a_1 \neq a_2$, $\alpha = 90°$. c) centered rectangular, $a_1 \neq a_2$, $\alpha = 90°$. d) hexagonal, $a_1 = a_2$, $\alpha = 60°$. e) oblique, $a_1 \neq a_2$, $\alpha \neq 90°$.

Real surface with structural defects



Overlayer structures

Wood’s notation: simple but limited

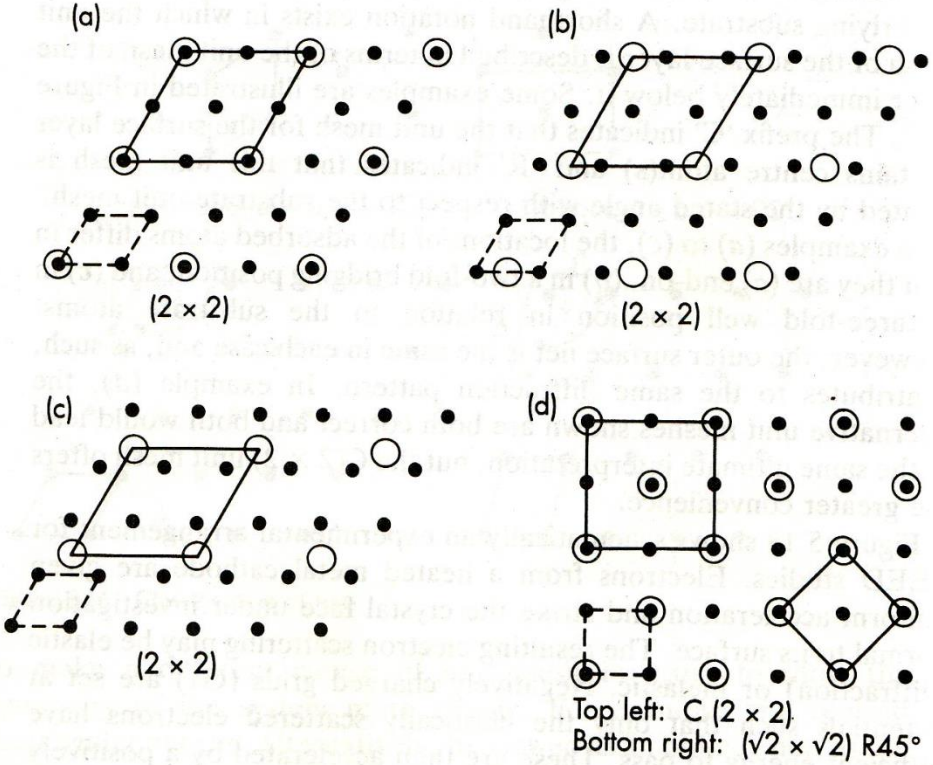
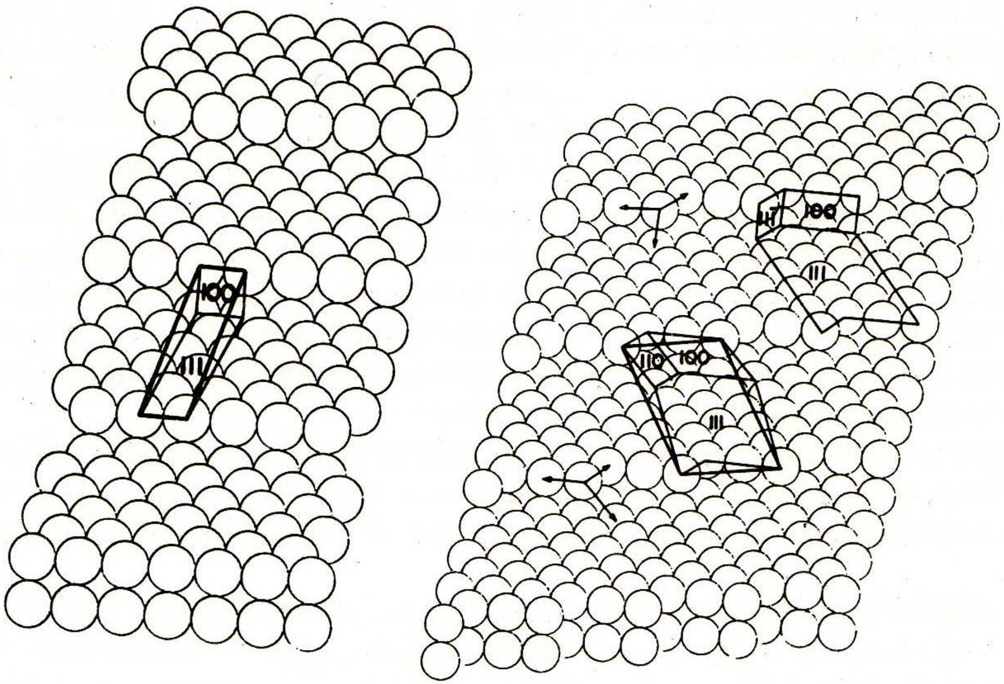


Figure 5.17 Examples and nomenclature of surface layers. Substrate atoms are represented by dots and adatoms by circles. The unit (1×1) mesh of the substrate is shown bottom left

Surfaces with periodic steps and kinks



fcc (755)

fcc (10,8,7)

Fig. 9.4. Structures of fcc (755) and fcc (10,8,7) surfaces. From Van Hove and Somorjai [28].

Matrix notation: can represent any structure

$$b_1 = m_{11} a_1 + m_{12} a_2 \qquad \text{in matrix notation,} \qquad b = \mathfrak{M} \cdot a \qquad \mathfrak{M} = \begin{pmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{pmatrix}$$

$$b_2 = m_{21} a_1 + m_{22} a_1$$

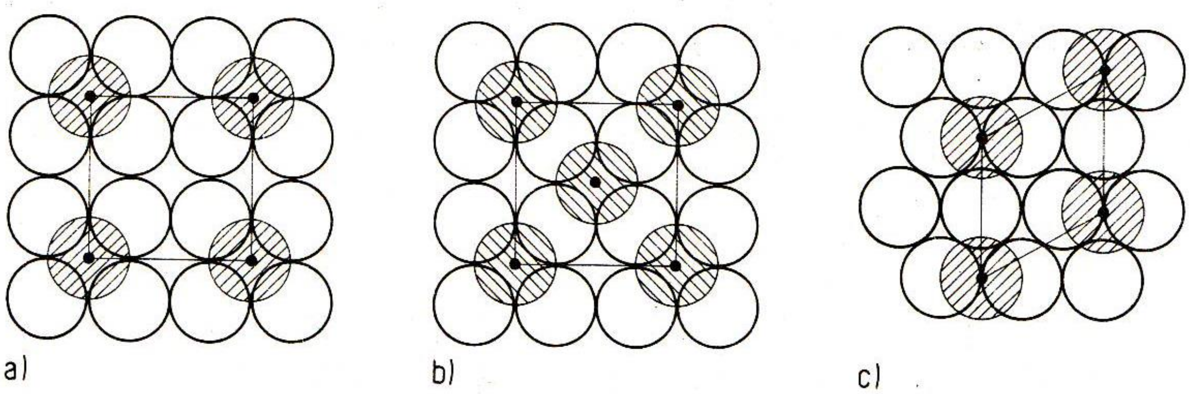
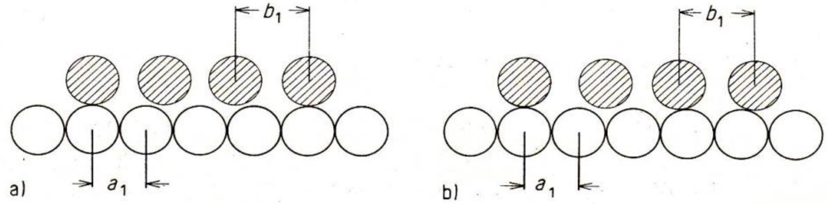


Fig. 9.2. Examples for overlayer structures. a) 2×2, b) c(2×2), c) $\sqrt{3} \times \sqrt{3}$/R 30°.

$$\mathfrak{M} = \begin{pmatrix} 2 & 0 \\ 0 & 2 \end{pmatrix}, \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix} \text{ and } \begin{pmatrix} 1 & 1 \\ -1 & 2 \end{pmatrix}$$

Coherent vs. incoherent structures



$m\, a_1 = n\, b_1$

n/m = rational # : coherent

irrational # : incoherent

2D real vs. reprociprocal lattices

$$b_1 = m_{11} a_1 + m_{12} a_2 \qquad b_1^* = m_{11}^* a_1^* + m_{12}^* a_2^*$$

$$b_2 = m_{21} a_1 + m_{22} a_2 \,. \qquad b_2^* = m_{21}^* a_1^* + m_{22}^* a_2^* \,.$$

$\mathfrak{M}^* = \tilde{\mathfrak{M}}^{-1}$, and so $\mathfrak{M} = \tilde{\mathfrak{M}}^{*-1}$

$$m_{11} = \frac{1}{\det \mathfrak{M}^*} \cdot m_{22}^*$$

$$m_{12} = -\frac{1}{\det \mathfrak{M}^*} \cdot m_{21}^*$$

$$m_{21} = -\frac{1}{\det \mathfrak{M}^*} \cdot m_{12}^*$$

$$m_{22} = \frac{1}{\det \mathfrak{M}^*} \cdot m_{11}^*$$

$$m_{11} = \frac{1}{\det \mathfrak{M}^*} \cdot m_{22}^*$$

$$m_{12} = -\frac{1}{\det \mathfrak{M}^*} \cdot m_{21}^*$$

$$m_{21} = -\frac{1}{\det \mathfrak{M}^*} \cdot m_{12}^*$$

$$m_{22} = \frac{1}{\det \mathfrak{M}^*} \cdot m_{11}^*$$

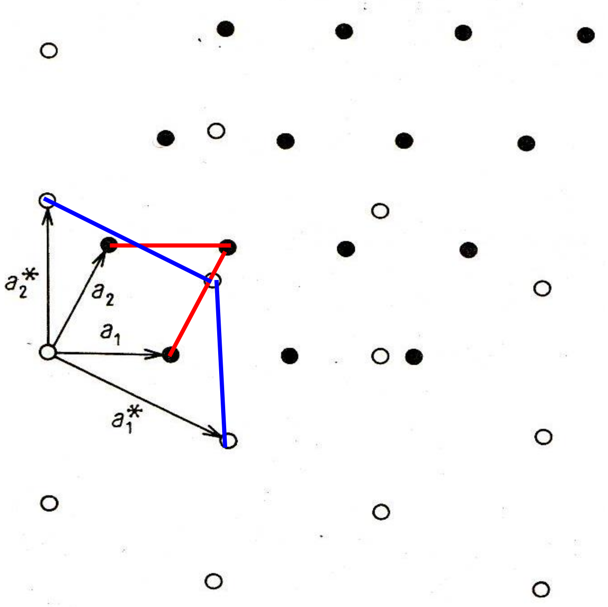


Fig. 9.11. A two-dimensional real lattice, described by a_1, a_2 (dark circles), and its reciprocal lattice a_1^*, a_2^* (open circles).

Diffraction pattern

$$\frac{1}{d^2_{h'k'}}=\frac{h'^2}{b_1^2\sin^2\gamma}+\frac{k'^2}{b_2^2\sin^2\gamma}-\frac{2h'k'\cos\gamma}{b_1b_2\sin^2\gamma} \tag{9.5}$$

where γ denotes the angle between the axes of the unit cell whose base vectors have lengths b_1 and b_2. If the unit cell is rectangular ($\gamma=90°$) eq. (9.5) simplifies to

$$\frac{1}{d^2_{h'k'}}=\left(\frac{h'}{b_1}\right)^2+\left(\frac{k'}{b_2}\right)^2 . \tag{9.6}$$

$$n\lambda=d_{h'k'}(\sin\varphi-\sin\varphi_0) .$$

$$\sin\varphi=\frac{n\lambda}{d_{h'k'}}=\frac{n}{d_{h'k'}}\cdot\sqrt{\frac{1.5}{U}}$$

$$\sin\varphi=\frac{1}{d_{hk}}\cdot\sqrt{\frac{1.5}{U}}$$

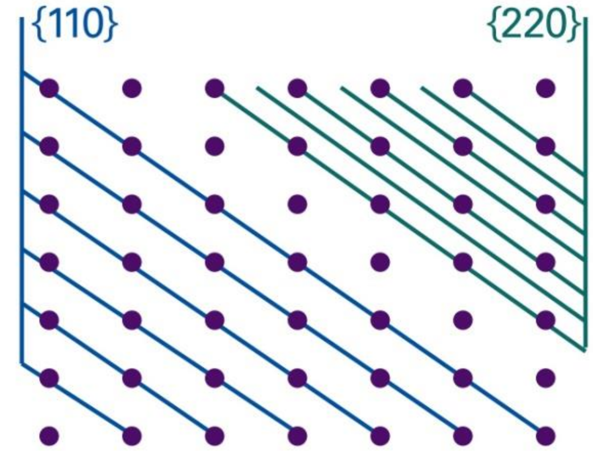


Figure 20-12
Atkins Physical Chemistry, Eighth Edition
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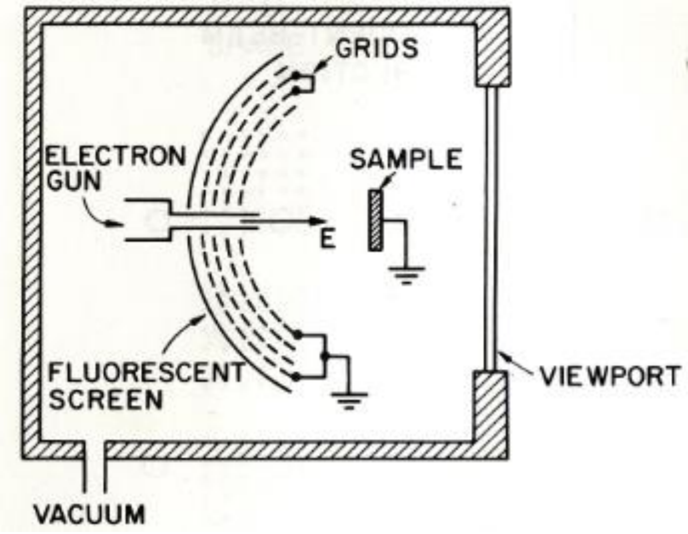
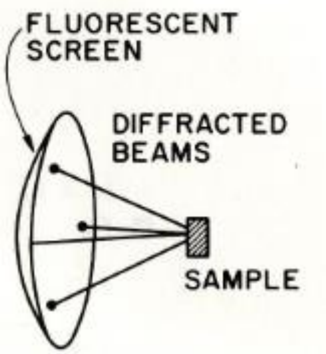
Low energy electron diffraction (LEED):

Why low energy electron used?

- The penetration depth of x-ray is ~ 1µm,
- So x-ray diffraction give structural information of a bulk solid (3D).
- It does not have any surface sensitivity.
- The penetration depth of low energy
- Electron is ≤ 20 Å; a rather good surface sensitivity.
- In any diffraction the employed wavelength λ should ~ d.

- De Broglie wavelength of **e**$^-$ is
- $\lambda = h/p = h/mv = h/(2mE_k)^{1/2}$
- If E_k)= 150 eV, λ =~ 1 Å.
- Since diffraction can be observed in elastic scattering,
- The inelastically scattered electrons have to be removed by setting up an potential barrier (grid assembly).
- The LEED pattern is usually recorded by taking a picture.





Instrument

(2x1) Cu(110)-O

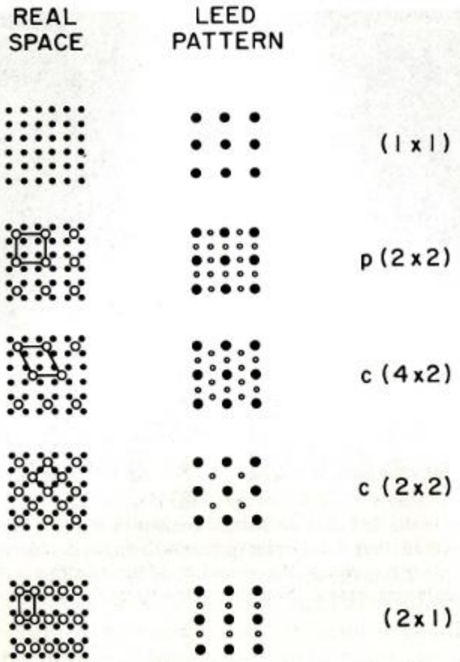


Figure 7.8 Overlayers on the (100) surface of a cubic crystal and the associated LEED patterns in reciprocal space. The notation for the various patterns is indicated on the right. [From Estrup and McRae, 1971.]

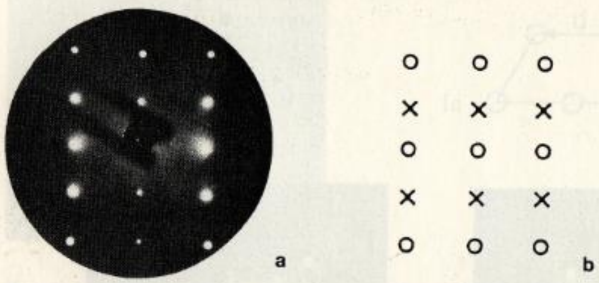
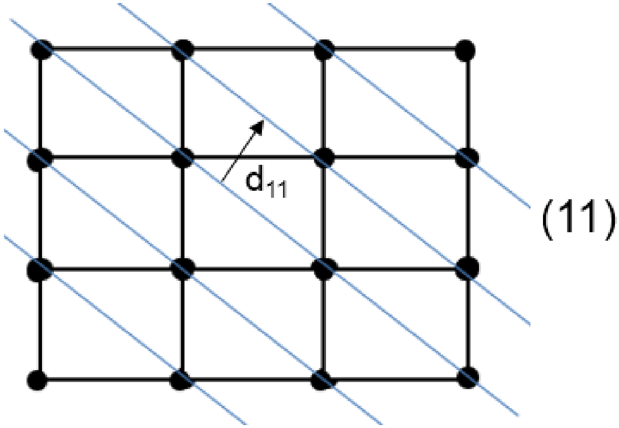
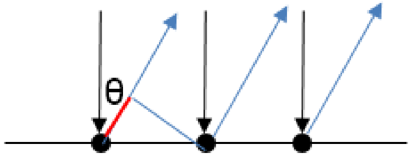


Fig. 4.8a,b. LEED pattern obtained after adsorption of atomic oxygen at low coverage on Cu(110). **(a)** (2×1) superstructure as seen on the phosphorus screen. **(b)** schematic of the (2×1) pattern with substrate spots as circles and half order spots as crosses [4.5]

Diffraction angle





Path difference $\Delta l = d \sin\theta$
Diffraction condition is
$d \sin\theta = n\lambda$; $n = 0,1,2,3 \ldots$