# Band structure and groundstate in weak potential approximation

Free electron energy spectrum is $\varepsilon_k^0 = \frac{\hbar^2 k^2}{2m}$

To represent the free electron energy spectrum in the "reduced zone" scheme, for each wavevector $\vec{k}$ we write

$$\vec{k} = \vec{q} + \vec{K}$$

where $\vec{q}$ is in the 1st BZ and $\vec{K}$ is in R.L. This decomposition is unique. We then plot $\varepsilon_k^0 = \hbar^2 (\vec{q} + \vec{K})^2 / 2m$ as a function of $\vec{q}$ in 1st BZ. This gives a separate curve for each RL vector $\vec{K}$, and this gives ε_k^0 represented as separate bands in the reduced zone scheme. When a weak potential is turned on, energy gaps are introduced wherever the free electron bands have a degeneracy (the degeneracies will occur when $\vec{q}+\vec{K}$ lies on a Bragg plane). In one dimension, the result looks like below:
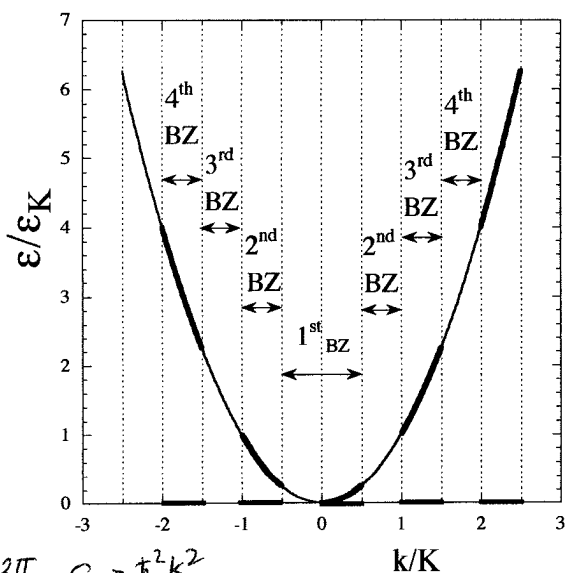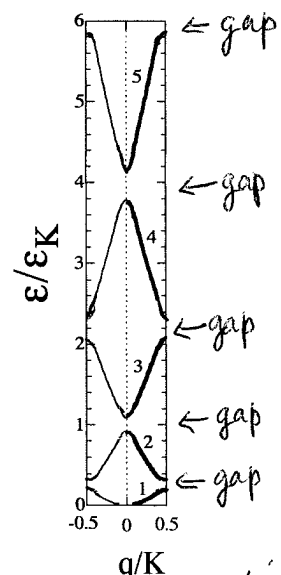

$K \equiv \frac{2\pi}{a}$, $\varepsilon_K \equiv \frac{\hbar^2 K^2}{2m}$

extended zone
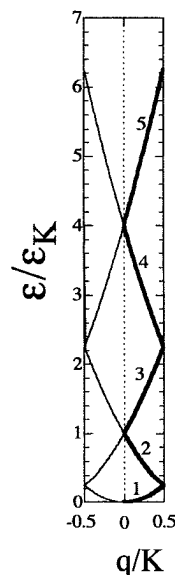
free electrons
reduced zone

weak potential

heavy lines are for $\vec{q}+\vec{K}$ with $0 \leq q \leq \frac{K}{2}$ — positive half 1st BZ
light lines are for $\vec{q}+\vec{K}$ with $-\frac{K}{2} \leq q \leq 0$ — negative half 1st BZ
In reduced zone plots, the numbers label the BZ that the band came from in the extended zone plot.

In 1-D the bands do not overlap ie

$$\max_q \, \mathcal{E}_n(q) < \min_q \, \mathcal{E}_{n+1}(q) \qquad n \text{ is band index}$$

When $\max_q \mathcal{E}_n(\bar{q})$ and $\min_q \mathcal{E}_{n+1}(\bar{q})$ occur at the same value of $\bar{q}$, we say there is a direct gap. When they occur at different $\bar{q}$, we say there is an indirect gap.

Ground State in 1-D weak potential

To construct the ground state one fills up the lowest energy single electron eigenstates to get the lowest total energy many electron state consistent with the Pauli exclusion principal.

From Born–van Karman boundary conditions we know that in a BL with N sites, there are N allowed $\vec{k}$ vectors in any primitive cell of the R.L. $\Rightarrow$ N allowed $\bar{q}$ vectors in the 1st BZ and hence $2N$ allowed electron states in each energy band (factor of 2 from spin $\uparrow$ or spin $\downarrow$ for each $\bar{q}$)

$\Rightarrow$ each energy band can hold 2 electrons per Bravais lattice site

Assume for simplicity we have a crystal structure with one ion at each BL site, with valence Z. ie each BL site contributes Z conduction electrons

In 1-D, since energy bands do not overlap:

① If $Z = 2m$ is <u>even</u>, then we completely fill up the lowest m bands and all other bands are completely empty

② If $Z = 2m+1$ is <u>odd</u>, then we completely fill up the lowest m bands, and the $(m+1)^{st}$ band is ½ filled. All higher bands are completely empty.

<u>Case ① Z even</u>: material is an <u>insulator</u>

At low T in equilibrium, bands are completely filled or completely empty $\Rightarrow$ there is an energy gap ε_g between the most energetic electron and the lowest unoccupied electron state (ie the first excited state)
$$\varepsilon_g = \min_q \varepsilon_{n+1}(q) - \max_q \varepsilon_n(q)$$

$\Rightarrow$ Unless electrons somehow receive an energy $\gtrsim \varepsilon_g$, they cannot scatter - no ~~nearby~~ empty states nearby in energy to scatter to! We will soon see that a filled band can carry no current
$\Rightarrow$ material is an insulator provided $k_B T \lesssim \varepsilon_g$ and $eE l \lesssim \varepsilon_g$ where l is the mean free path

When $k_B T \gtrsim \varepsilon_g$, the equilibrium state will have some electrons, with density $\sim e^{-\varepsilon_g/k_B T}$ excited over the gap ε_g from the top of the $m = Z/2$ band into the bottom of the $m+1$

band. Now these electrons at bottom of m+1 band
at at top of m band will have nearly empty
states they can scatter into. Applying an $\vec{E}$ field
will scatter electrons and create a non equilibrium
distribution that carries a finite current.

$$\Rightarrow \begin{cases} k_B T \ll \varepsilon_g \Rightarrow \text{insulator} \\ k_B T \gtrsim \varepsilon_g \Rightarrow \underline{\text{semiconductor}} - \text{carrier} \\ \qquad\qquad\qquad\qquad \text{density} \sim e^{-\varepsilon_g / k_B T} \end{cases}$$

case ② Z odd : Material is a metal
The highest band containing electrons is partially
(half) filled at T=0,

$\Rightarrow$ at any T there are empty states nearby in
energy ~~to scatter into more energy gap~~
to the most energetic electrons at ε_F.
There is no energy gap. When applying
electric field $\vec{E}$ one will set up a
non-equilibrium distribution carry a current

So for 1-D weak potential, Z odd $\Rightarrow$ metal
Z even $\Rightarrow$ insulator
This was a consequence of the non-overlapping bands.

But in 2-D or 3-D (or even perhaps 1-D when
potential is NOT weak) bands <u>can</u> overlap,

ie we may have the case that

$$\max_q \varepsilon_n(q) > \min_q \varepsilon_{n+1}(q)$$

In such a case, as one constructs the ground state, one will start to fill up the $n+1$ band before one has completely filled the n band.

Thus Z even <u>need not be an insulator</u> — we might have more than one partially filled band containing the most energetic electrons at ε_F

$\Rightarrow$ metal.
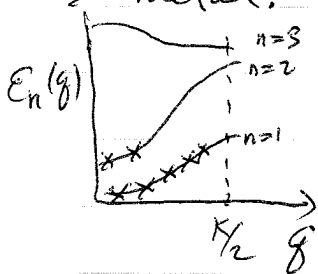
{when bands overlap, can have several partially filled bands before completely filling a given band

However, we still <u>would expect</u> that if a material is an <u>insulator</u>, it must have only completely filled bands and completely empty bands (so no scattering possible). Since each filled band holds 2 electrons per Bravais lattice site, we would still expect Z must be <u>even</u>.

Thus we would expect that Z even is a necessary but not sufficient condition to have an insulator.

But it turns out that even this is not always true. While most insulators do have Z even, it was known in 1940's that some transition metal oxides, such as NiO and CoO, have Z odd but are still insulators!

Such materials, where Z is odd but material is an insulator, are called __Mott insulators__. It is believed that in these cases strong electron-electron interactions are responsible for the effect, invalidating the conclusions of the independent electron approximation that is the basis of band theory. To study such problems the simple __Hubbard model__ is often ~~used~~ (the Hubbard model is simple to state, but very difficult to solve!)

2D weak potential band structure — single square BL

R.L. in square with $\vec{K} = K(n\hat{x} + m\hat{y})$ n, m integers

$K = 2\pi/a$

$a = $ lattice constant BL

The smallest R.L. vectors are

$\vec{K}_0 = 0$

$\{\vec{K}_1\} = \{ K\hat{x}, -K\hat{x}, K\hat{y}, -K\hat{y} \}$

$\{\vec{K}_2\} = \{ K(\hat{x}+\hat{y}), K(\hat{x}-\hat{y}), K(-\hat{x}+\hat{y}), K(-\hat{x}-\hat{y}) \}$
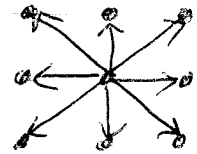
For $\vec{q} = q\hat{x}$ in 1st BZ, ie $0 \le q \le \frac{K}{2}$, we will plot the band structure, in the reduced zone scheme, for all bands corresponding the above 8 R.L. vectors.

$$\mathcal{E}_i(\vec{q}) = \frac{\hbar^2}{2m}(\vec{q} + \vec{K}_i)^2 \quad \text{measure energy in units of} \quad \mathcal{E}_x = \frac{\hbar^2}{2m}\left(\frac{K}{2}\right)^2$$

R.L. vector	energy		degeneracy	
$\vec{K}_0 = 0$	$\varepsilon = \frac{\hbar^2 q^2}{2m}$	$\mathcal{E}/\mathcal{E}_x = 4(q/K)^2$	1	(a)

$\{\vec{K}_1\}$

$-K\hat{x}$	$\varepsilon = \frac{\hbar^2}{2m}(q-K)^2$	$\mathcal{E}/\mathcal{E}_x = 4\left(\frac{q}{K}-1\right)^2$	1	(b)
$+K\hat{x}$	$\varepsilon = \frac{\hbar^2}{2m}(q+K)^2$	$\mathcal{E}/\mathcal{E}_x = 4\left(\frac{q}{K}+1\right)^2$	1	(c)
$\pm K\hat{y}$	$\varepsilon = \frac{\hbar^2}{2m}(q^2+K^2)$	$\mathcal{E}/\mathcal{E}_x = 4\left(\left(\frac{q}{K}\right)^2+1\right)$	2	(d)

$\{\vec{K}_2\}$

$K(-\hat{x}\pm\hat{y})$	$\varepsilon = \frac{\hbar^2}{2m}\left[(q-K)^2+K^2\right]$	$\mathcal{E}/\mathcal{E}_x = 4\left[\left(\frac{q}{K}-1\right)^2+1\right]$	2	(e)
$K(+\hat{x}\pm\hat{y})$	$\varepsilon = \frac{\hbar^2}{2m}\left[(q+K)^2+K^2\right]$	$\mathcal{E}/\mathcal{E}_x = 4\left[\left(\frac{q}{K}+1\right)^2+1\right]$	2	(f)

we plot the above curves of $\mathcal{E}/\mathcal{E}_x$ vs q/K
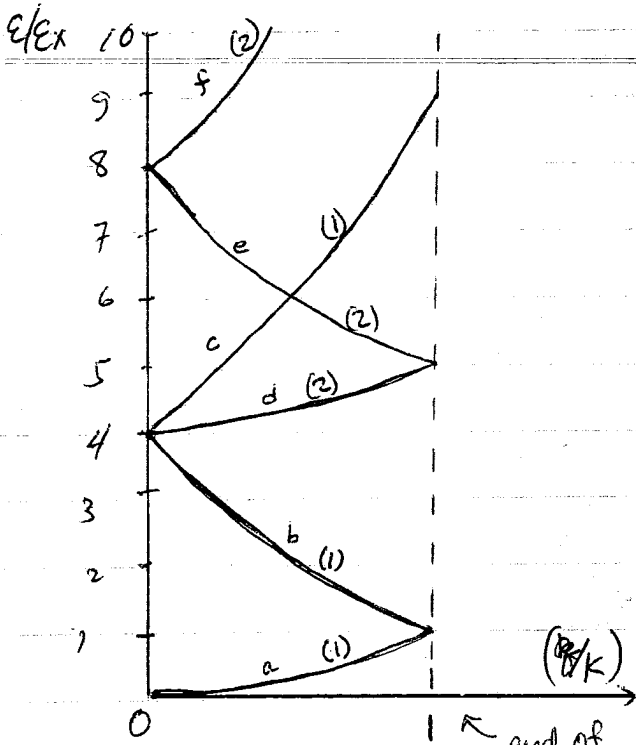in reduced zone scheme

Reciprocal Lattice and k-space for a two-dimensional square Bravais Lattice of lattice constant *a*.
Bragg planes are labeled by the reciprocal lattice vector that they bisect, **K** = (2π/a)(n, m) .

1st BZ   2nd BZ   3rd BZ   4th BZ
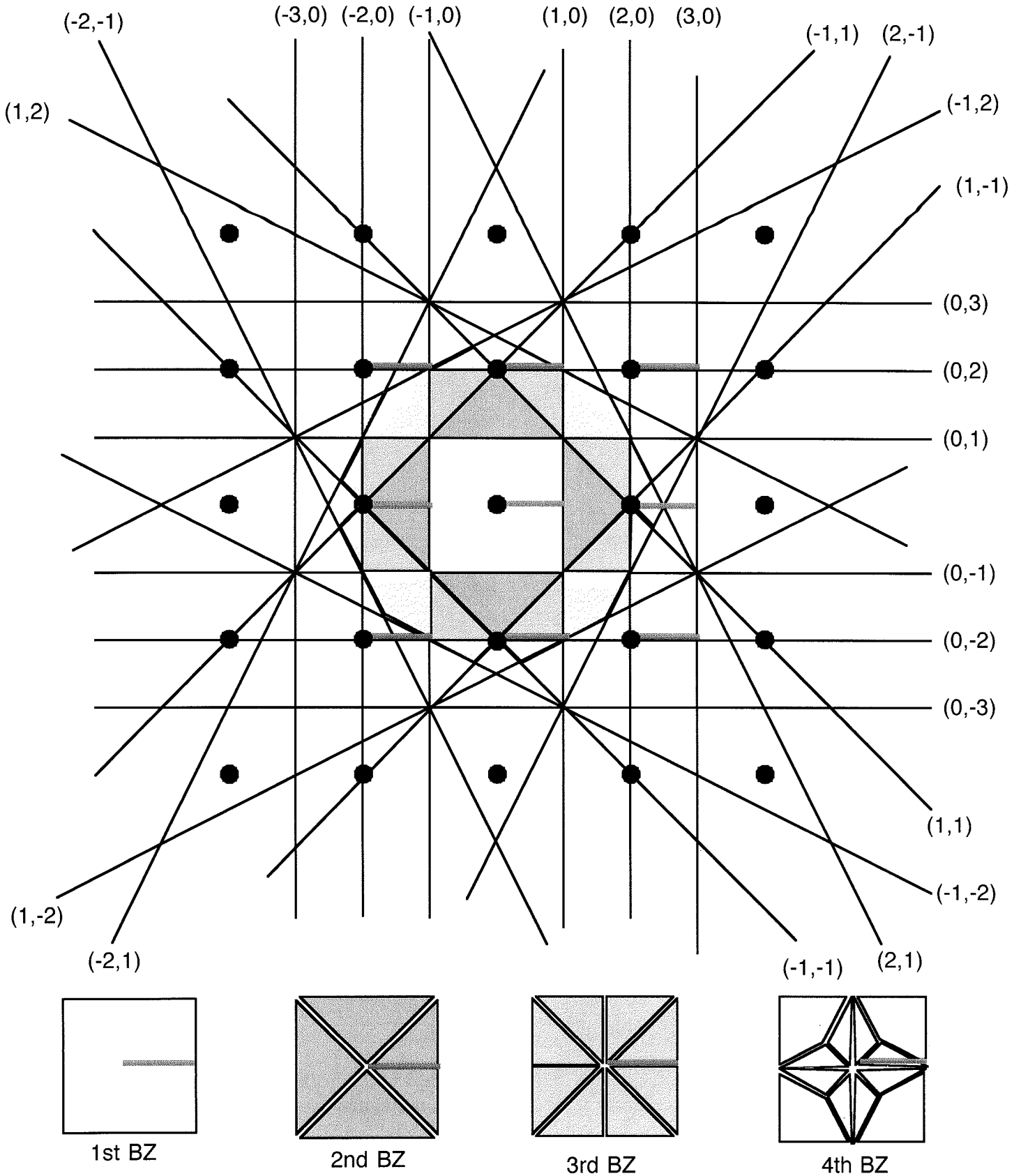
Pieces of the nth Brillouin Zone translated back into the 1st BZ

Red lines indicate values of $\vec{k}$ for free electron states
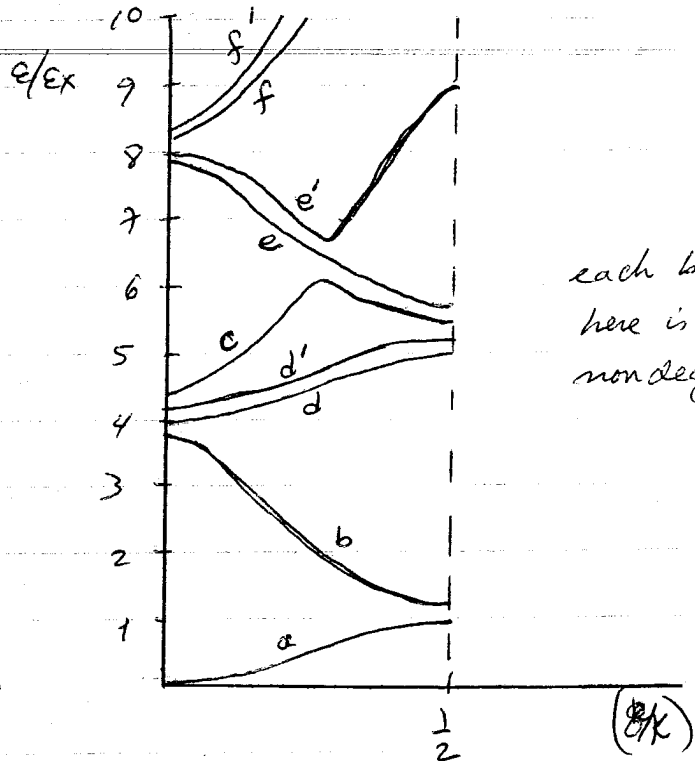giving rise to the band structure plotted in reduced ~~set~~ zone
scheme on preceding page.

free electrons graph: $\varepsilon/\varepsilon_x$ axis with markings 1–10, curves labeled a (1), b (1), c, d (2), e, f (2), with (1) and (2) degeneracy labels. x-axis (k/K), from 0 to $\frac{1}{2}$.

reduced zone scheme

$\frac{1}{2}$ ← end of 1st BZ in $\hat{x}$ direction

weak potential graph: $\varepsilon/\varepsilon_x$ axis 1–10, curves labeled a, b, c, d, d', e, e', f, f'. x-axis (k/K), $\frac{1}{2}$.

each band here is non degenerate

free electrons	weak potential
a) 1st BZ	a) 1st BZ
b) 2nd BZ	b) 2nd BZ
d) 3rd + 4th BZs	d) 3rd BZ
c) 5th + 7th BZs	d') 4th BZ
e) 5th, 6th + 7th BZs	c) 5th BZ
f) 8th + 9th BZ + higher	e) 6th BZ
	e') 7th BZ
	f) 8th BZ
	f') 9th BZ

Weak potential splits degeneracies
More complicated band structure than in 1 dimension
Not necessarily true that $\max[\varepsilon_n(\vec{k})] \leq \min[\varepsilon_{n+1}(\vec{k})]$

We can do the same thing for wave vectors along the $\underline{\text{diagonal}}$ of the 1st BZ, ie $\vec{q} = g(\hat{x} + \hat{y})$, $0 \le g \le K/2$

R.L.	energy		degeneracy
$\vec{K}_0 = 0$	$\varepsilon = \dfrac{\hbar^2 g^2}{2m}(2)$	$\varepsilon/\varepsilon_x = 8(g/K)^2$	1 (a)

$\{\vec{K}_1\}$
$$\begin{cases} -K\hat{x}, -K\hat{y} & \varepsilon = \dfrac{\hbar^2}{2m}\left[(g-K)^2 + g^2\right] & \varepsilon/\varepsilon_x = 4\left[\left(\tfrac{g}{K}-1\right)^2 + \left(\tfrac{g}{K}\right)^2\right] & 2\ (b) \\[4mm] +K\hat{x}, +K\hat{y} & \varepsilon = \dfrac{\hbar^2}{2m}\left[(g+K)^2 + g^2\right] & \varepsilon/\varepsilon_x = 4\left[\left(\tfrac{g}{K}+1\right)^2 + \left(\tfrac{g}{K}\right)^2\right] & 2\ (c) \end{cases}$$

$\{\vec{K}_2\}$
$$\begin{cases} -K\hat{x} - K\hat{y} & \varepsilon = \dfrac{\hbar^2}{2m}\left[2(g-K)^2\right] & \varepsilon/\varepsilon_x = 8\left[\tfrac{g}{K}-1\right]^2 & 1\ (d) \\[4mm] +K\hat{x} + K\hat{y} & \varepsilon = \dfrac{\hbar^2}{2m}\left[2(g+K)^2\right] & \varepsilon/\varepsilon_x = 8\left[\tfrac{g}{K}+1\right]^2 & 1\ (e) \\[4mm] \left.\begin{array}{c} -K\hat{x} + K\hat{y} \\ K\hat{x} - K\hat{y} \end{array}\right\} & \varepsilon = \dfrac{\hbar^2}{2m}\left[(g+K)^2 + (g-K)^2\right] & \varepsilon/\varepsilon_x = 4\left[\left(\tfrac{g}{K}+1\right)^2 + \left(\tfrac{g}{K}-1\right)^2\right] & 2\ (f) \end{cases}$$

free electrons   weak potential

gaps open up where free electron states are degenerate

weak potential "lifts" degeneracies

$\left[\begin{array}{l}\text{To represent band structure in 2D or 3D one picks } \vec{q} \text{ in certain} \\ \text{symmetry directions, and plots } \varepsilon_n(\vec{q}) \text{ vs } |\vec{q}| \text{ along these} \\ \text{directions, as done above.}\end{array}\right]$

$(\vec{g}+K_x)^2$

$(\vec{g}-K_x')^2$

$(\vec{g}+K_L)^2$

$(\vec{g}-K_L)^2$

$(\vec{g}-K_x)^2$

g^2
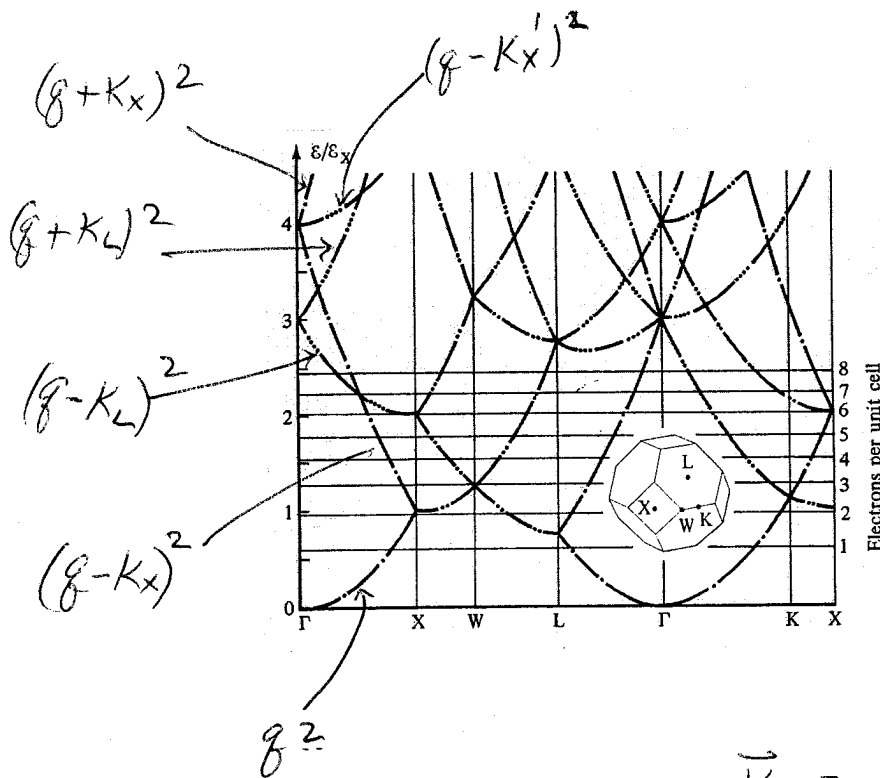
A & M

Figure 9.5
Free electron energy levels for an fcc Bravais lattice. The energies are plotted along lines in the first Brillouin zone joining the points $\Gamma(\mathbf{k} = 0)$, K, L, W, and X. ε_x is the energy at point X $([\hbar^2/2m][2\pi/a]^2)$. The horizontal lines give Fermi energies for the indicated numbers of electrons per primitive cell. The number of dots on a curve specifies the number of degenerate free electron levels represented by the curve. (From F. Herman, in *An Atomistic Approach to the Nature and Properties of Materials*, J. A. Pask, ed., Wiley, New York, 1967.)

plot $\varepsilon^0_{\vec{g}-k}$ for
$\vec{g}$ in special directions
for all $\vec{K}$ in R-L.

$\vec{K}_x = (1,0,0)$

$\vec{K}_L = \left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right)$

$\vec{g}_x = \left(\frac{1}{2},0,0\right)$
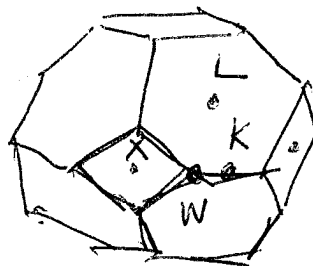
$X' \leftarrow$ 1st BZ of fcc

A+M

Figure 15.11

Burdick's calculated bands for copper, illustrating that the absorption threshold for transitions up from the conduction band is about 4 eV, while the threshold for transitions from the *d*-band to the conduction band is only about 2 eV. (The energy scale is in tenths of a rydberg (0.1 Ry = 1.36 eV).) Note the resemblance of the bands other than the *d*-bands to the free electron bands plotted below.

→ s band - free electron like

} d bands - tight binding like

$Cu = [Ar] 3d^{10} 4s^1$
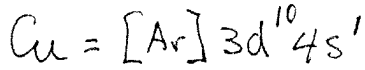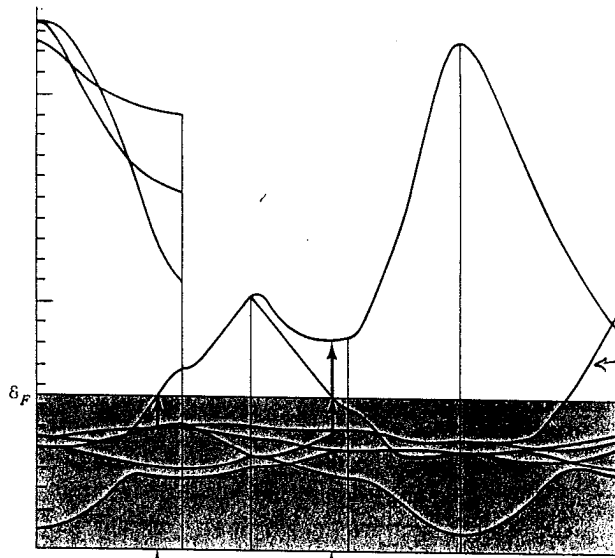
free electron bands →
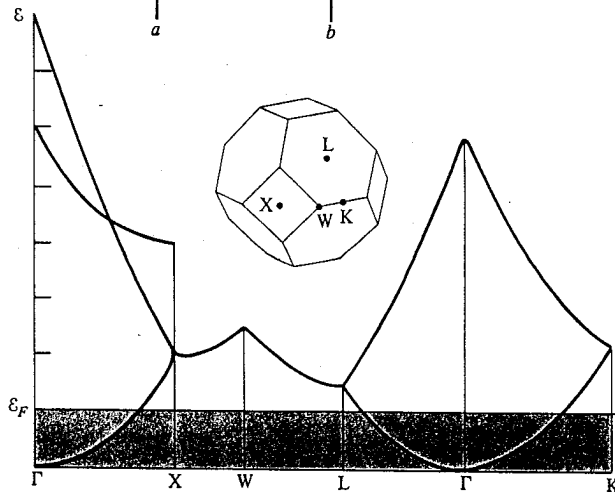
A+M

Figure 11.9

Calculated valence bands for aluminum (three electrons outside of a closed-shell neon configuration) compared with *free* electron bands (dashed lines). The bands are computed by the KKR method. (B. Segall, *Phys. Rev.* **124**, 1797 (1961).)

$AL = [Ne] 3s^2 3p^1$
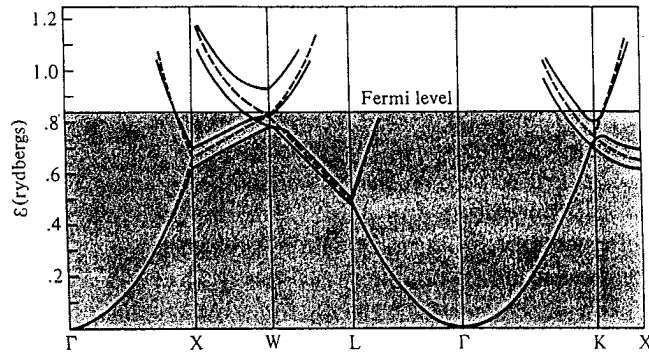
$Z = 3$

Bravais Lattice with a basis

Suppose we have a monatomic BL with a basis (all atoms identical). If $\phi(\vec{r} - \vec{r_0})$ is the potential from the ion centered at $\vec{r_0}$, then the periodic ion potential is

$$U(\vec{r}) = \sum_i \sum_j \phi(\vec{r} - \vec{R_i} - \vec{d_j})$$

since ions are located at positions $\vec{R_i} + \vec{d_j}$

Fourier transform is:

$$U_K = \frac{1}{v} \int_{\substack{primitive \\ cell}} d^3r \; e^{-i\vec{K}\cdot\vec{r}} \sum_{ij} \phi(\vec{r} - \vec{R_i} - \vec{d_j})$$

$$= \frac{1}{V} \int_{\substack{all \\ space}} d^3r \; e^{-i\vec{K}\cdot\vec{r}} \sum_{ij} \phi(\vec{r} - \vec{R_i} - \vec{d_j})$$

$$= \sum_i \frac{1}{V} \int_{\substack{all \\ space}} d^3r \; e^{-i\vec{K}\cdot\vec{r}} \sum_j \phi(\vec{r} - \vec{R_i} - \vec{d_j})$$

let $\vec{r}' = \vec{r} - \vec{R_i}$ and do change of integration variable

$$U_K = \sum_i \frac{1}{V} \int_{\substack{all \\ space}} d^3r' \; e^{-i\vec{K}\cdot(\vec{r}' + \vec{R_i})} \sum_j \phi(\vec{r}' - \vec{d_j})$$

$$= \sum_i \frac{1}{V} \int_{\substack{all \\ space}} d^3r' \; e^{-i\vec{K}\cdot\vec{r}'} \sum_j \phi(\vec{r}' - \vec{d_j})$$

since $\vec{K}\cdot\vec{R_i} = 2\pi$

$$= \frac{N}{V} \int_{\substack{all \\ space}} d^3r' \; e^{-i\vec{K}\cdot\vec{r}'} \sum_j \phi(\vec{r}' - \vec{d_j})$$

Since all the terms in the $\sum_i$ are now identical

$$u_K = \frac{1}{v} \int_{\substack{\text{all} \\ \text{space}}} d^3r \; e^{-i\vec{K}\cdot\vec{r}} \sum_j \phi(\vec{r}-\vec{d_j}) \qquad \text{as } v \equiv \frac{V}{N}$$

substitute in F.T. of $\phi(\vec{r})$

$$\phi(\vec{r}-\vec{d_j}) = \int \frac{d^3k'}{(2\pi)^3} e^{i\vec{k}'\cdot(\vec{r}-\vec{d_j})} \phi_{k'}$$

So

$$u_K = \frac{1}{v} \int d^3k' \; \phi_{k'} \underbrace{\int_{\substack{\text{all} \\ \text{space}}} \frac{d^3r}{(2\pi)^3} e^{i(\vec{k}'-\vec{K})\cdot\vec{r}}}_{\delta(\vec{k}'-\vec{K})} \sum_j e^{-i\vec{k}'\cdot\vec{d_j}}$$

$$= \frac{1}{v} \phi_K \sum_j e^{-i\vec{K}\cdot\vec{d_j}}$$

$$u_K = \frac{1}{v} \phi_K S_K \qquad \text{proportional to geometric structure factor } S_K$$

If S_K vanishes — we saw that there will be no diffraction peak in x-ray scattering at $\vec{K}$.

Now we see the analogous result, when $S_K = 0$ then $u_K = 0$, and there will be no energy gap opening up for electron states with $\vec{k}$ that lie on the Bragg plane bisecting $\vec{K}$.

An important case where this happens is for hcp crystals

For hcp $\quad \vec{a}_1 = a\hat{x}$, $\vec{a}_2 = \frac{a}{2}\hat{x} + \frac{\sqrt{3}a}{2}\hat{y}$, $\vec{a}_3 = c\hat{z}$

two point basis $\quad \vec{d}_1 = 0$, $\vec{d}_2 = \frac{1}{3}(\vec{a}_1 + \vec{a}_2) + \frac{1}{2}\vec{a}_3$
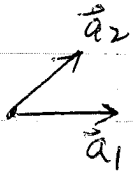
↑ lies in center of cells of triangular lattice in xy plane, and halfway between the two triangular layers

R.L.

$$\vec{K} = n_1\vec{b}_1 + n_2\vec{b}_2 + n_3\vec{b}_3 \qquad \begin{cases} \vec{b}_1 = \frac{4\pi}{\sqrt{3}a}\left(\frac{1}{2}\hat{x} - \frac{\sqrt{3}}{2}\hat{y}\right) \\[2mm] \vec{b}_2 = \frac{4\pi}{\sqrt{3}a}\hat{y} \\[2mm] \vec{b}_3 = \frac{2\pi}{c}\hat{z} \end{cases}$$
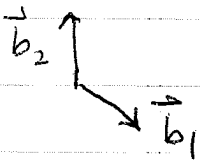
Then $\quad S_K = e^{-i\vec{K}\cdot\vec{d}_1} + e^{-i\vec{K}\cdot\vec{d}_2}$

$$= 1 + e^{-i(n_1\vec{b}_1 + n_2\vec{b}_2 + n_3\vec{b}_3)\cdot\left(\frac{\vec{a}_1}{3} + \frac{\vec{a}_2}{3} + \frac{\vec{a}_3}{2}\right)}$$

$$S_K = 1 + e^{-2\pi i\left(\frac{n_1}{3} + \frac{n_2}{3} + \frac{n_3}{2}\right)}$$

If, for example, $n_1 = n_2 = 0$, $n_3 = \pm 1$, then $S_K = 0$. So no gap opens on the Bragg plane that bisects $\vec{K} = \pm\frac{2\pi}{c}\hat{z}$ — i.e. the top and bottom surfaces of the 1st BZ.

1st BZ $\qquad$ } no gap on these Bragg planes !
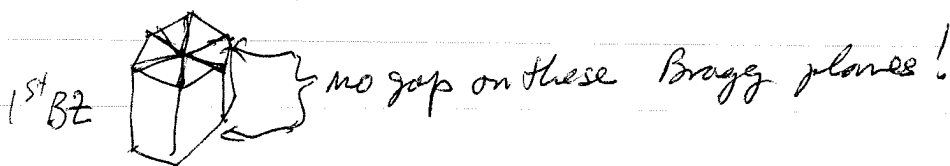
(and Fermi Surface)

Zones in Two dimensions   —single square BZ
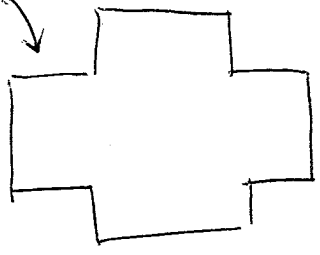
Draw in Bragg planes
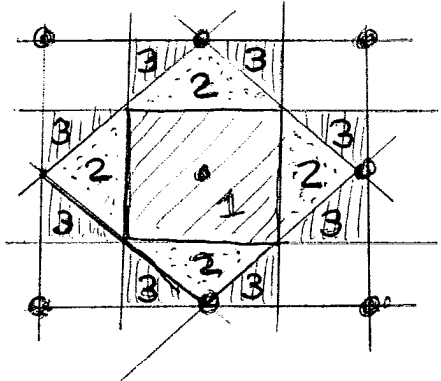
so <u>outer</u> surface 1st zone looks like

1
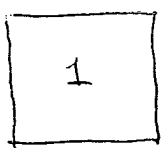
outer surface 2nd zone is →

2
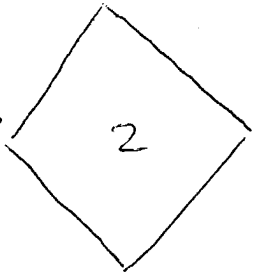
outer surface 3rd zone is ↘

surface of nth zone gets more complicated as n increases

To find shape of constant energy surface (fermi surface) in weak potential approx:

1) Draw free fermi sphere corresponding to desired energy

2) See ~~state~~ which zones surface of sphere intersects. There will be branches of surface in each ~~state~~ ~~zones~~ <u>band, corresponding to ~~one~~ the</u>

3) deform free energy sphere where it intersects zone boundary so that it is ⊥ to Bragg plane (HW problem #2)
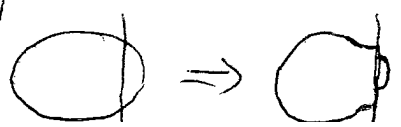
(often ignore this step as 1st approx)

4) This gives constant energy surface in _extended_ zone scheme. Translate branches of surface in nth zone back to 1st zone (by adding appropriate recip lattice vector) to get branches of surface in _reduced_ zone scheme. _On_ translate through all recip lattice vectors to get _repeated_ zone scheme.
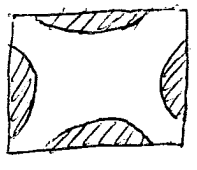
example

extended zone scheme
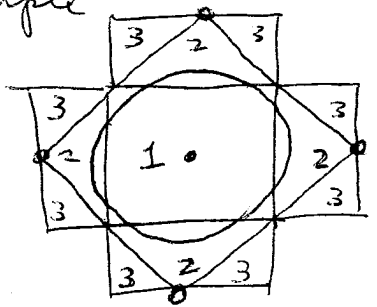
This free electron surface intersects _of energy ε_0_ 1st & 2nd zones only

Translate pieces of curves back to 1st B

branches of surface in 1st ~~zone~~ band.
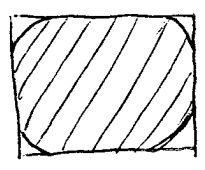
reduced zone scheme

branches of surface in 2nd ~~zone~~ band translated back to _1st BZ_

Branches of curve in _reduced_ zone scheme shaded areas are states of lower energy $\varepsilon < \varepsilon_0$. unshaded areas are states of greater energy $\varepsilon > \varepsilon_0$

In _repeated_ ~~extended~~ zone scheme, branches look like

holes
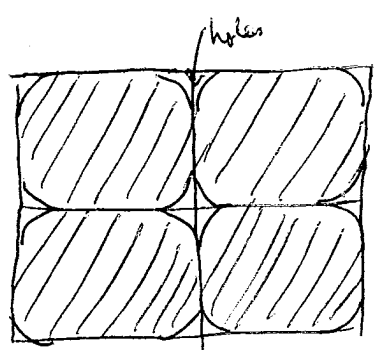
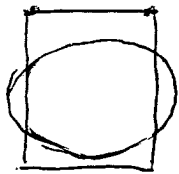...ches in 1st zone
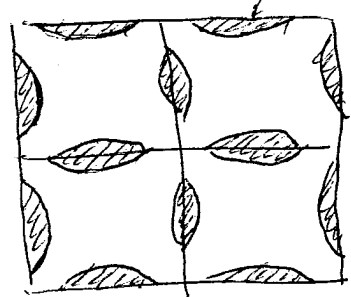
electrons

branches in 2nd zone

branches of fermi surface are closed curves

If surface we have drawn is fermi surface, then shaded areas are filled states.
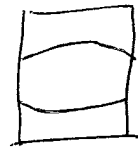
In 1st band we have small pockets of holes ⎫ more meaning
In 2nd band we have small pockets of electrons ⎬ to this when
  we get to dynamics

In both cases, the constant energy surface in the repeated zone scheme is a <u>closed</u> curve. This need not be the case for a less symmetric crystal
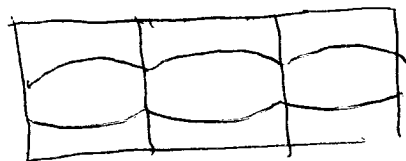
1st BZ

in this case, branches in 1st zone are

when we extend to repeated zone scheme we get

surface of constant energy is an <u>open</u> curve

the distinction between open and closed surfaces will be very important when we consider the dynamics (motion in magnetic field – energy conserved – electron moves on const energy surface). See text for pictures in 3-D.

Note that in 2 + 3 dimensions, one always has partially full bands. ⇒ weak potential method does not give insulators or semiconductors.

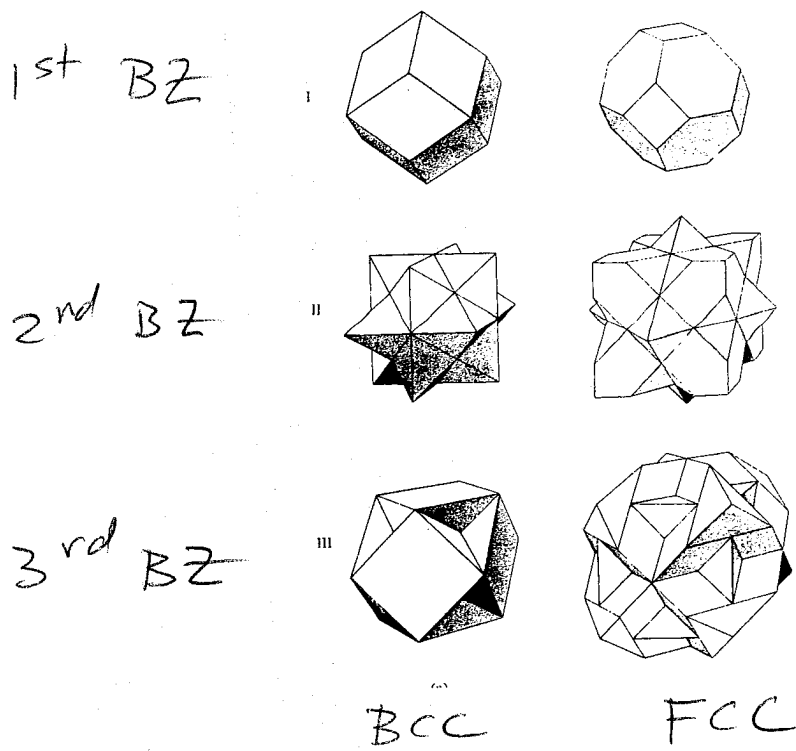See Ashcroft + Mermin Figs 9.8 and 9.9 for BZ's and Fermi surface branches in 3D

1st BZ

2nd BZ

3rd BZ

BCC   FCC

Free electron
Fermi surface
FCC

Z = 4
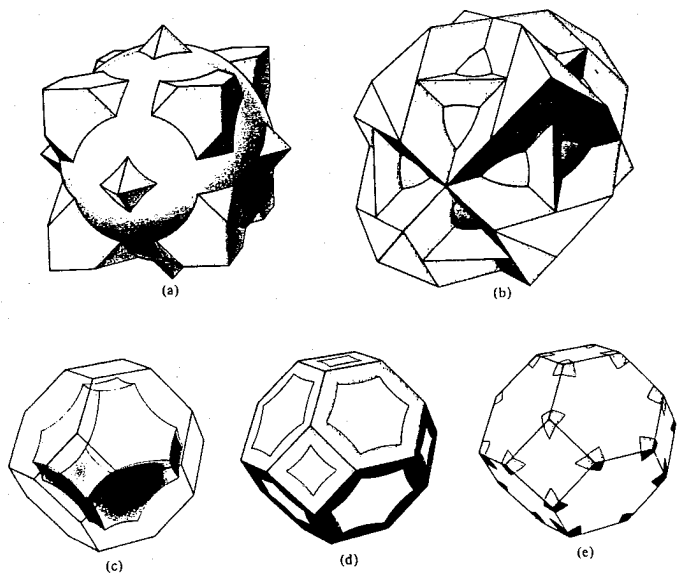

(a)   (b)

(c)   (d)   (e)

Figure 9.9
The free electron Fermi sphere for a face-centered cubic metal of valence 4. The first zone lies entirely within the interior of the sphere, and the sphere does not extend beyond the fourth zone. Thus the only zone surfaces intersected by the surface of the sphere are the fourth zone. Thus the only zone surfaces intersected by the surface of the sphere are the (exterior) surfaces of the second and third zones (cf. Figure 9.8b). The second-zone Fermi surface consists of those parts of the surface of the sphere lying entirely within the polyhedron bounding the second zone (i.e., all of the sphere except the parts extending beyond the polyhedron in (a)). When translated through reciprocal lattice vectors into the first zone, the pieces of the second-zone surface give the simply connected figure shown in (c). (It is known as a "hole surface"; the levels it encloses have higher energies than those outside). The third-zone Fermi surface consists of those parts of the surface of the sphere lying outside of the second zone (i.e., the parts extending beyond the polyhedron in (a)) that do not lie outside the third zone (i.e., that are contained within the polyhedron shown in (b)). When translated through reciprocal lattice vectors into the first zone, these pieces of sphere give the multiply connected structure shown in (d). The fourth-zone Fermi surface consists of the remaining parts of the surface of the sphere that lie outside the third zone (as shown in (b)). When translated through reciprocal lattice vectors into the first zone they form the "pockets of electrons" shown in (e). For clarity (d) and (e) show only the intersection of the third and fourth zone Fermi surfaces with the surface of the first zone. (From R. Lück, *op. cit.*)