Part I Fundamentals

Electron Theory : Matter Waves

Chap. 1 Introduction

Chap. 2 The Wave-Particle Duality

Chap. 3 The Schördinger Equation

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

Chap. 5 Energy Bands in Crystals

Chap. 6 Electrons in a Crystal

Electromagnetic Theory : Maxwell Equations

Chap. 4 Light Waves

(Electrons in Solids, 3rd Ed., R. H. Bube)

5. Energy Bands in Crystals

5.1 One-Dimensional Zone Schemes

Energy E vs momentum of the electrons p (or k)

For free electrons, the wave number in 1-dim

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

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

In a crystal

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

$\cos \alpha a = \cos k_x a \equiv \cos(k_x a + n2\pi)$: more general form in 1-dim

$n = 0, \pm 1, \pm 2, \ldots$ $\quad \alpha a = k_x a + n2\pi$ $\quad \Big\}$ $\quad k_x + n\frac{2\pi}{a} = \sqrt{\frac{2m}{\hbar^2}}E^{1/2}$

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

5. Energy Bands in Crystals

5.1 One-Dimensional Zone Schemes

$$k_x + n\frac{2\pi}{a} = \sqrt{\frac{2m}{\hbar^2}}E^{1/2}$$

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

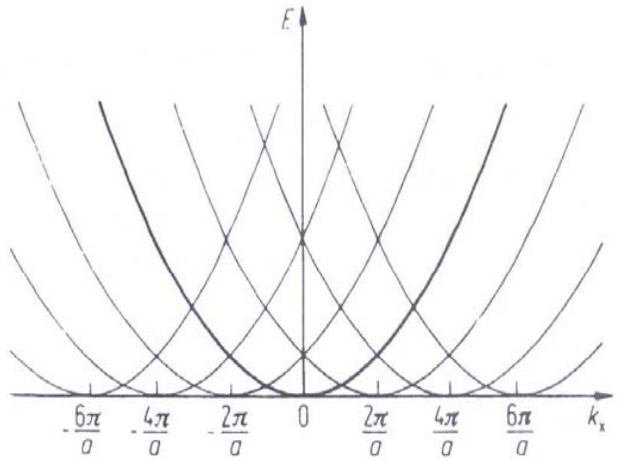

Figure 5.2. Periodic repetition of Fig. 5.1 at the points $k_x = n \cdot 2\pi/a$. The figure depicts a family of free electron parabolas having a periodicity of $\pm 2\pi/a$.

If an electron propagates in *a periodic potential*, discontinuities of the electron energies are observed when $\cos k_x a$ has a maximum or a minimum, i.e., when $\cos k_x a = \pm 1$

$$k_x a = n\pi, \qquad n = \pm 1, \pm 2, \pm 3, \ldots, \qquad \text{or} \qquad k_x = n \cdot \frac{\pi}{a}$$

At these singularities, a deviation from the parabolic *E vs* k_x occurs and the branches of the individual parabolas merge into the neighboring ones (see Fig.5.3)

5. Energy Bands in Crystals

5.1 One-Dimensional Zone Schemes

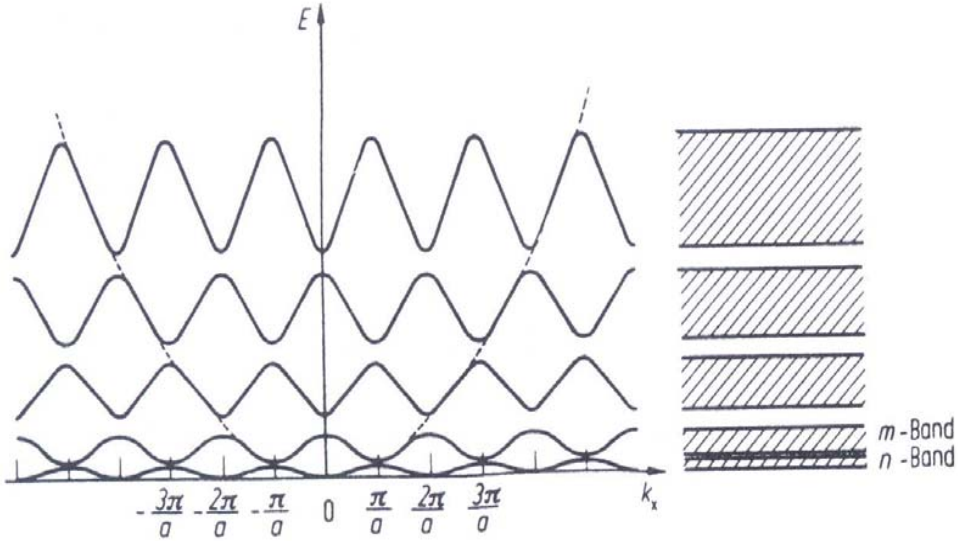

Figure 5.3. Periodic zone scheme.

The electrons in a crystal behave like free electrons for most k_x value except $k_x \rightarrow n\,\pi/a$

periodic zone scheme (see Fig 5.3)

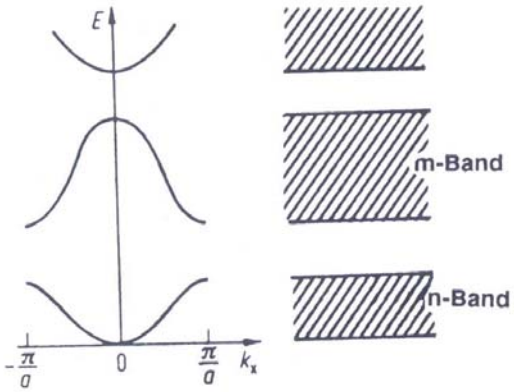

Figure 5.4. Reduced zone scheme. (This is a section of Fig. 5.3 between $-\pi/a$ and $+\pi/a$.)

reduced zone scheme (see Fig 5.4)

$$\pi/a \leq k_x \leq \pi/a$$

5. Energy Bands in Crystals

5.1 One-Dimensional Zone Schemes

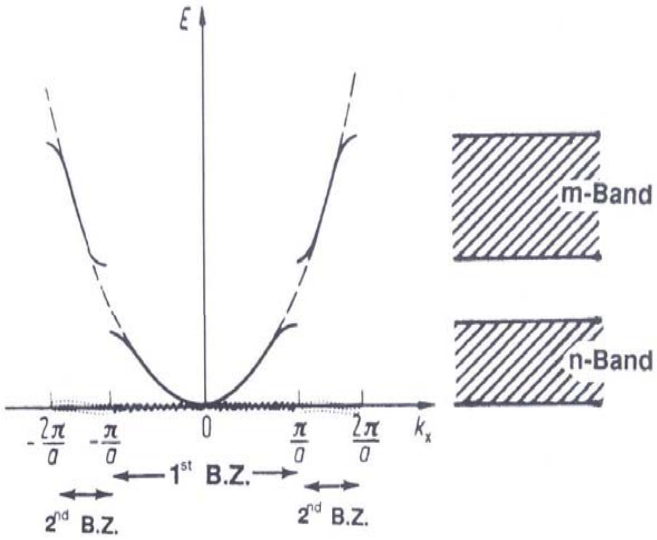

Figure 5.5. Extended zone scheme. The first and second Brillouin zones (BZ) are shown, see Section 5.2.

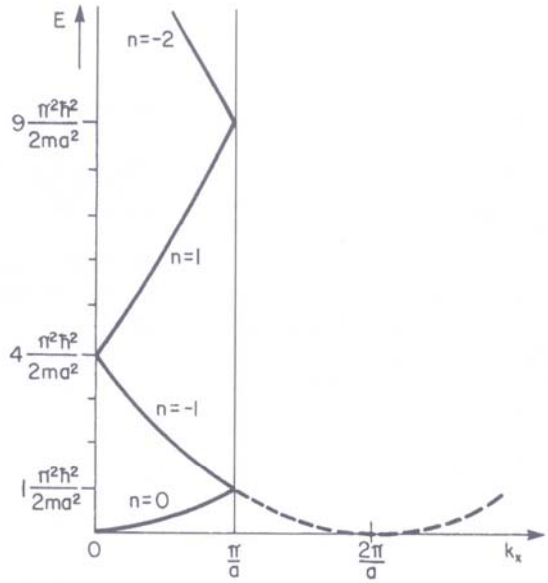

Figure 5.6. "Free electron bands" plotted in the reduced zone scheme (cubic primitive crystal structure). Compare this figure with the central portion of Fig. 5.2, that is, with the region from zero to π/a. Note the sameness of the individual bands.

extended zone scheme (see Fig 5.5)

the deviations from the free electron parabola at the critical points $k_x = n\,\pi/a$ are particularly easy to identify.

free electron bands (see Fig 5.6)

free electrons in a reduced zone scheme

from $$k_x + n\frac{2\pi}{a} = \sqrt{\frac{2m}{\hbar^2}}E^{1/2}$$

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

5. Energy Bands in Crystals

5.1 One-Dimensional Zone Schemes

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

By inserting different *n*-values, one can calculate the shape of branches of the free electron bands

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

$$n = -1, \quad E = \frac{\hbar^2}{2m}(k_x - \frac{2\pi}{a})^2 \quad (parabola \ \ with \ \ \frac{2\pi}{a} \ \ \text{as origin})$$

$$\text{For } k_x = 0, \quad E = 4\frac{\pi^2\hbar^2}{2ma^2}$$

$$\text{For } k_x = \frac{\pi}{a}, \quad E = 1\frac{\pi^2\hbar^2}{2ma^2}$$

5. Energy Bands in Crystals

5.2 One- and Two-Dimensional Brillouin Zones

1-d Brillouin Zone

- The first Brillouin Zone (BZ) :

$\pi/a \leq k_x \leq \pi/a$: n-Band

- The second Brillouin Zone (BZ):

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

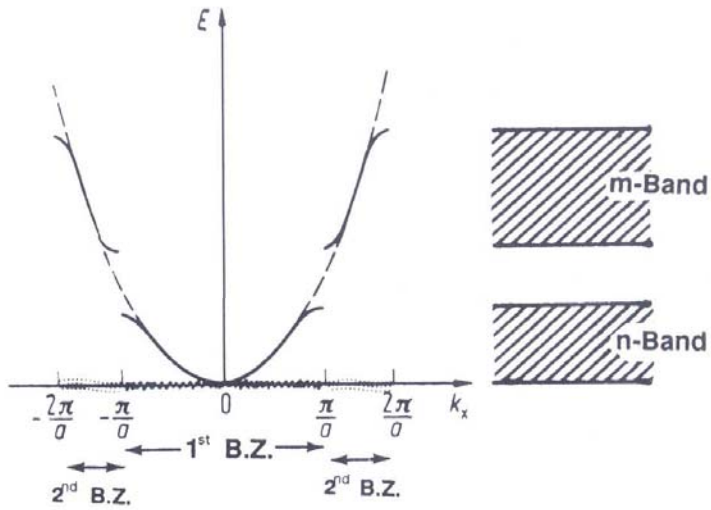

Figure 5.5. Extended zone scheme. The first and second Brillouin zones (BZ) are shown, see Section 5.2.

- 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 2nd 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 3rd BZ, and all BZ (because of the $2\pi/a$ periodicity) → relevant information of all BZ can be contained in the 1st BZ (a reduced zone scheme)

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 $\boldsymbol{k} = (k_x, k_y)$: 2-d reciprocal lattice (Fig 5.7)

- A 2-d field of allowed energy regions which correspond to the allowed energy band → 2-d BZ

-1st zone in 2-d: the area enclosed by four "Bragg planes" having four shortest lattice vectors, $\mathbf{G_1}$**:** bisectors on the lattice vectors

- For the following zone → construct the bisectors of the next shortest lattice vectors, $\mathbf{G_2}$**,** $\mathbf{G_3}$**…**

- For the zone of higher order the extended limiting lines of the zones of lower order are used as additional limiting lines.

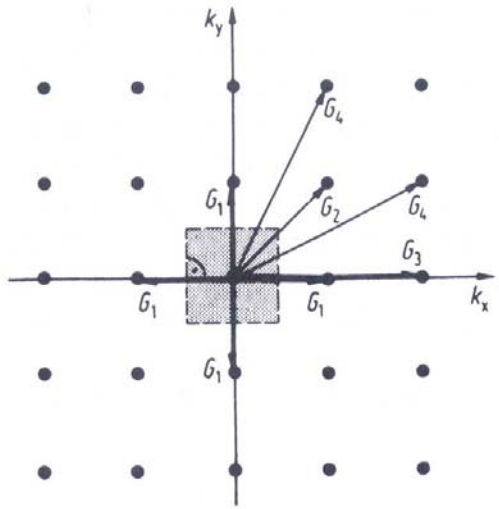

Figure 5.7. Four shortest lattice vectors in a $k_x - k_y$ coordinate system and the first Brillouin zone in a two-dimensional reciprocal lattice. (Cubic primitive crystal structure.)

5. Energy Bands in Crystals

5.2 One- and Two-Dimensional Brillouin Zones

The first four BZ shown in Fig 5.8

"Usefulness of BZ"

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

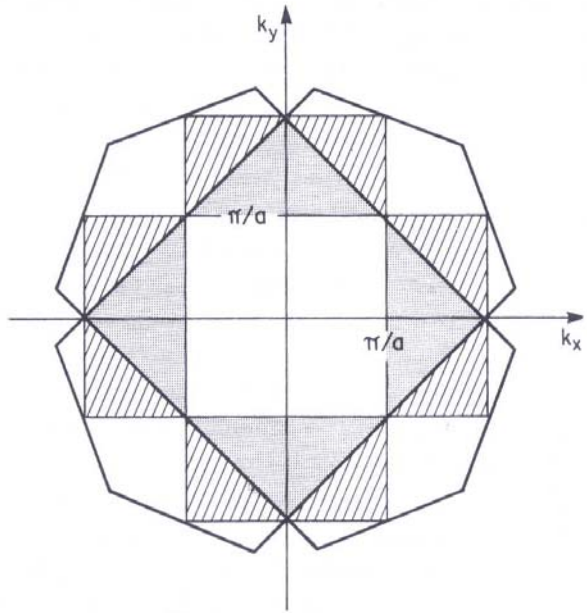

Figure 5.8. The first four Brillouin zones of a two-dimensional, cubic primitive reciprocal lattice.

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

according to Fig 5.8, for $k_{crit} = \frac{\pi}{a}\sqrt{2}$

this yields with (4.8) 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 $E_{\max} = \frac{1}{2}\left(\frac{\pi^2\hbar^2}{a^2 m}\right)$

5. Energy Bands in Crystals

5.2 One- and Two-Dimensional Brillouin Zones

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

- Overlapping of energy bands: bands are drawn in different directions in *k*-space (Fig 5.9) :

the consequence of

$$k_{crit} = \frac{\pi}{a} \quad \text{and} \quad k_{crit} = \frac{\pi}{a}\sqrt{2}$$

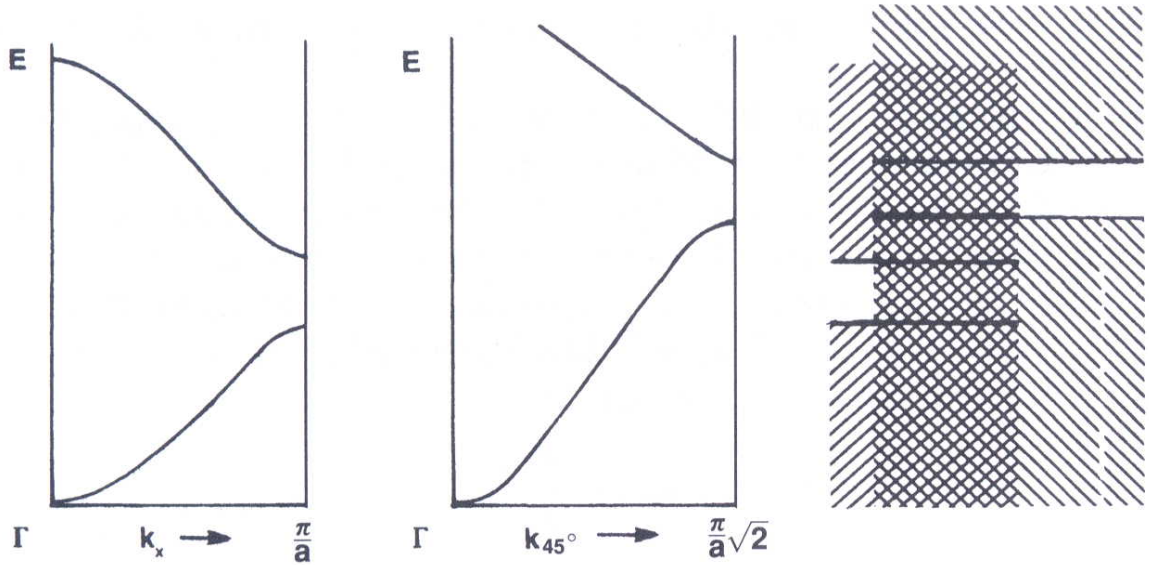

Figure 5.9. Overlapping of allowed energy bands.

5. Energy Bands in Crystals

5.2 One- and Two-Dimensional Brillouin Zones

A different illustration of the occurrence of critical energies at which a reflection of the electron wave takes place :

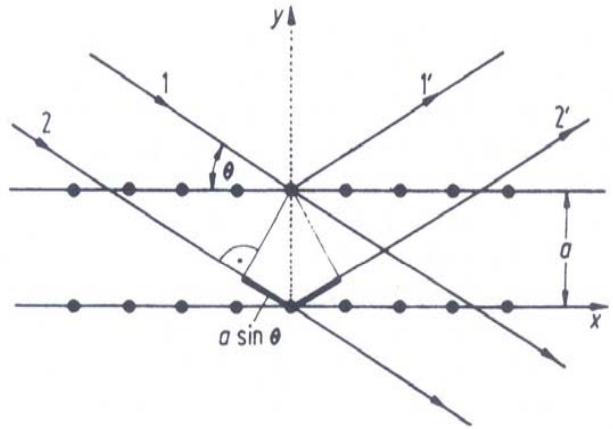

Figure 5.10. Bragg reflection of an electron wave in a lattice. The angle of incidence is θ.

Bragg relation

$$2a\sin\theta = n\lambda, \qquad n = 1,2,3,...$$

Since $\lambda = 2\pi/k$

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

For a perpendicular incidence, $\theta = 90^{o}$, $k_{crit} = \frac{\pi}{a}$

If $\theta = 45^{o}$, $k_{crit} = \frac{\pi}{a}\sqrt{2}$

For increasing electron energies, a critical k-value is finally reached for which "reflection" of the electron wave at the lattice plane occurs. At k_{crit}, the transmission of electron beam through the lattice is prevented.

5. Energy Bands in Crystals

5.3 Three-Dimensional Brillouin Zones

- In previous section, it was shown that at the boundaries of the zones the electron waves are Bragg-reflected by the crystal.

- The wave vector, $|\boldsymbol{k}| = 2\pi/\lambda$, was seen to have the unit of reciprocal length and thus is defined in the reciprocal lattice.

- The construction of 3-d Brillouin zones for two important crystal structures of face centered cubic (FCC) and body centered cubic (BCC) : important features in common with "**Wigner- Seitz cells**"

5. Energy Bands in Crystals

5.4 Wigner - Seitz Cells

Crystals have symmetrical properties

- An accumulation of "**unit cell**"
- Smallest possible cell "**primitive cell**" (consist of 1 atom)
- BCC, FCC : conventional non-primitive unit cells

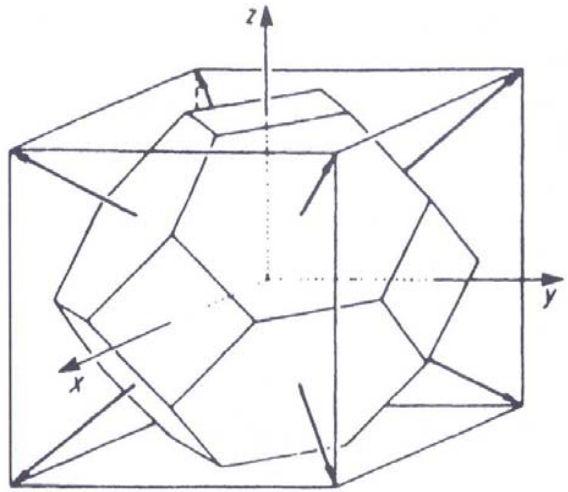

Figure 5.11. Wigner–Seitz cell for the body-centered cubic (bcc) structure.

- Wigner-Seitz cell : a special type of primitive unit cell that shows the cubic symmetry of cubic cells

- 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. For BCC (Fig 5.11) & FCC (Fig. 5. 13)

5. Energy Bands in Crystals

5.4 Wigner - Seitz Cells

- The atoms arrangement of FCC:
corners and faces of cube,
or center points of the edges and the
center of the cell (Fig 5.12)
-The W-S cell for FCC shown
in Fig 5.13

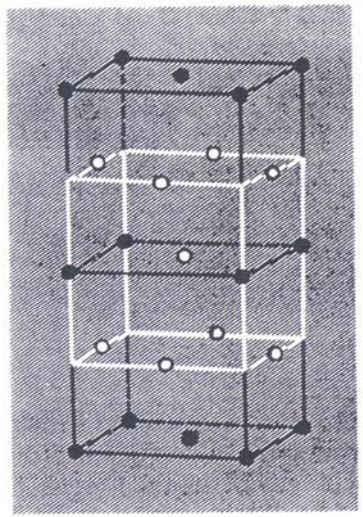

Figure 5.12. Conventional unit cell of the fcc structure. In the cell which is marked black, the atoms are situated on the corners and faces of the cubes. In the white cell, the atoms are at the centers of the edges and the center of the cell.

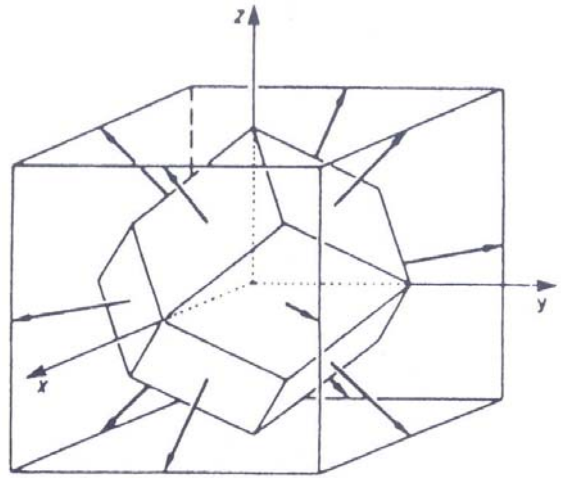

Figure 5.13. Wigner–Seitz cell for the fcc structure. It is constructed from the white cell which is marked in Fig. 5.12.

5. Energy Bands in Crystals

5.5 Translation Vectors and the Reciprocal Lattice

Fundamental vectors or primitive vectors : $\mathbf{t}_1, \mathbf{t}_2, \mathbf{t}_3$

Translation vectors, **R :** combination of primitive vectors

$$\mathbf{R} = n_1\mathbf{t}_1 + n_2\mathbf{t}_2 + n_3\mathbf{t}_3$$

where n_1, n_2, and n_3 are integers.

Three vectors for the reciprocal lattice: $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$

a translation vector for the reciprocal lattice, **G**

$$\mathbf{G} = 2\pi(h_1\mathbf{b}_1 + h_2\mathbf{b}_2 + h_3\mathbf{b}_3)$$

where h_1,h_2, and h_3 is integer

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

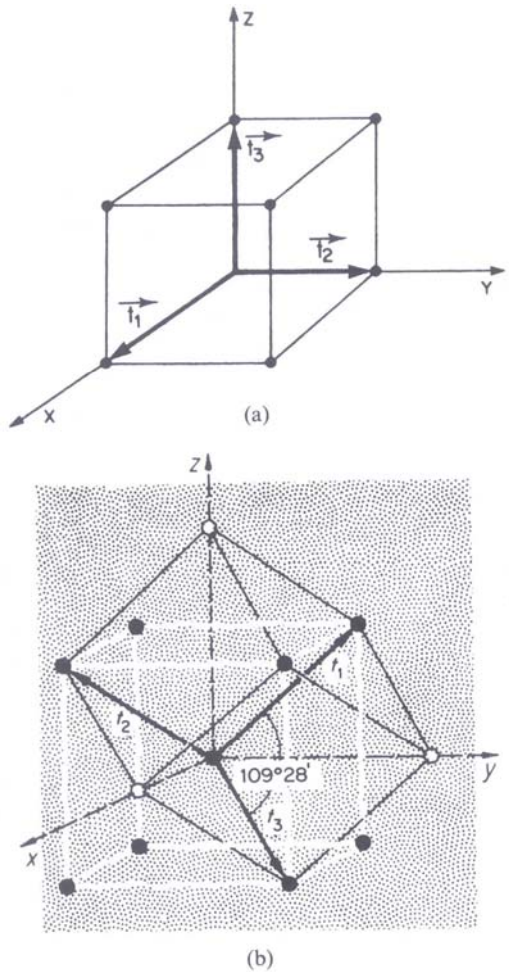

Figure 5.14. (a) Fundamental lattice vectors $\mathbf{t}_1, \mathbf{t}_2, \mathbf{t}_3$ in a cubic primitive lattice. (b) Fundamental lattice vectors in a conventional (white) and primitive, noncubic unit cell (black) of a bcc lattice. The axes of the primitive (noncubic) unit cell form angles of 109° 28′.

5. Energy Bands in Crystals

5.5 Translation Vectors and the Reciprocal Lattice

The relation between real and reciprocal lattices

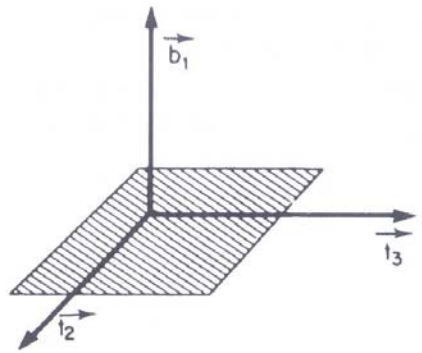

Figure 5.15. Plane formed by $\mathbf{t}_2$ and $\mathbf{t}_3$ with perpendicular vector $\mathbf{b}_1$.

$$\left.\begin{aligned} \mathbf{b}_1 \bullet \mathbf{t}_1 &= 1, \\ \mathbf{b}_1 \bullet \mathbf{t}_2 &= 0, \\ \mathbf{b}_1 \bullet \mathbf{t}_3 &= 0. \end{aligned}\right\} \quad \mathbf{b}_n \mathbf{t}_m = \delta_{nm},$$

Kronecker-Delta symbol,

$$\text{where } \delta_{nm} = 1 \text{ for } n = m \text{ and } \delta_{nm} = 0 \text{ for } n \neq m$$

$$\mathbf{b}_1 = const.\ \mathbf{t}_2 \times \mathbf{t}_3 \longrightarrow \mathbf{b}_1 \bullet \mathbf{t}_1 = const.\ \mathbf{t}_1 \bullet \mathbf{t}_2 \times \mathbf{t}_3 = 1 \longrightarrow const = \frac{1}{\mathbf{t}_1 \bullet \mathbf{t}_2 \times \mathbf{t}_3}$$

$$\mathbf{b}_1 = \frac{\mathbf{t}_2 \times \mathbf{t}_3}{\mathbf{t}_1 \bullet \mathbf{t}_2 \times \mathbf{t}_3} \qquad \mathbf{b}_2 = \frac{\mathbf{t}_3 \times \mathbf{t}_1}{\mathbf{t}_1 \bullet \mathbf{t}_2 \times \mathbf{t}_3} \qquad \mathbf{b}_3 = \frac{\mathbf{t}_1 \times \mathbf{t}_2}{\mathbf{t}_1 \bullet \mathbf{t}_2 \times \mathbf{t}_3}$$

5. Energy Bands in Crystals

5.5 Translation Vectors and the Reciprocal Lattice

Calculation for the reciprocal lattice of a BCC crystal

Real crystal

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

i, j, 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, $\mathbf{t}_1 = \frac{a}{2}(\bar{1}\,1\,1)$ $\mathbf{t}_2 = \frac{a}{2}(1\,\bar{1}\,1)$ $\mathbf{t}_3 = \frac{a}{2}(1\,1\,\bar{1})$

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

$$= \frac{a^2}{4}(2\mathbf{j}+2\mathbf{l}) = \frac{a^2}{2}(\mathbf{j}+\mathbf{l})$$

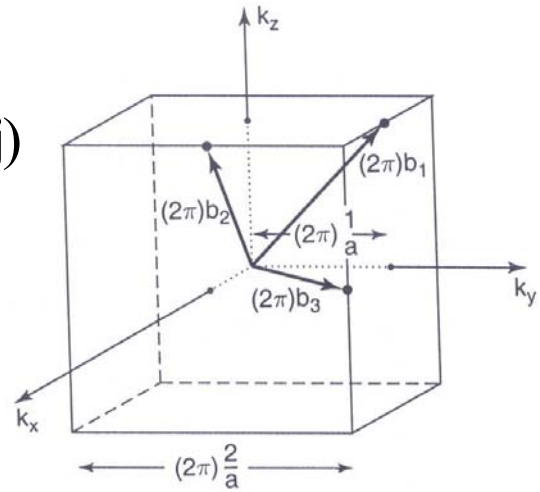

Figure 5.16. Lattice vectors in reciprocal space of a bcc crystal. The primitive vectors in the reciprocal lattice are (because of (5.13)) larger by a factor of 2π. The lattice constant of the cube then becomes $2\pi \cdot 2/a$.

5. Energy Bands in Crystals

5.5 Translation Vectors and the Reciprocal Lattice

(continued)

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

$$\mathbf{b}_1 = \frac{\mathbf{t}_2 \times \mathbf{t}_3}{\mathbf{t}_1 \bullet \mathbf{t}_2 \times \mathbf{t}_3} \longrightarrow \mathbf{b}_1 = \frac{\frac{a^2}{2}(\mathbf{j}+\mathbf{l})}{\frac{a^3}{2}} = \frac{1}{a}(\mathbf{j}+\mathbf{l}),$$

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

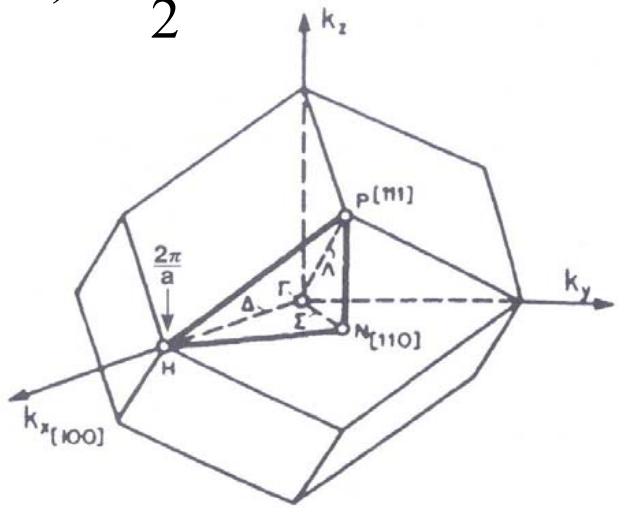

Figure 5.17. First Brillouin zone of the bcc crystal structure.

BCC (reciprocal lattice) ⟶ **FCC (real lattice)**

1st Brillouin zone for BCC ⟶ **Wigner-Seitz cell for FCC**

⟵

Vice versa

5.6 Free electron Bands

Periodicity of E(**k**) → all information of electron contained in the 1st Brillouin Zone (BZ)

$E_{\mathbf{k}'}$ for **k'** for outside 1st BZ → $E_{\mathbf{k}}$ with in 1st BZ with a suitable translation vector **G**

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

"Energy band are not alike in different directions in **k**-space"

for the demonstration, "Free electron band" is used (Fig 5.6 **).**

In 3-D, from (5.7) $$E_{k'} = \frac{\hbar^2}{2m}(\mathbf{k} + \mathbf{G})^2$$

5. Energy Bands in Crystals

5.6 Free electron Bands

In Fig 5.17

[100] from Γ(origin) to point H : Δ

[110] from Γ to N : Σ

[111] from Γ to P: Λ

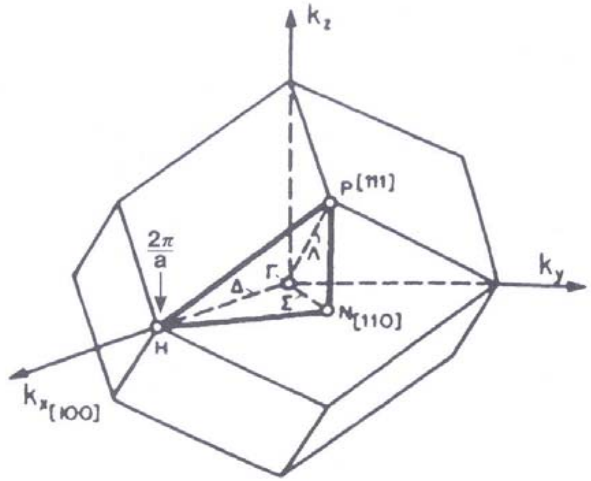

Figure 5.17. First Brillouin zone of the bcc crystal structure.

Fig 5.18 calculated by using the following equation

$$E_{k'} = \frac{\hbar^2}{2m}(\mathbf{k}+\mathbf{G})^2$$

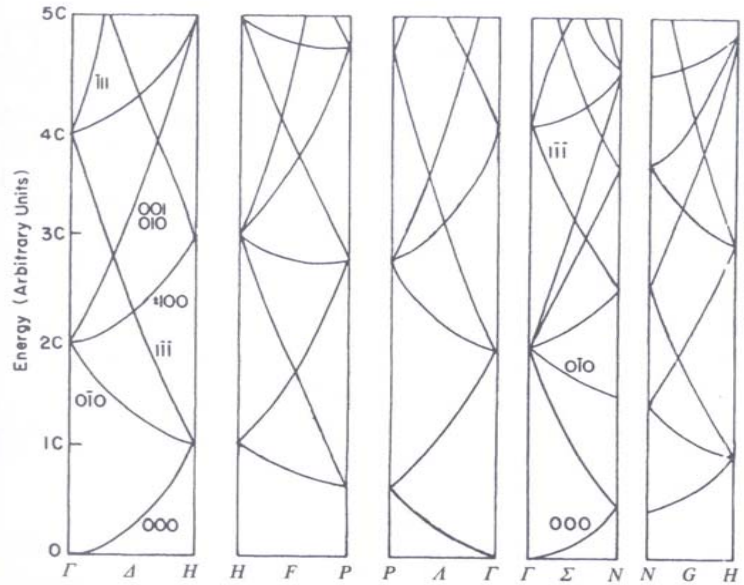

Figure 5.18. Energy bands of the free electrons for the bcc structure. The numbers given on the branches are the respective h_i values (see the calculation in the text). Compare to Fig. 5.6. $C = \hbar^2 2\pi^2/ma^2$, see (5.38).

5. Energy Bands in Crystals

5.6 Free electron Bands

band calculation for BCC $\Gamma - H \quad [100]$ direction

$\mathbf{k}_{\Gamma-H} \equiv \mathbf{k}_x$ between 0 and $2\pi/a$ (boundary of BZ)

For this direction (5.35) becomes

$$E = \frac{\hbar^2}{2m}\left(\frac{2\pi}{a}x\mathbf{i} + \mathbf{G}\right)^2$$

Where x may take values between 0 and 1. to start with, let $\mathbf{G} = 0$, then

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

this curve is labeled (000) in Fig 5. 18 since $h_1,h_2,h_3 = 0,0,0$ for $\mathbf{G}=0$

5. Energy Bands in Crystals

5.6 Free electron Bands

For the case of $h_1,h_2,h_3 = 0,-1,0$

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

combined (5.36) and (5.38)

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

$$C = [(x-1)^2+1] = C(x^2-2x+2)$$

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

and for $x=1 \rightarrow E=1C$

The band labeled $(0\,\bar{1}\,0)$

in Fig 5.18 obtained.

Similarly, For FCC, see

Figs. 5.19 & 5. 20

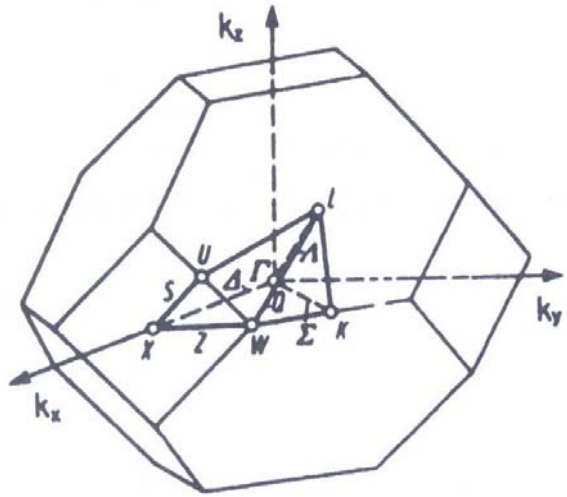

Figure 5.19. First Brillouin zone of the fcc structure.

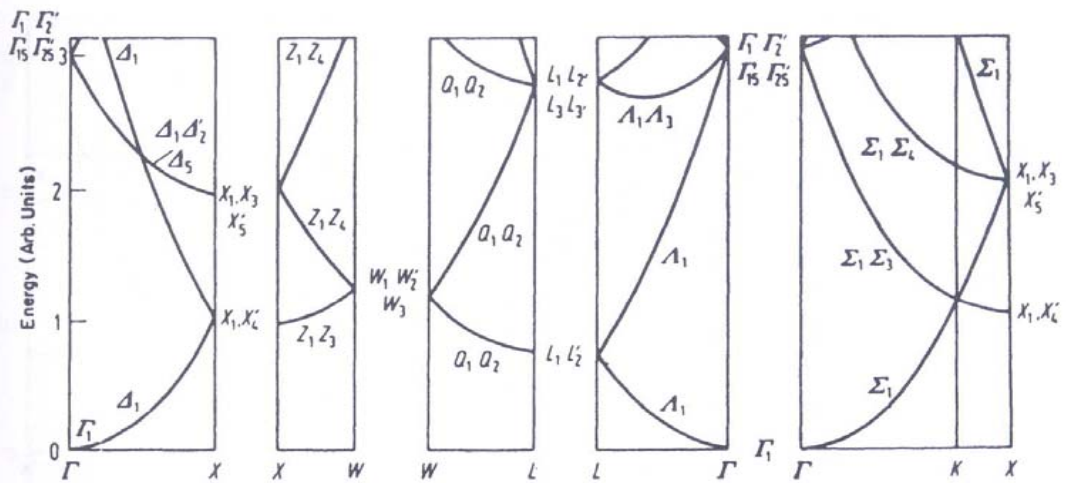

Figure 5.20. Free electron bands of the fcc structure. The letters on the bottom of the graphs correspond to letters in Fig. 5.19 and indicate specific symmetry points in *k*-space.

5. Energy Bands in Crystals

5.7 Band Structures for Some Metals and Semiconductors

- Band structure of actual solids : Figs. 5.21~5.24 (results of extensive, computer-aided calculations)

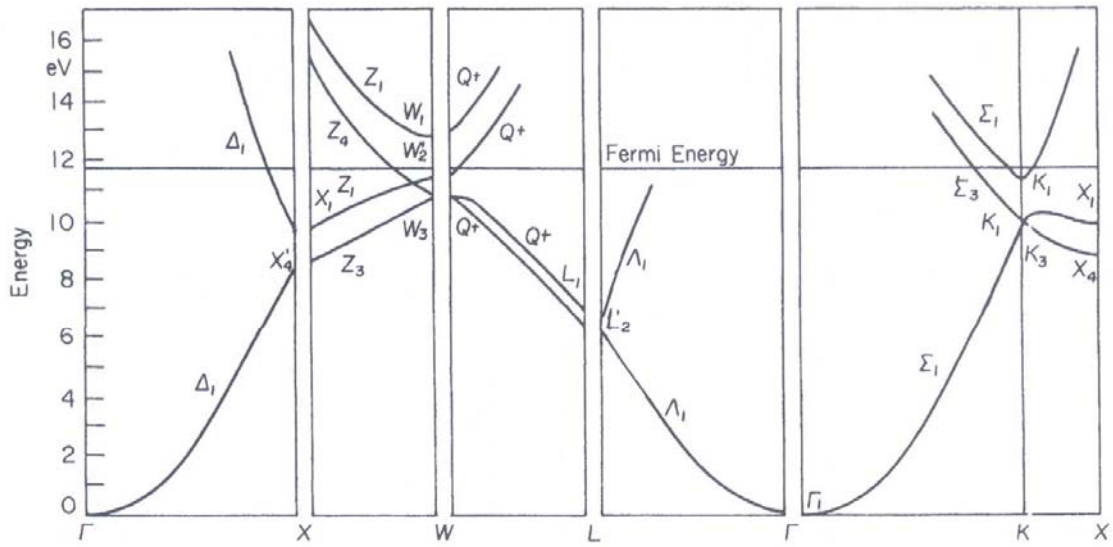

Figure 5.21. Energy bands for aluminum. Adapted from B. Segal, *Phys. Rev.* **124**, 1797 (1961). (The meaning of the Fermi energy will be explained in Section 6.1.)

- Directions in *k*-space

[100] : $\Gamma - X$

[110] : $\Gamma - K$

[111]: $\Gamma - L$

Band diagram for aluminum

- parabola-shaped band: free- electron like

5. Energy Bands in Crystals

5.7 Band Structures for Some Metals and Semiconductors

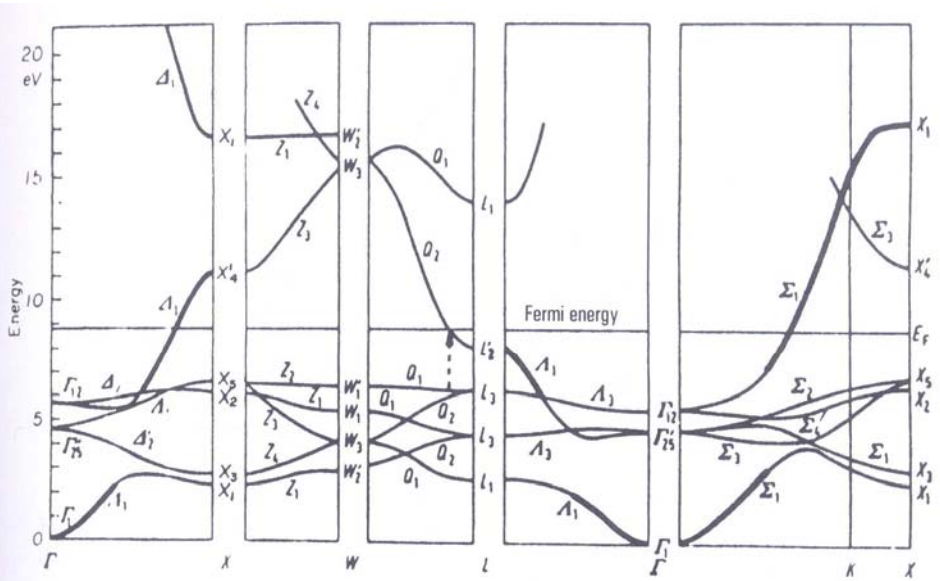

Figure 5.22. Band structure of copper (fcc). Adapted from B. Segal, *Phys. Rev.* **125**, 109 (1962). The calculation was made using the *l*-dependent potential. (For the definition of the Fermi energy, see Section 6.1.)

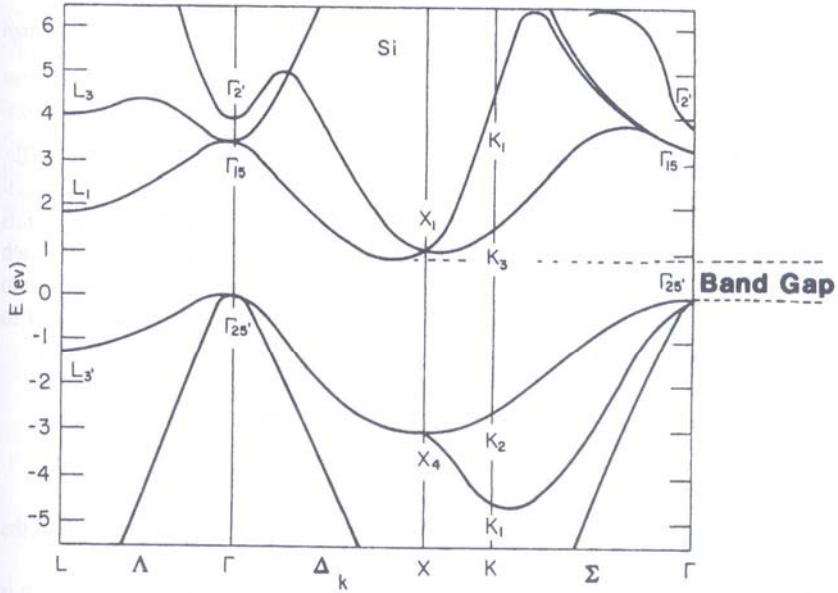

Figure 5.23. Calculated energy band structure of silicon (diamond-cubic crystal structure). Adapted from M.L. Cohen and T.K. Bergstresser, *Phys. Rev.* **14**, 789 (1966). See also J.R. Chelikowsky and M.L. Cohen, *Phys. Rev.* **B14**, 556 (1976).

Band diagram for copper

-Lower half of the diagram closely spaced and flat running bands (due to 3d-bands of Cu)

Band diagram for silicon

- band gap : near 0~ 1eV → "semiconductor properties"

5. Energy Bands in Crystals

5.7 Band Structures for Some Metals and Semiconductors

-Band diagram gallium arsenide

: so called III – IV semiconductor

Important for “optoelectonic devices”

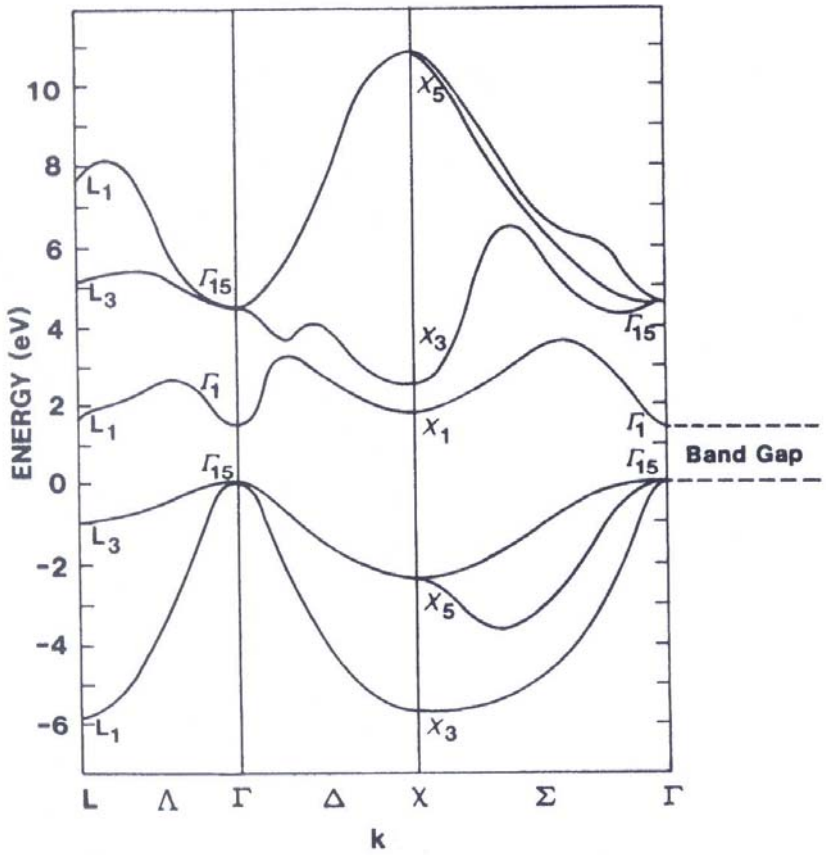

Figure 5.24. Calculated energy band structure of GaAs. Adapted from F. Herman and W.E. Spicer, *Phys. Rev.* **174**, 906 (1968).

5. Energy Bands in Crystals

5.8 Curves and Planes of Equal Energy

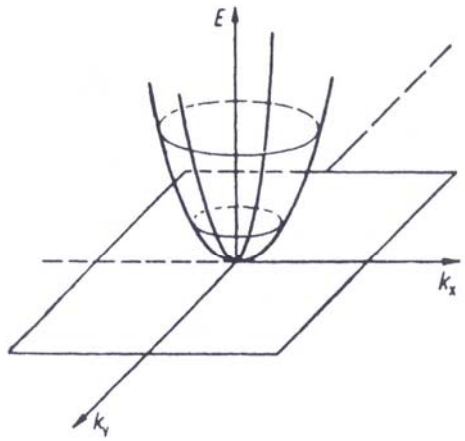

Figure 5.25. Electron energy E versus wave vector $\mathbf{k}$ (two-dimensional). This figure demonstrates various curves of equal energy for free electrons.

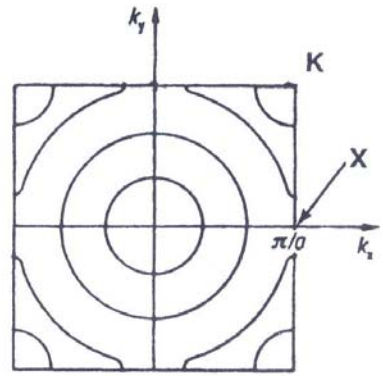

Figure 5.26. Curves of equal energy inserted into the first Brillouin zone for a two-dimensional square lattice.

Energy vs. wave vector, *k*

Fig 5.25: 3-d curves equal energy

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

Fig 5.27: 3-d BZ for Cu

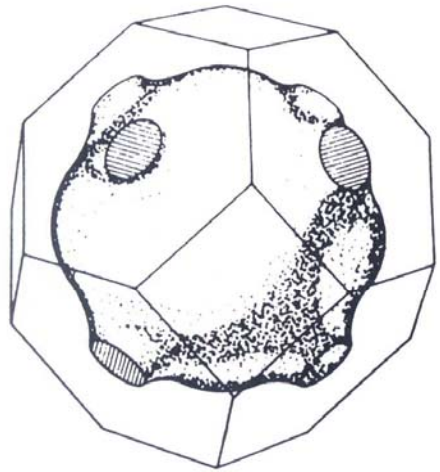

Figure 5.27. A particular surface of equal energy (Fermi surface, see Section 6.1) and the first Brillouin zone for copper. Adapted from A.B. Pippard, *Phil. Trans. Roy. Soc. London*, **A 250**, 325 (1957).