



# Part I Fundamentals

## Electron Theory : Matter Waves

Chap. 3 The Schrödinger Equation

Chap. 4 Solution of the Schrödinger Equation for  
Four Specific Problems

**Chap. 5 Energy Bands in Crystals**

Chap. 6 Electrons in a Crystal



# 5. Energy Bands in Crystals

## 5.1 1-D Zone Schemes

\* For Free electron

$$E = \frac{\hbar^2}{2m} k_x^2 \quad \rightarrow \quad k_x = \text{const.} E^{1/2}.$$

In a crystal

$$P \frac{\sin \alpha a}{\alpha a} + \cos \alpha a \quad \rightarrow \quad \text{If } P = 0, \cos \alpha a = \cos k a$$

$$\cos \alpha a = \cos k_x a \equiv \cos(k_x a + 2\pi n)$$

$$n = 0, \pm 1, \pm 2, \dots$$

$$\alpha a = k_x a + 2\pi n$$

$$\alpha = \sqrt{\frac{2m}{\hbar^2}} E^{1/2}$$

$$\left. \begin{array}{l} \alpha a = k_x a + 2\pi n \\ \alpha = \sqrt{\frac{2m}{\hbar^2}} E^{1/2} \end{array} \right\} k_x + \frac{2\pi}{a} n = \sqrt{\frac{2m}{\hbar^2}} E^{1/2}$$

$E$  is a periodic function of  $k_x$  with the periodicity of  $2\pi/a$



Figure 5.1. Electron energy  $E$  versus the wave vector  $k_x$  for free electrons.



If an electron propagates in a periodic potential we always observe discontinuities of the energies when  $\cos k_x a$  has a maximum or a minimum from Fig.4.11

$$k_x a = n\pi, \quad n = \pm 1, \pm 2, \pm 3, \dots,$$

$$k_x = \frac{\pi}{a} n$$

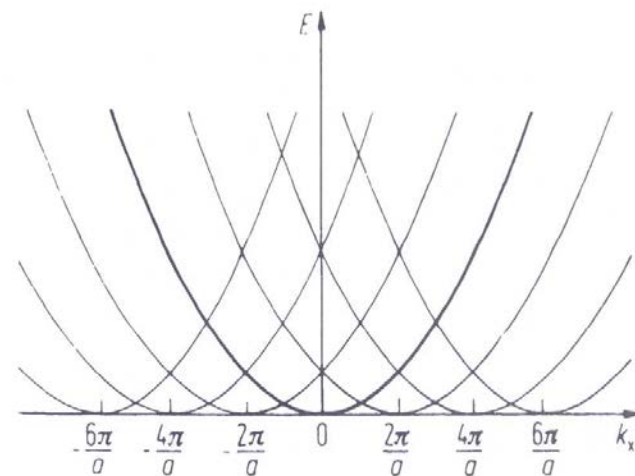


Figure 5.2. Periodic repetition of Fig. 5.1 at the points  $k_x = n \cdot 2\pi/a$ . The figure depicts a family of free electron parabolas having a periodicity of  $\pm 2\pi/a$ .

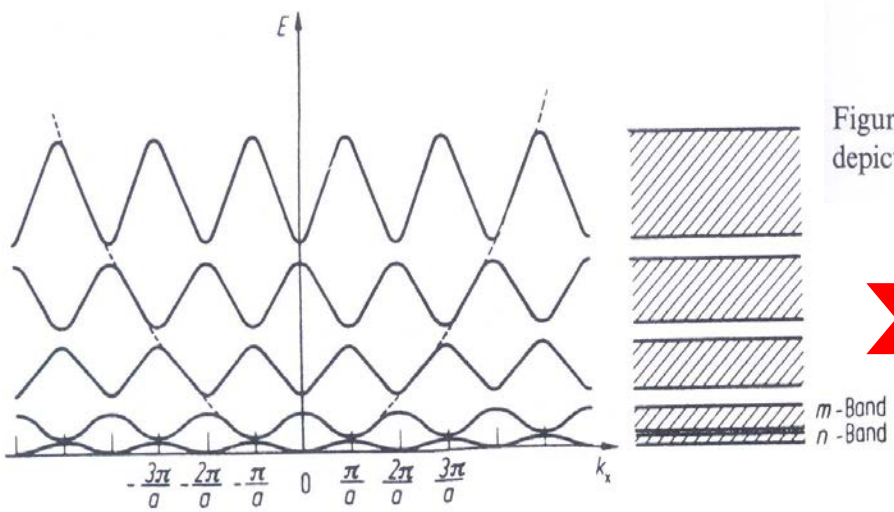


Figure 5.3. Periodic zone scheme.



This discontinuities of the energies come from the fact that periodic potential is not perfectly zero. In other words, it is not a perfect free electron.



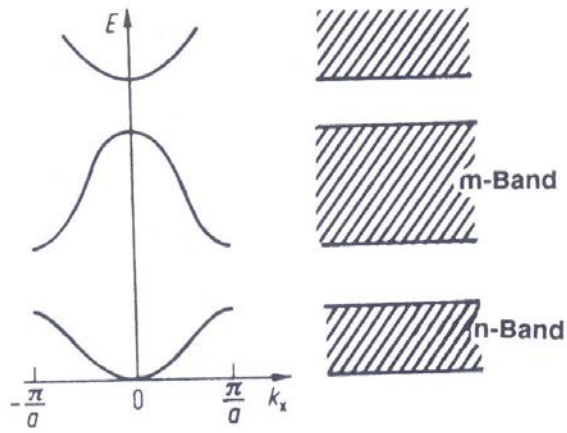


Figure 5.4. Reduced zone scheme. (This is a section of Fig. 5.3 between  $-\pi/a$  and  $+\pi/a$ .)

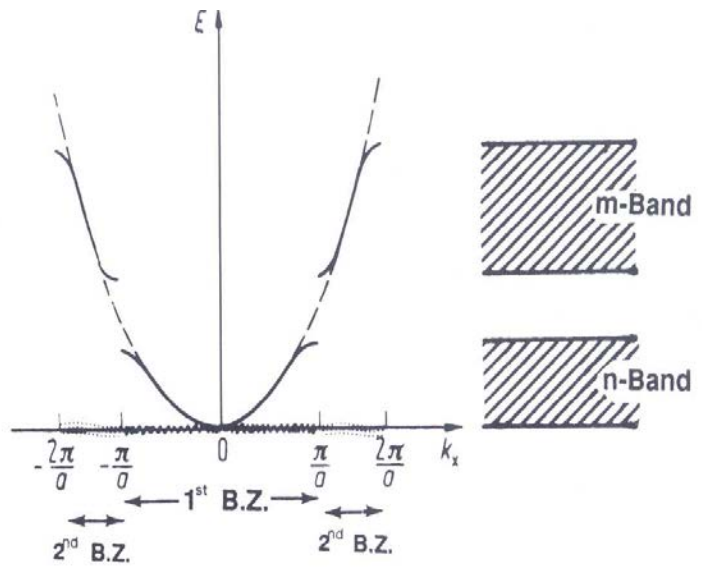


Figure 5.5. Extended zone scheme. The first and second Brillouin zones (BZ) are shown, see Section 5.2.

We call the allowed bands, for the time being, the n-band or the m-band, and so forth. In later sections and particularly in semiconductor physics, we will call one of these bands the **valence band** and the next higher one the **conduction band**.





### Free electron bands (see Fig 5.6)

$$E = \frac{\hbar^2}{2m} \left( k_x^2 + n \frac{2\pi}{a} \right)^2 \quad n = 0, \pm 1, \pm 2, \dots$$

$n = 0$  yields  $E = \frac{\hbar^2}{2m} k_x^2$  (parabola with 0 as origin);

$n = -1$  yields  $E = \frac{\hbar^2}{2m} \left( k_x - \frac{2\pi}{a} \right)^2$  (parabola with  $\frac{2\pi}{a}$  as origin);

specifically, for  $k_x = 0$  follows  $E = 4 \frac{\pi^2 \hbar^2}{2ma^2}$ ;

and for  $k_x = \frac{\pi}{a}$  follows  $E = 1 \frac{\pi^2 \hbar^2}{2ma^2}$ .

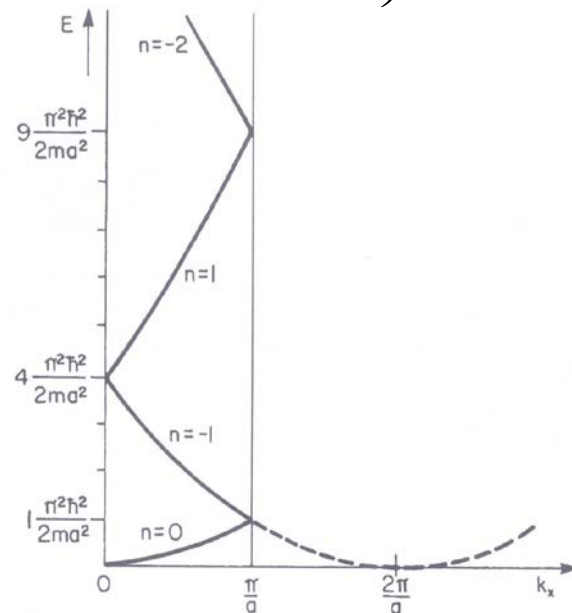


Figure 5.6. “Free electron bands” plotted in the reduced zone scheme (cubic primitive crystal structure). Compare this figure with the central portion of Fig. 5.2, that is, with the region from zero to  $\pi/a$ . Note the sameness of the individual bands.



# 5. Energy Bands in Crystals

## 5.2 One- and Two-Dimensional Brillouin Zones

### 1-d Brillouin Zone

The first Brillouin Zone (BZ) :

$$\pi/a \leq k_x \leq \pi/a : \text{n-Band}$$

The second Brillouin Zone (BZ):

$$\pi/a \leq k_x \leq 2\pi/a, -\pi/a \leq k_x \leq -2\pi/a : \text{m-band}$$

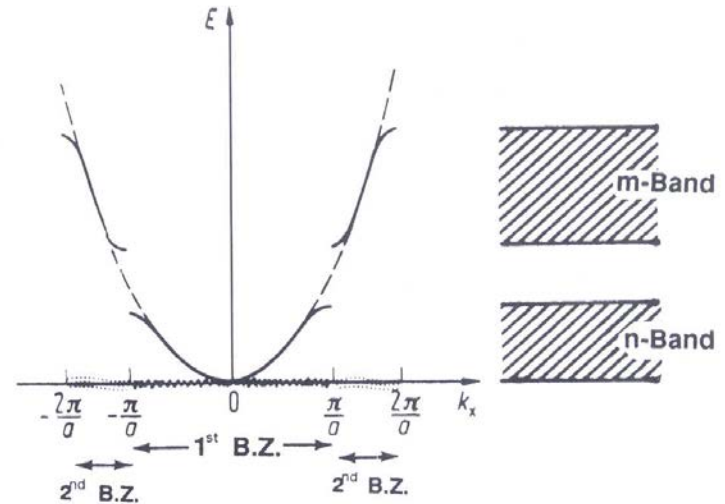


Figure 5.5. Extended zone scheme. The first and second Brillouin zones (BZ) are shown, see Section 5.2.

- Individual branches in an extended zone

scheme (Fig. 5.5) can be shifted by  $2\pi/a$  to left or to right.

Shift the branches of 2<sup>nd</sup> BZ to the positive side of  $E-k_x$  diagram by  $2\pi/a$  to the left, and likewise the left band by  $2\pi/a$  to the right → The result is shown in Fig. 5.4 (a reduced zone scheme)

- The same can be done in 3<sup>rd</sup> BZ and all BZ (because of the  $2\pi/a$  periodicity) →

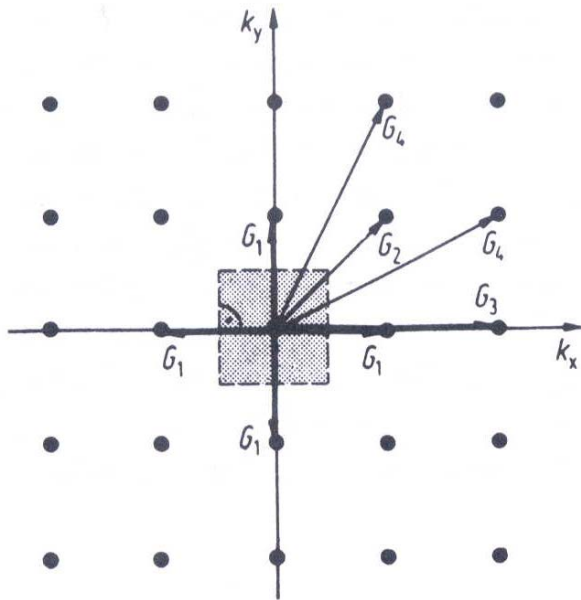
relevant information of all BZ can be contained in the 1<sup>st</sup> BZ (a reduced zone scheme)



# 5. Energy Bands in Crystals

## 5.2 One-and Two-Dimensional Brillouin Zones

### 2-d Brillouin Zone



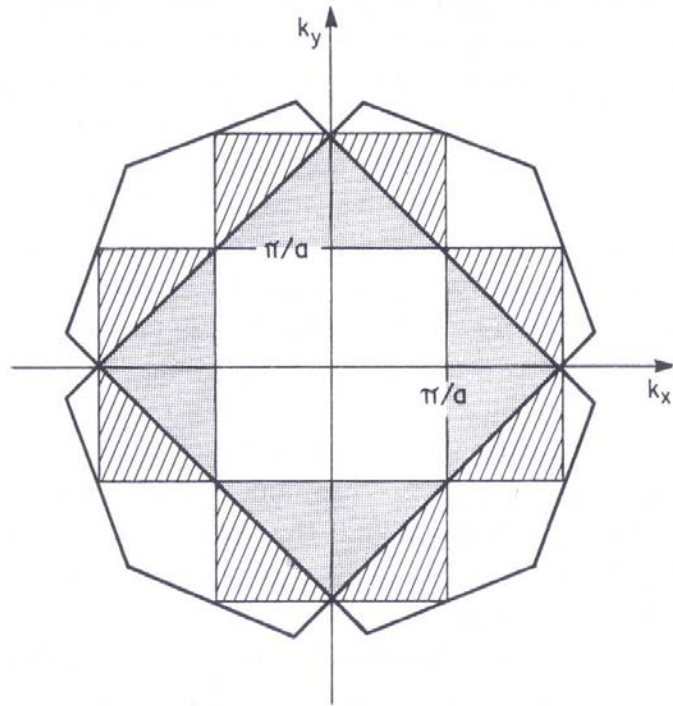
Between the boundaries  $-\pi/a$  and  $\pi/a$ , corresponds to the first electron band, which we arbitrarily labeled as n-band. This region in  $k$ -space between  $-\pi/a$  and  $\pi/a$  is called **the first Brillouin zone (BZ)**. Accordingly the area between  $\pi/a$  and  $2\pi/a$ , and also between  $-\pi/a$  and  $-2\pi/a$ , which corresponds to the m-band, is called **the second Brillouin zone**.

Figure 5.7. Four shortest lattice vectors in a  $k_x - k_y$  coordinate system and the first Brillouin zone in a two-dimensional reciprocal lattice. (Cubic primitive crystal structure.)

# 5. Energy Bands in Crystals

## 5.2 One-and Two-Dimensional Brillouin Zones

### 2-d Brillouin Zone



Description for the movement of an electron in the potential of 2-d lattice

- Wave vector  $k = (k_x, k_y)$  : 2-d reciprocal lattice (Fig 5.7)
- A 2-d field of allowed energy regions which correspond to the allowed energy band  $\rightarrow$  2-d BZ
- 1st zone in 2-d: the area enclosed by four "Bragg planes" having four shortest lattice vectors,  $G_1$ : bisectors on the lattice vectors
- For the following zone, construct the bisectors of the next shortest lattice vectors,  $G_2, G_3, \dots$
- For the zone of higher order the extended limiting lines of the zones of lower order are used as additional limiting lines.

Figure 5.8. The first four Brillouin zones of a two-dimensional, cubic primitive reciprocal lattice.





## “Usefulness of BZ”

- Energy bands of solids (discussed in later section)
- The behavior of electrons which travel in a specific direction in reciprocal space

Example: in 2-d lattice, an electron travels at 45° to  $k_x$ -axis, then the boundary

of the BZ is reached for  $k_{crit} = \frac{\pi}{a}\sqrt{2}$

this yields a maximal attainable energy of  $E_{max} = \frac{\pi^2 \hbar^2}{a^2 m}$

If the boundary of a BZ is reached at  $k_{crit} = \frac{\pi}{a}$

the largest energy of electrons moving parallel to  $k_x$  or  $k_y$  axis  $E_{max} = \frac{1}{2} \left( \frac{\pi^2 \hbar^2}{a^2 m} \right)$

- Once the maximal energy has been reached, the electron waves (those of the incident and the Bragg-reflected electrons) form standing waves (or equivalently, the electrons are reflected back into the BZ.)



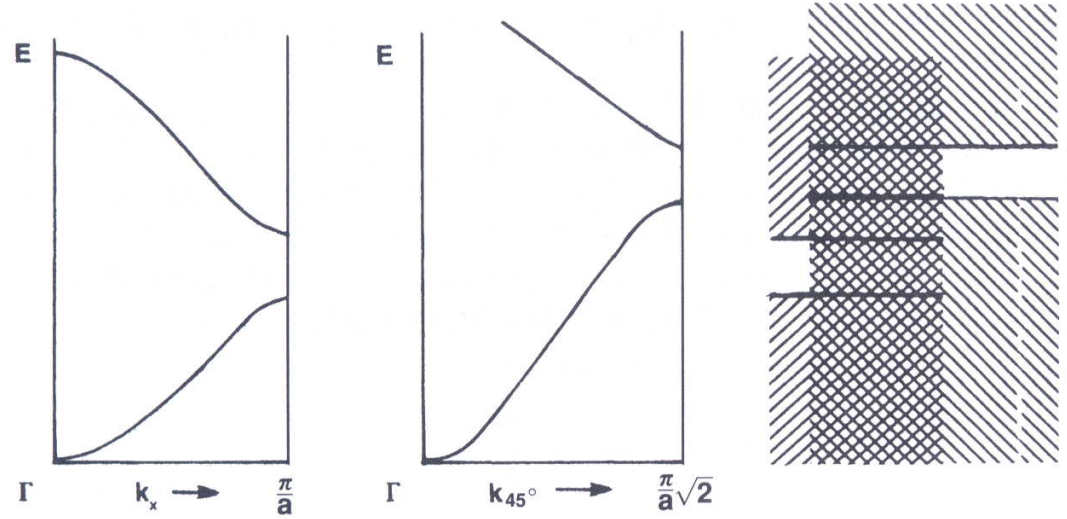


Figure 5.9. Overlapping of allowed energy bands.

In previous pages we have seen an electron **traveling in a specific direction**. When we consider energies with all directions, **overlapping of allowed energy bands** occur

**(Bragg Reflection)**

$$2a \sin \theta = n\lambda, \quad n = 1, 2, 3, \dots$$

$$2a \sin \theta = n \frac{2\pi}{k}$$

$$k_{\text{crit}} = n \frac{\pi}{a \sin \theta}$$

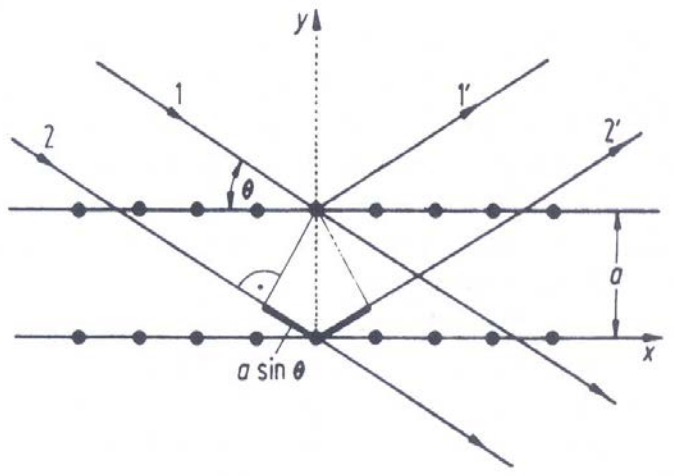


Figure 5.10. Bragg reflection of an electron wave in a lattice. The angle of incidence is  $\theta$ .

At  $k_{\text{crit}}$ , the transmission of an electron beam through the lattice is prevented, and then the incident and the Bragg-reflected electron wave form a standing wave.



# 5. Energy Bands in Crystals

## 5.3-4 3-D Brillouin Zone and Wigner-Seitz Cells

Crystals have symmetrical properties. Therefore, a crystal can be described as an accumulation of “unit cells”. There are two kinds of unit cell, “primitive unit cell” means a smallest possible cell, and “conventional unit cell” is a nonprimitive unit cell having the advantage that the symmetry can be better recognized,

➔ **Wigner-Seitz Cell** is a special type of primitive unit cell that shows the cubic symmetry of the cubic cells

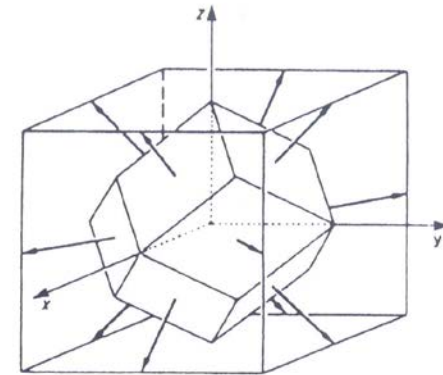
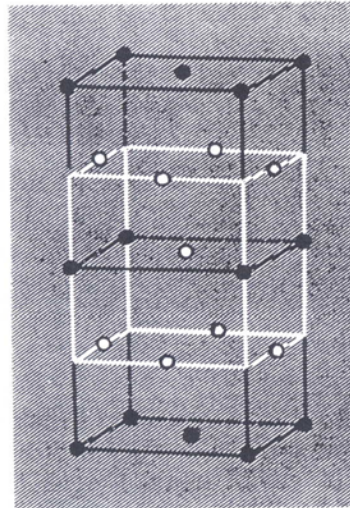
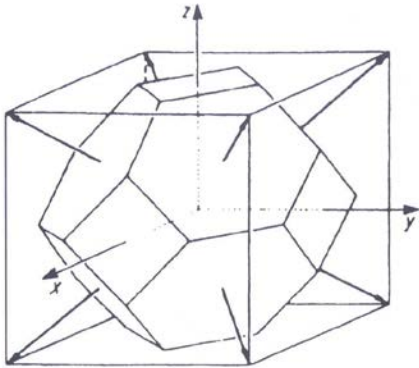


Figure 5.11. Wigner–Seitz cell for the body-centered cubic (bcc) structure.

Figure 5.13. Wigner–Seitz cell for the fcc structure. It is constructed from the white cell which is marked in Fig. 5.12.

W-S cell construction: bisects the vectors from a given atom to its nearest neighbors and place a plane perpendicular to these vectors at the bisecting points.

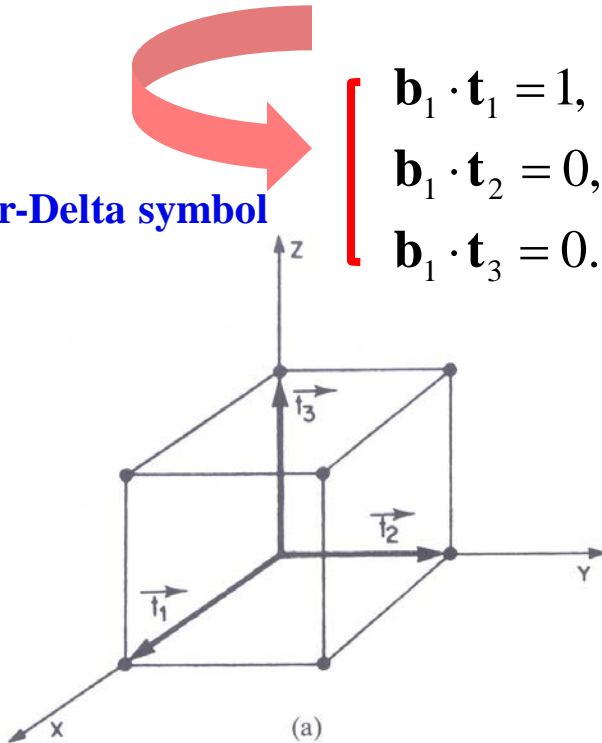
Figure 5.12. Conventional unit cell of the fcc structure. In the cell which is marked black, the atoms are situated on the corners and faces of the cubes. In the white cell, the atoms are at the centers of the edges and the center of the cell.

# 5. Energy Bands in Crystals

## 5.5 Translation Vectors and the Reciprocal Lattice

**Translation vectors**  $\mathbf{R} = n_1 \mathbf{t}_1 + n_2 \mathbf{t}_2 + n_3 \mathbf{t}_3$ ,  $\mathbf{t}_1, \mathbf{t}_2, \mathbf{t}_3$  : Primitive (or fundamental) vectors  
**vectors**  $\mathbf{G} = 2\pi(h_1 \mathbf{b}_1 + h_2 \mathbf{b}_2 + h_3 \mathbf{b}_3)$ ,  $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$  : reciprocal lattice vectors

Kronecker-Delta symbol



$\mathbf{b}_n \cdot \mathbf{t}_m = \delta_{nm},$   
 where  $\delta_{nm} = 1$  for  $n = m$  and  $\delta_{nm} = 0$  for  $n \neq m$

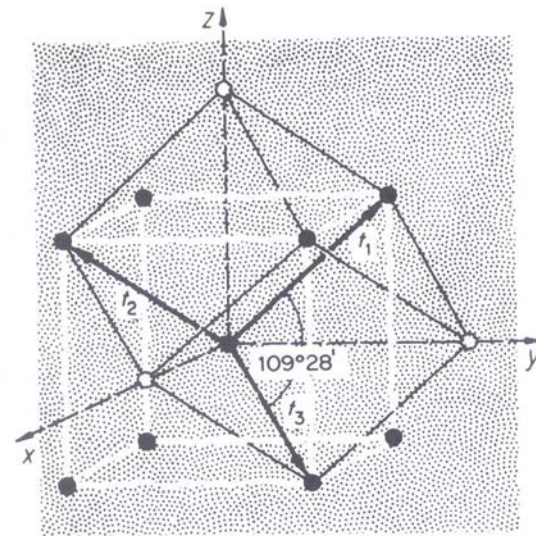
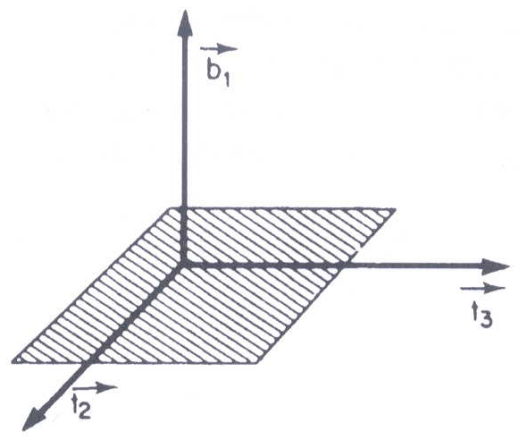


Figure 5.14. (a) Fundamental lattice vectors  $\mathbf{t}_1, \mathbf{t}_2, \mathbf{t}_3$  in a cubic primitive lattice. (b) Fundamental lattice vectors in a conventional (white) and primitive, noncubic unit cell (black) of a bcc lattice. The axes of the primitive (noncubic) unit cell form angles of  $109^\circ 28'$ .



$$\mathbf{b}_1 = \text{const.} \cdot \mathbf{t}_2 \times \mathbf{t}_3.$$

$$\mathbf{b}_1 \cdot \mathbf{t}_1 = \text{const.} \cdot \mathbf{t}_1 \cdot \mathbf{t}_2 \times \mathbf{t}_3 = 1.$$

$$\text{const.} = \frac{1}{\mathbf{t}_1 \cdot \mathbf{t}_2 \times \mathbf{t}_3} \quad \therefore \mathbf{b}_1 = \frac{\mathbf{t}_2 \times \mathbf{t}_3}{\mathbf{t}_1 \cdot \mathbf{t}_2 \times \mathbf{t}_3}.$$

$$\rightarrow \mathbf{b}_2 = \frac{\mathbf{t}_3 \times \mathbf{t}_1}{\mathbf{t}_1 \cdot \mathbf{t}_2 \times \mathbf{t}_3}, \quad \mathbf{b}_3 = \frac{\mathbf{t}_1 \times \mathbf{t}_2}{\mathbf{t}_1 \cdot \mathbf{t}_2 \times \mathbf{t}_3}.$$

Figure 5.15. Plane formed by  $\mathbf{t}_2$  and  $\mathbf{t}_3$  with perpendicular vector  $\mathbf{b}_1$ .

## Calculation for the reciprocal lattice of a BCC crystal

Real crystal

$a$ : lattice constant,  $\mathbf{t}_1, \mathbf{t}_2, \mathbf{t}_3$ : primitive lattice vectors,

$\mathbf{i}, \mathbf{j}, \mathbf{l}$ : unit vectors in the  $x, y, z$  coordinate system (see Fig. 5.14(b))

$$\mathbf{t}_1 = \frac{a}{2}(-\mathbf{i} + \mathbf{j} + \mathbf{l}),$$

Abbreviated,

$$\mathbf{t}_1 = \frac{a}{2}(\bar{1}11) \quad \mathbf{t}_2 = \frac{a}{2}(1\bar{1}1), \quad \mathbf{t}_3 = \frac{a}{2}(11\bar{1}).$$







$$\mathbf{t}_2 \times \mathbf{t}_3 = \frac{a^2}{4} \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{l} \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{vmatrix} = \frac{a^2}{4} (\mathbf{i} + \mathbf{j} + \mathbf{l} + \mathbf{l} - \mathbf{i} + \mathbf{j}) = \frac{a^2}{4} (2\mathbf{j} + 2\mathbf{l})$$

$$= \frac{a^2}{2} (\mathbf{j} + \mathbf{l})$$

$$\mathbf{t}_1 \cdot \mathbf{t}_2 \times \mathbf{t}_3 = \frac{a^3}{4} (-\mathbf{i} + \mathbf{j} + \mathbf{l}) \cdot (0 + \mathbf{j} + \mathbf{l}) = \frac{a^3}{4} (0 + 1 + 1) = \frac{a^3}{2}$$

$$\mathbf{b}_1 = \frac{\frac{a^2}{2} (\mathbf{j} + \mathbf{l})}{\frac{a^3}{2}} = \frac{1}{a} (\mathbf{j} + \mathbf{l}),$$

$$\mathbf{b}_1 = \frac{1}{a} (011), \quad \mathbf{b}_2 = \frac{1}{a} (101), \quad \mathbf{b}_3 = \frac{1}{a} (110).$$

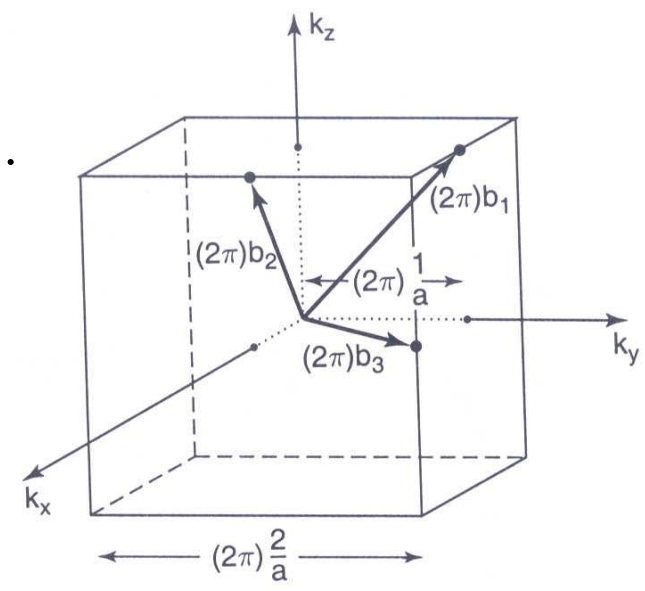


Figure 5.16. Lattice vectors in reciprocal space of a bcc crystal. The primitive vectors in the reciprocal lattice are (because of (5.13)) larger by a factor of  $2\pi$ . The lattice constant of the cube then becomes  $2\pi \cdot 2/a$ .



The end points of the reciprocal lattice vectors of a bcc crystal are at the center of the edges of a cube. This means that **reciprocal lattice of the bcc structure** are identical to the lattice points **in a real lattice of the fcc structure**





# 5. Energy Bands in Crystals

## 5.6 Free Electron Bands for BCC

In Fig 5.17, three important directions

[100] from  $\Gamma$  (origin) to point  $H$ :  $\Delta$

[110] from  $\Gamma$  to  $N$ :  $\Sigma$

[111] from  $\Gamma$  to  $P$ :  $\Lambda$

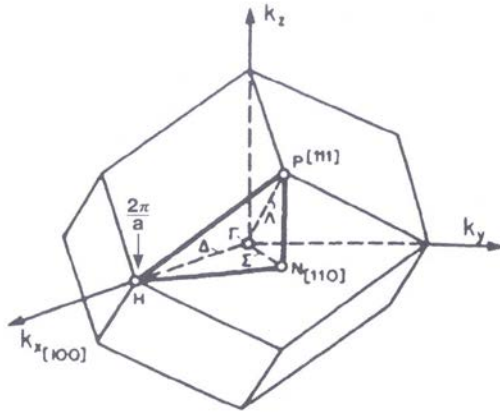


Figure 5.17. First Brillouin zone of the bcc crystal structure.

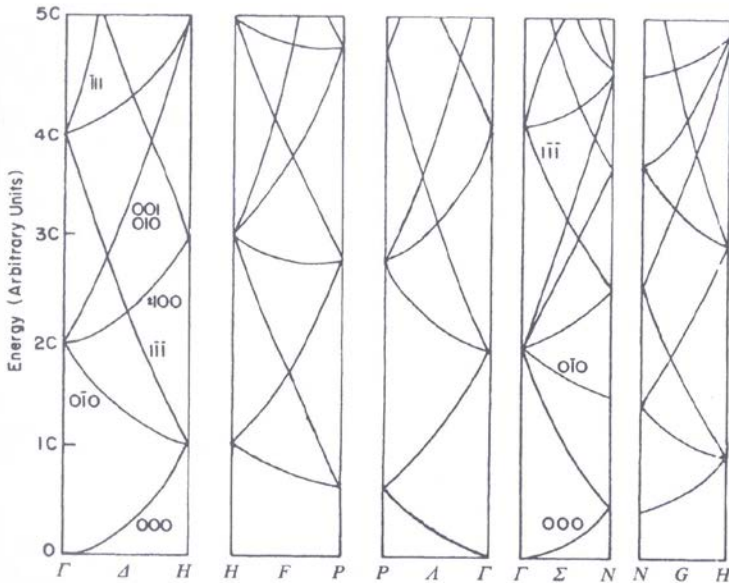


Figure 5.18. Energy bands of the free electrons for the bcc structure. The numbers given on the branches are the respective  $h_i$  values (see the calculation in the text). Compare to Fig. 5.6.  $C = \hbar^2 2\pi^2 / ma^2$ , see (5.38).

$$\mathbf{k}' = \mathbf{k} + \mathbf{G}.$$

$$E_{\mathbf{k}'} = \frac{\hbar^2}{2m} (\mathbf{k} + \mathbf{G})^2. \quad E = \frac{\hbar^2}{2m} \left( \frac{2\pi}{a} x\mathbf{i} + \mathbf{G} \right)^2,$$

$$E = \frac{\hbar^2}{2m} \left( \frac{2\pi}{a} \right)^2 (x\mathbf{i})^2 \equiv Cx^2, \quad C = \frac{\hbar^2}{2m} \left( \frac{2\pi}{a} \right)^2 = \frac{2\hbar^2 \pi^2}{ma^2}$$

$$\mathbf{G} = -\frac{2\pi}{a} (\mathbf{i} + \mathbf{l}).$$

$$\begin{aligned} E &= \frac{\hbar^2}{2m} \left[ \frac{2\pi x}{a} \mathbf{i} - \frac{2\pi}{a} (\mathbf{i} + \mathbf{l}) \right]^2 = C [\mathbf{i}(x-1) - \mathbf{l}]^2 \\ &= C [(x-1)^2 + 1] = C(x^2 - 2x + 2) \end{aligned}$$

$$x = 0 \rightarrow E = 2C$$

$$x = 1 \rightarrow E = 1C.$$

# 5. Energy Bands in Crystals

## 5.6 Free Electron Bands for FCC

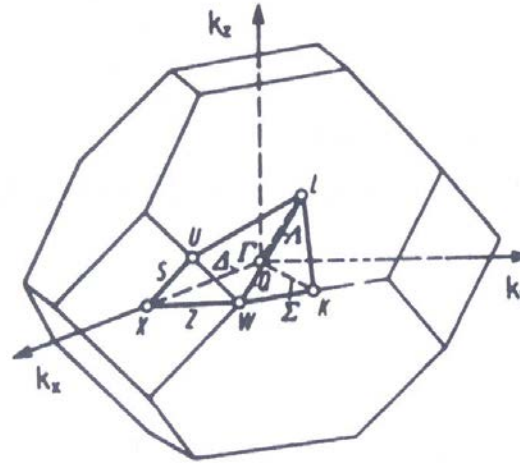


Figure 5.19. First Brillouin zone of the fcc structure.

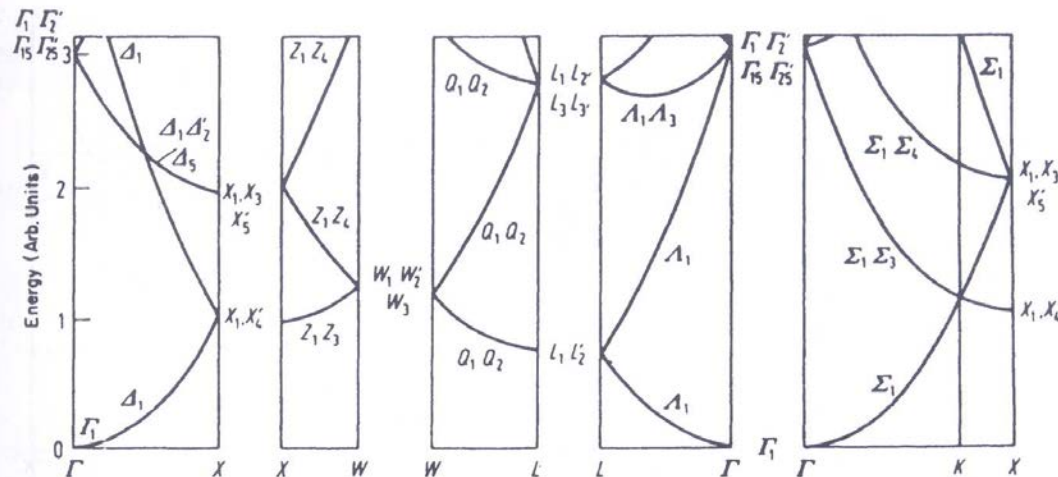


Figure 5.20. Free electron bands of the fcc structure. The letters on the bottom of the graphs correspond to letters in Fig. 5.19 and indicate specific symmetry points in  $k$ -space.

# 5. Energy Bands in Crystals

## 5.7 Band Structures for Some Metals and Semiconductors

Band structure of actual solids: Figs. 5.21-24  
(results of extensive, computer-aided calculations)

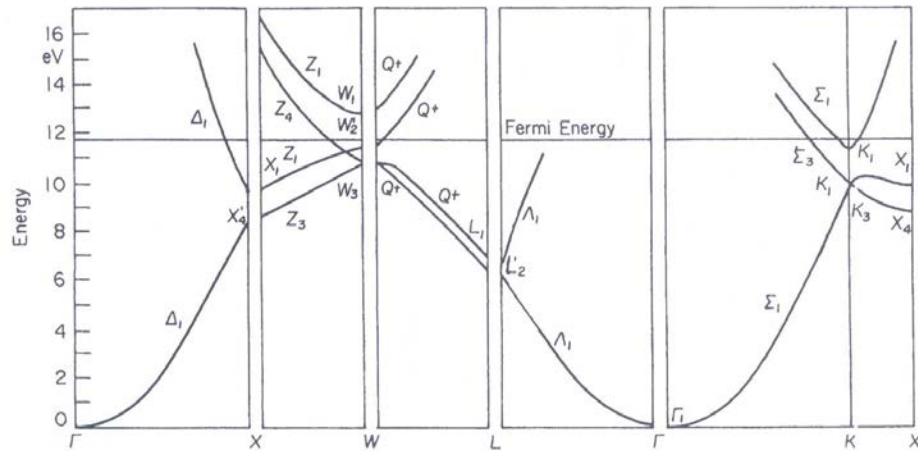


Figure 5.21. Energy bands for aluminum. Adapted from B. Segal, *Phys. Rev.* **124**, 1797 (1961). (The meaning of the Fermi energy will be explained in Section 6.1.)

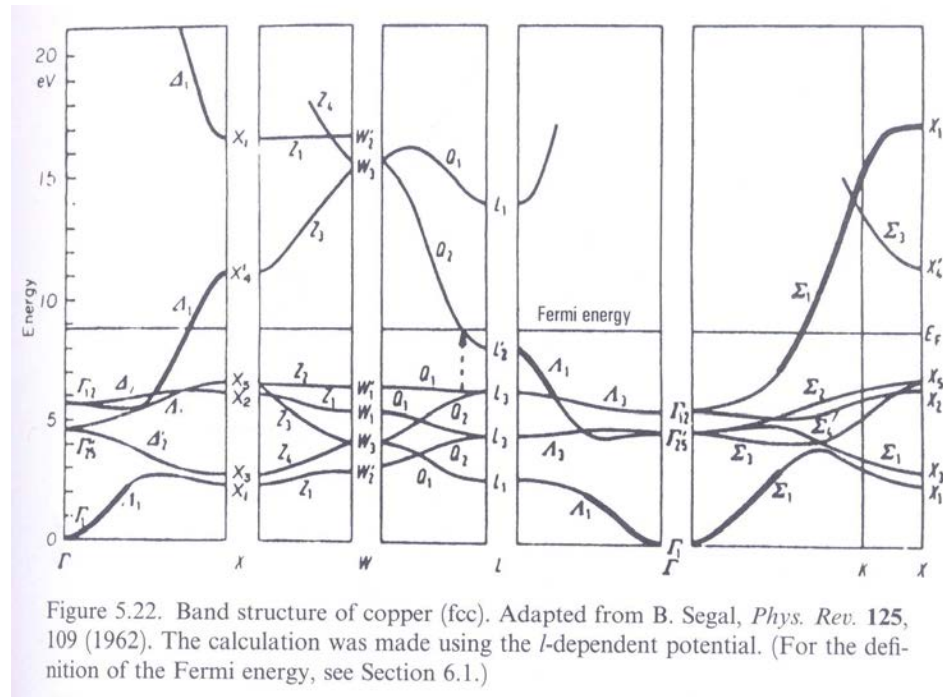


Figure 5.22. Band structure of copper (fcc). Adapted from B. Segal, *Phys. Rev.* **125**, 109 (1962). The calculation was made using the  $l$ -dependent potential. (For the definition of the Fermi energy, see Section 6.1.)

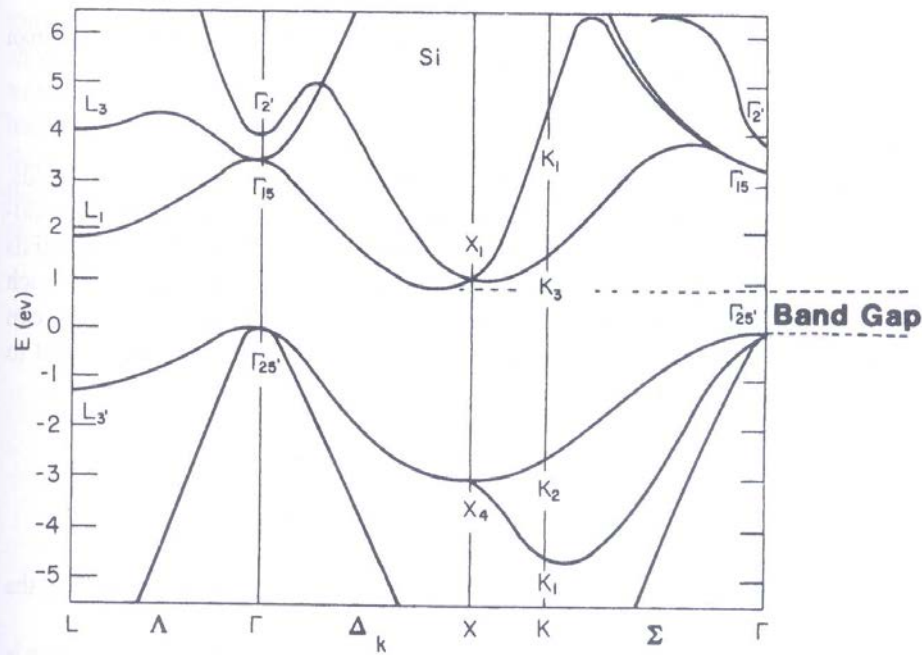


Figure 5.23. Calculated energy band structure of silicon (diamond-cubic crystal structure). Adapted from M.L. Cohen and T.K. Bergstresser, *Phys. Rev.* **14**, 789 (1966). See also J.R. Chelikowsky and M.L. Cohen, *Phys. Rev.* **B14**, 556 (1976).

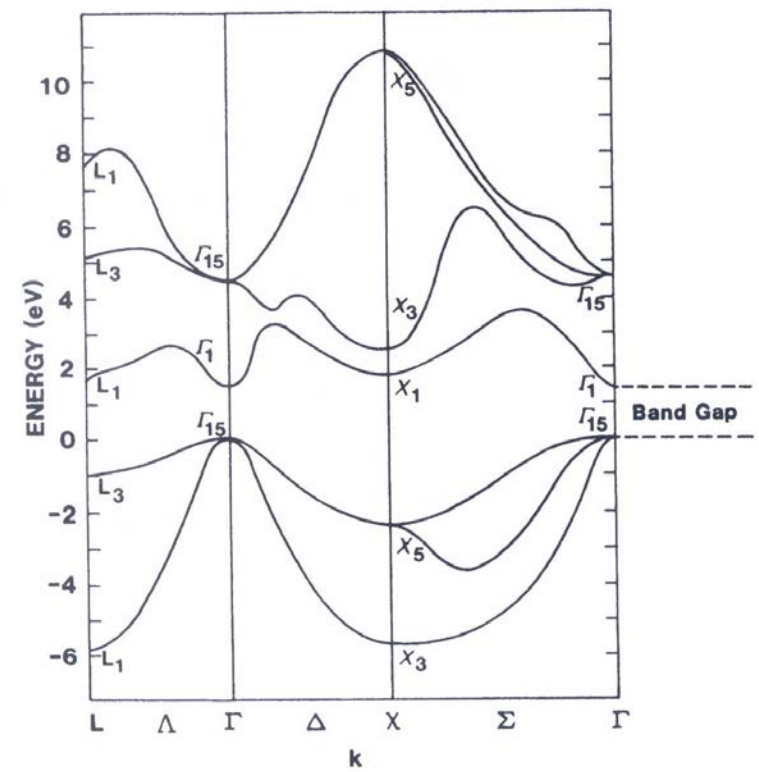


Figure 5.24. Calculated energy band structure of GaAs. Adapted from F. Herman and W.E. Spicer, *Phys. Rev.* **174**, 906 (1968).





# 5. Energy Bands in Crystals

## 5.8 Curves and Planes of Equal Energy

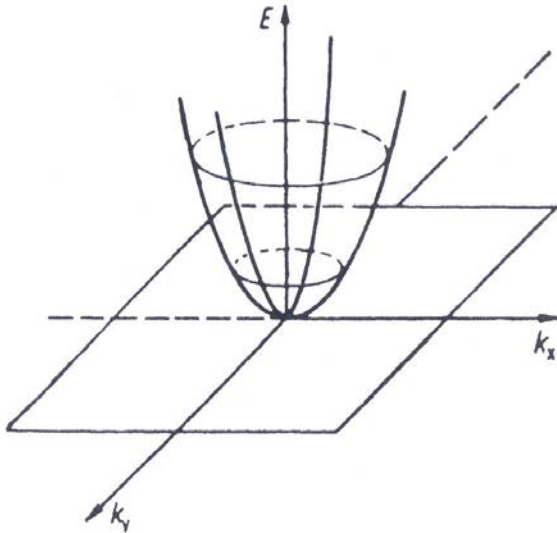


Figure 5.25. Electron energy  $E$  versus wave vector  $\mathbf{k}$  (two-dimensional). This figure demonstrates various curves of equal energy for free electrons.

$E(k)$  curves

Fig 5.25: curves of equal energy for free electrons

Fig 5.26: near boundary of BZ- deviation from a circular form (2-d)

Fig 5.27: 3-d BZ for Cu

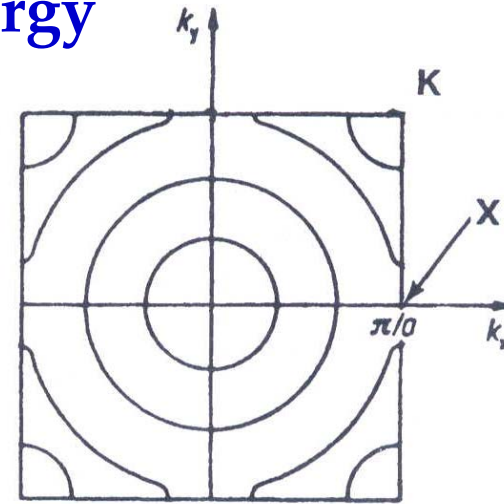


Figure 5.26. Curves of equal energy inserted into the first Brillouin zone for a two-dimensional square lattice.

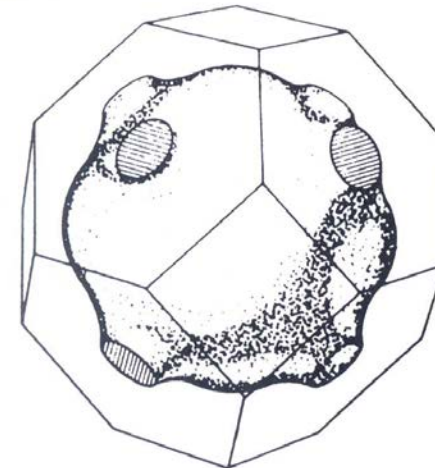


Figure 5.27. A particular surface of equal energy (Fermi surface, see Section 6.1) and the first Brillouin zone for copper. Adapted from A.B. Pippard, *Phil. Trans. Roy. Soc. London, A* **250**, 325 (1957).

