

Real metals

Monovalent metals

(1A)	<u>Alkali's</u>	(bcc)	(1B)	<u>Noble's</u>	(fcc)
Li	$[1s^2]2s^1$			-	
Na	$[Ne]3s^1$			-	
K	$[Ar]4s^1$		Cu	$[Ar]3d^{10}4s^1$	
Rb	$[Kr]5s^1$		Ag	$[Kr]4d^{10}5s^1$	
Cs	$[Xe]6s^1$		Au	$[Xe]4f^{14}5d^{10}6s^1$	

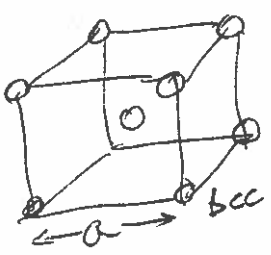
Rare earth configuration is tightly bound core, electrons here are in very low lying, narrow, filled tight binding bands. Can generally ignore them.

bcc) Alkalies - If we assume the single conduction electron moves completely freely in metal, the Fermi surface is a sphere of radius k_F

$$2 \times \frac{\frac{4}{3}\pi k_F^3}{(2\pi)^3} = \frac{k_F^3}{3\pi^2} = n = \frac{2}{a^3} \leftarrow \text{side of unit cell}$$

↑ spins

↑ density of ions



$$k_F = (6\pi^2)^{1/3} \frac{1}{a} = \left(\frac{6\pi^2}{(2\pi)^3}\right) \left(\frac{2\pi}{a}\right) = \left(\frac{3}{4\pi}\right)^{1/3} \left(\frac{2\pi}{a}\right)$$

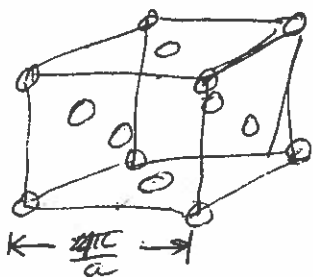
bcc unit cell has 2 atoms $\Rightarrow n = \frac{2}{a^3}$

$$\Rightarrow k_F = \left(\frac{3}{4\pi}\right)^{1/3} \left(\frac{2\pi}{a}\right) = 0.620 \left(\frac{2\pi}{a}\right)$$

↑ one half of side of unit cell in recip lattice.

unit cell of RL has side of length $\frac{4\pi}{a}$

1st BZ is Wigner Seitz cell of fcc lattice of unit cell size $\frac{4\pi}{a}$



nearest neighbor is $\frac{4\pi}{a} \sqrt{(\frac{1}{2})^2 + (\frac{1}{2})^2}$ away, so shortest distance to surface of 1st BZ is

$$k_0 = \frac{1}{2} \sqrt{\frac{1}{4} + \frac{1}{4}} \left(\frac{4\pi}{a}\right) = 0.707 \left(\frac{2\pi}{a}\right)$$

↳ bisect R-L vector to get dist to Bragg plane

so $\frac{k_F}{k_0} = \frac{0.620}{0.707} = 0.877$

fermi surface goes 0.877 of the way to closest pt on zone boundary

If weak potential, approx good, expect fermi surface to be very spherical - since not near Bragg plane (zone boundary) corrections to free electrons are only $O(U^2)$

That is the case. Sommerfeld model is ~~extremely~~ good in explaining Alkali's (Li not clear) (charge density wave?)

	Li	Na	K	Rb	Cs
-1/R _{Hall} nec	0.8	1.2	1.1	1.0	0.9

(Charge density waves in Li?)

magneto-resistance also ~~shows~~ is less ^H field dependant than other materials (Sommerfeld gives indep of H)

Low temp specific heat $C_v = \gamma T + O(T^3)$

$\gamma = \frac{\pi^2}{2} \left(\frac{k_B^2}{\epsilon_F}\right) n$ Free elec

γ measures $g(\epsilon_F)$

	γ free electron	γ expt
Li	1.8	4.2
Na	2.6	3.5
K	4.0	4.7
Rb	4.6	5.8
Cs	5.3	7.7

$\gamma = \frac{\pi^2}{3} k_B g(\epsilon_F)$
in general

~~Alkali~~ Noble Metals (fcc)

as in Alkalais, rare earth core is tightly bound + can be ignored. (also 4f electrons of Au)

Conduction electrons are the 11 $d^{10}s^1$ electrons.

⇒ need 6 bands at least (each band holds 2 elec's per B-lattice site)

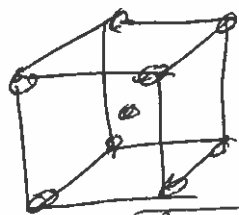
turns out 6 bands are enough. 5 lowest bands completely filled, 6th band half full. Bands look like 5 narrow bands (d-like tight binding) and one (s-band) nearly free electron like. However the nearly free electron s-band is mixed with narrow d-bands.

[Show Fig 15.4]

Fermi surface passes through 6th band (s-band) where it looks very free electron like - above narrow d-bands. Try free electron approx for the Fermi surface of half filled 6th band - $2 \cdot \frac{4\pi k_F^3}{(2\pi)^3} = n = \frac{4}{a^3}$ ← 4 con's per cubic cell of fcc BL

As before, add 1 electron per site to 6th band

$$\Rightarrow k_F = \left(\frac{2\pi}{a}\right) \left(\frac{3}{2}\right)^{1/3} = 0.782 \left(\frac{2\pi}{a}\right)$$



$$k_{\text{small}} = \sqrt{\left(\frac{1}{2}\right)^2 + \left(\frac{1}{2}\right)^2 + \left(\frac{1}{2}\right)^2} \left(\frac{4\pi}{a}\right)$$

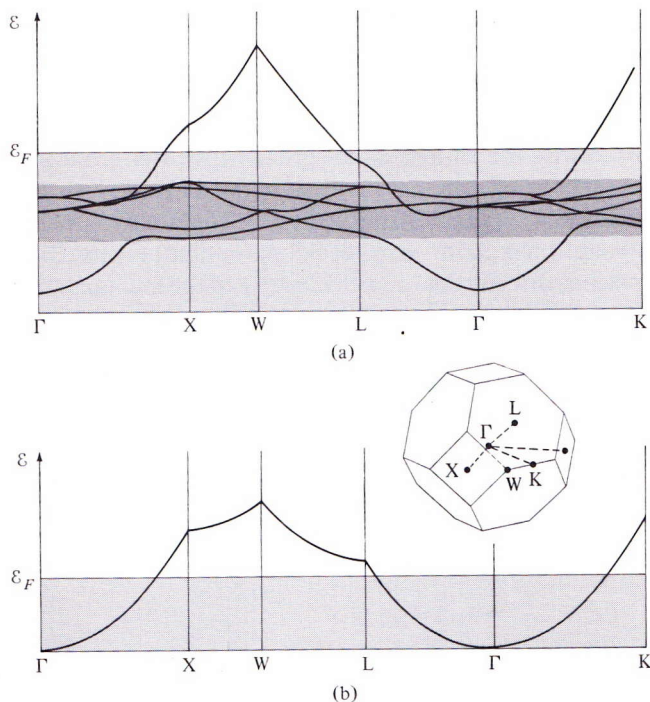
1st BZ is Wigner Seitz cell of bcc, closest pt

$$\text{on boundary from origin is at } k_0 = \frac{1}{2} \sqrt{\left(\frac{1}{2}\right)^2 + \left(\frac{1}{2}\right)^2 + \left(\frac{1}{2}\right)^2} \left(\frac{4\pi}{a}\right)$$

$$k_0 = \sqrt{\frac{3}{4}} \left(\frac{2\pi}{a}\right) = 0.866 \left(\frac{2\pi}{a}\right)$$

Figure 15.4

(a) Calculated energy bands in copper. (After G. A. Burdick, *Phys. Rev.* **129**, 138 (1963).) The ϵ vs. k curves are shown along several lines in the interior and on the surface of the first zone. (The point Γ is at the center of the zone.) The d -bands occupy the darkest region of the figure, whose width is about 3.5 eV. (b) The lowest-lying free electron energies along the same lines as in (a). (The energy scales in (a) and (b) are not the same.)



Note that the k dependence of the s -band levels, except where they approach the d -bands, bears a remarkable resemblance to the lowest free electron band for an fcc crystal (plotted in Figure 15.4b for comparison), especially if one allows for the expected modifications near the zone faces characteristic of a nearly free electron calculation (Chapter 9). Note also that the Fermi level lies far enough above the d -band for the s -band to intersect ϵ_F at points where the resemblance to the free electron band is still quite recognizable.⁴ Thus the calculated band structure indicates that for purposes of Fermi surface determination one might still hope for some success with a nearly free electron calculation. However, one must always keep in mind that not too far below the Fermi energy lurks a very complex set of d -bands, which can be expected to influence the metallic properties far more strongly than do any of the filled bands in the alkali metals.⁵

The Fermi surface for a single half-filled free electron band in an fcc Bravais lattice is a sphere entirely contained within the first Brillouin zone, approaching the surface of the zone most closely in the $\langle 111 \rangle$ directions, where it reaches 0.903 of the distance from the origin to the center of the hexagonal face. The de Haas-van Alphen

⁴ However, the Fermi level is close enough to the d -band to make the s -band nomenclature somewhat dubious for conduction band levels on the Fermi surface. A more precise specification of how s -like or d -like a level is must be based on a detailed examination of its wave function. In this sense most, but by no means all, levels at the Fermi surface are s -like.

⁵ The atomic ionization potentials provide a convenient reminder of the different roles played by filled bands in the alkali and noble metals. To remove the first ($4s$) and then the second ($3p$) electron from atomic potassium requires 4.34 and 31.81 eV, respectively. The corresponding figures for copper are 7.72 eV ($4s$) and 20.29 eV ($3d$).

$$k_F/k_0 = .782 / .866$$

$k_F/k_0 = .903 \Rightarrow$ nearly spherical might be expected

However in this direction of closest approach $\langle 111 \rangle$, Fermi surface distorts from sphere to touch zone boundary + give neck. Fermi surface in repeated zone scheme is multiply connected with open orbits as well as closed orbits



de Haas van Alphen expts with H in $\langle 111 \rangle$ direction have 2 period corresp to small area neck + wide area sphere

[Show Fig 15.5
Fig 15.6
Fig 15.7]

Magneto resistance shows dramatic effect ~~seen~~ in H dependence ~~the field is a function~~ with orientation of current wrt open orbits

	Cu	Ag	Au	
$-1/(R\mu_0)_{mec}$	1.5	1.3	1.5	} not bad
δ free elect	1.2	1.5	1.5	
δ expt	1.6	1.6	1.6	

← open orbits can cause problems!

$$R = \frac{-1}{mec(1+\lambda)} \text{ from single model (see later notes)}$$

$$\frac{-1}{Rmec} = \frac{mec(1+\lambda)}{mec} \approx 1+\lambda > 1 \text{ as above}$$

effect in all three noble metals reveals that their Fermi surfaces are closely related to the free electron sphere; however, in the $\langle 111 \rangle$ directions contact is actually made with the zone faces, and the measured Fermi surfaces have the shape shown in Figure 15.5. Eight “necks” reach out to touch the eight hexagonal faces of the zone, but otherwise the surface is not grossly distorted from spherical. The existence of these necks is most strikingly evident in the de Haas–van Alphen oscillations for magnetic fields in the $\langle 111 \rangle$ directions, which contain two periods, determined by the extremal “belly” (maximum) and “neck” (minimum) orbits (Figure 15.6). The ratio of the two periods directly determines the ratio of the maximal to minimal $\langle 111 \rangle$ cross sections.⁶

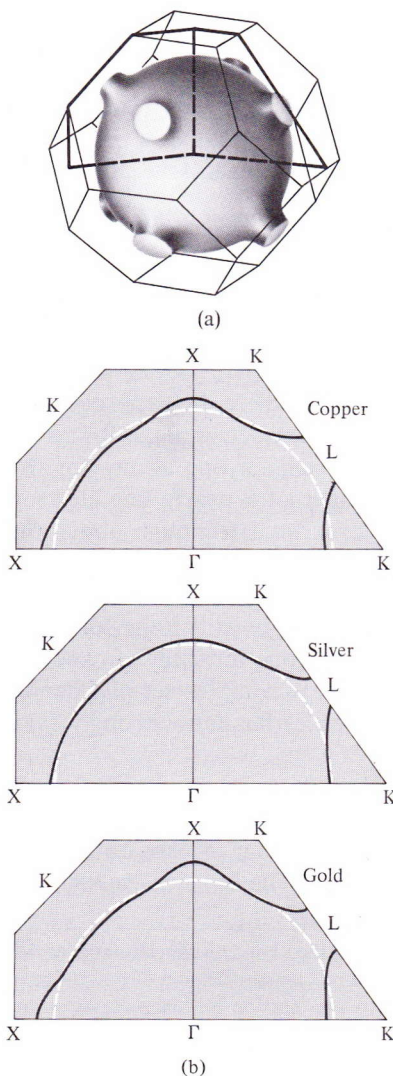


Figure 15.5

(a) In the three noble metals the free electron sphere bulges out in the $\langle 111 \rangle$ directions to make contact with the hexagonal zone faces. (b) Detailed cross sections of the surface for the separate metals. (D. Shoenberg and D. J. Roaf, *Phil. Trans. Roy. Soc.* **255**, 85 (1962).) The cross sections may be identified by a comparison with (a).

⁶ M. R. Halse, *Phil. Trans. Roy. Soc.* **A265**, 507 (1969). The entry for silver can be read directly from the experimental curve in Figure 15.6.

METAL	$A_{111}(\text{BELLY})/A_{111}(\text{NECK})$
Cu	27
Ag	51
Au	29

Although a distorted sphere, bulging out to make contact with the hexagonal zone faces, is still a fairly simple structure, when viewed in the repeated-zone scheme the noble metal Fermi surface reveals a variety of exceedingly complex orbits. Some of the simplest are shown in Figure 15.7. The open orbits are responsible for the very dramatic behavior of the magnetoresistance of the noble metals (Figure 15.8), whose

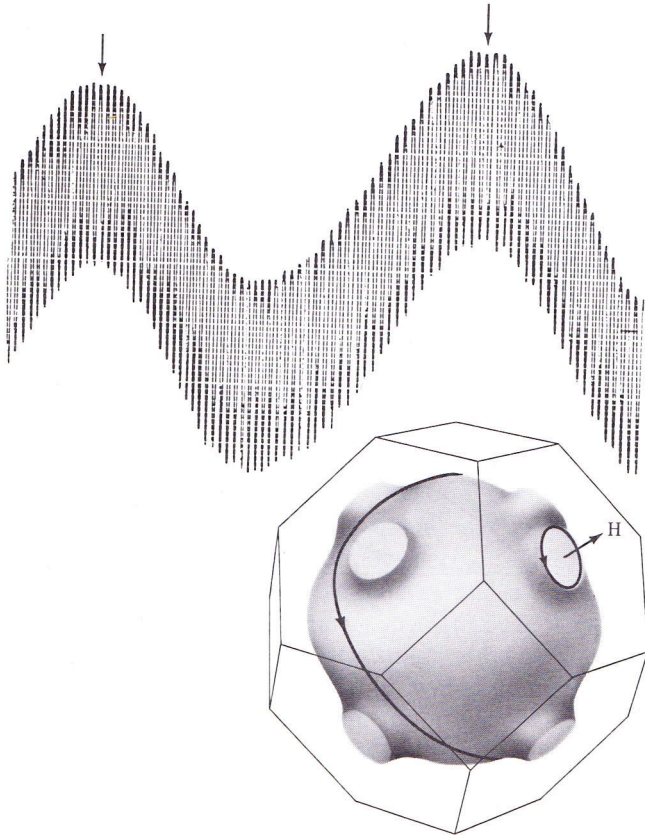
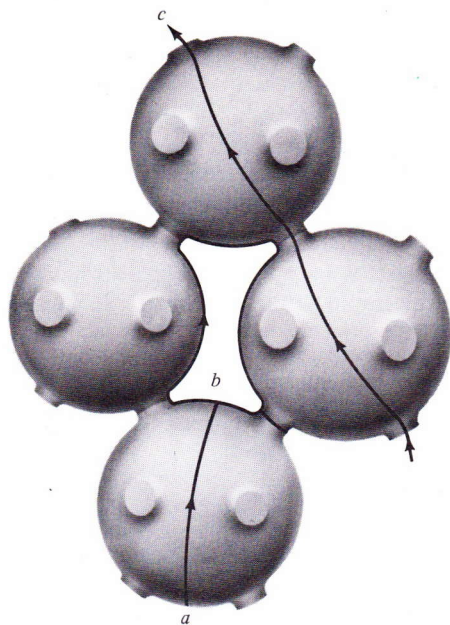
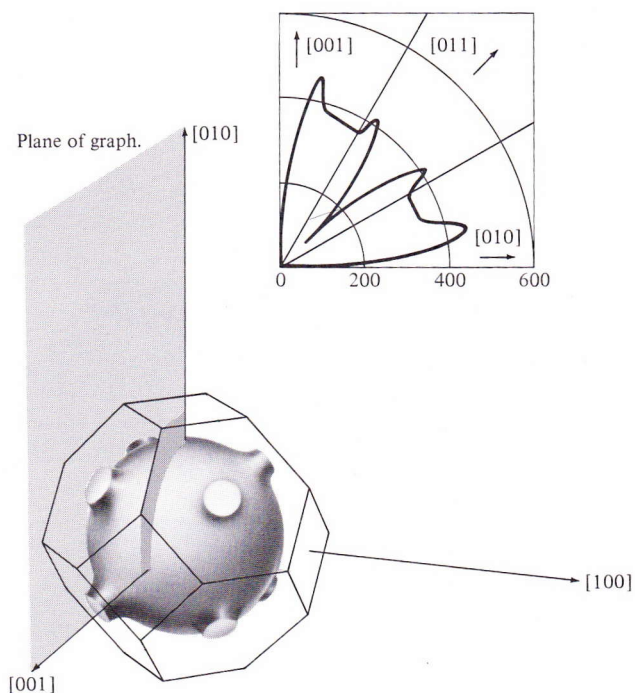


Figure 15.6

De Haas-van Alphen oscillations in silver. (Courtesy of A. S. Joseph.) The magnetic field is along a $\langle 111 \rangle$ direction. The two distinct periods are due to the neck and belly orbits indicated in the inset, the high-frequency oscillations coming from the larger belly orbit. By merely counting the number of high-frequency periods in a single low-frequency period (i.e., between the two arrows) one deduces directly that $A_{111}(\text{belly})/A_{111}(\text{neck}) = 51$. (Note that it is not necessary to know either the vertical or horizontal scales of the graph to determine this fundamental piece of geometrical information!)

**Figure 15.7**

Indicating only a few of the surprisingly many types of orbits an electron can pursue in k -space when a uniform magnetic field is applied to a noble metal. (Recall that the orbits are given by slicing the Fermi surface with planes perpendicular to the field.) The figure displays (a) a closed particle orbit; (b) a closed hole orbit; (c) an open orbit, which continues in the same general direction indefinitely in the repeated-zone scheme.

**Figure 15.8**

The spectacular direction dependence of the high-field magnetoresistance in copper that is characteristic of a Fermi surface supporting open orbits. The [001] and [010] directions of the copper crystal are as indicated in the figure, and the current flows in the [100] direction perpendicular to the graph. The magnetic field is in the plane of the graph. Its magnitude is fixed at 18 kilogauss, and its direction varied continuously from [001] to [010]. The graph is a polar plot of

$$\frac{\rho(H) - \rho(0)}{\rho(0)}$$

vs. orientation of the field. The sample is very pure and the temperature very low (4.2 K—the temperature of liquid helium) to insure the highest possible value for $\omega_c\tau$. (J. R. Klauder and J. E. Kunzler, *The Fermi Surface*, Harrison and Webb, eds., Wiley, New York, 1960.)

Read ArM about Divalent - hcp, fcc, bcc

Trivalent $z=3$ Aluminum fcc

Fermi surface is close to free electron sphere for fcc BL with 3 conduction electrons per ion

If N is number of ions, then $3N$ is number of conduction electrons

Free electron Fermi sphere completely encloses 1st BZ and extends into the 2nd, 3rd, and 4th BZ. In reduced zone scheme, branch of the Fermi surface in 2nd zone encloses "holes", i.e. unoccupied states. The branch of the Fermi surface in the 3rd zone consists of connected tubes enclosing filled states, "electrons". In 4th zone the branch of Fermi surface is small isolated pockets enclosing occupied states.

In Al, the ion potential is strong enough that it causes the small pockets of electrons in the 4th zone to disappear.

Fermi surface lies just in the 2nd and 3rd zones (bands)

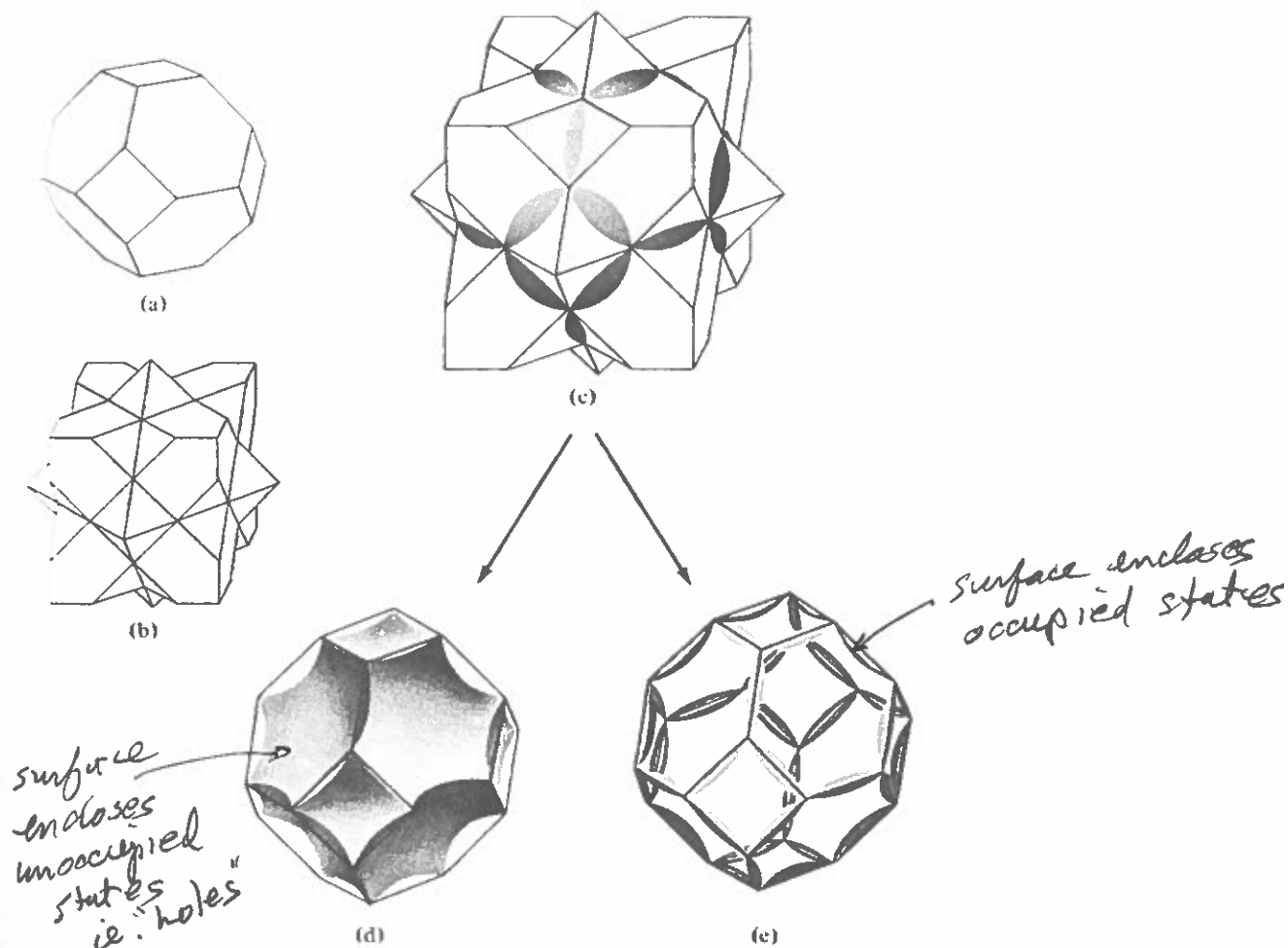
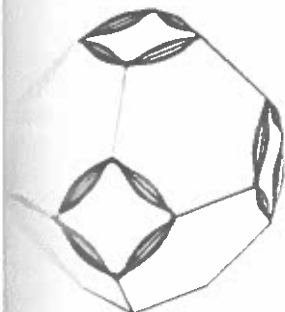


Figure 15.14

(a) First Brillouin zone for an fcc crystal. (b) Second Brillouin zone for an fcc crystal. (c) The free electron sphere for a trivalent monatomic fcc Bravais lattice. It completely encloses the first zone, passing through and beyond the second zone into the third and (at the corners) ever so slightly into the fourth. (d) Portion of the free electron sphere in the second zone when translated back into the first zone. The convex surface encloses holes. (e) Portion of the free electron sphere in the third zone when translated back into the first zone. The surface encloses particles. (The fourth-zone surface translates into microscopic pockets of electrons at all corner points.) (From R. Lück, doctoral dissertation, Technische Hochschule, Stuttgart, 1965.)

Figure 15.15

The third-zone surface of aluminum, in a reduced-zone scheme. (From N. W. Ashcroft, *Phil. Mag.* 8, 2055 (1963).)



← In Al, the con potential is strong enough that it eliminates the pockets of electrons on certain edges

Al is fcc BL with valence $Z = 3$

If N is # unit cells, then # conduction electrons is $3N$

Each band can hold $2N$ electrons

\Rightarrow lowest band completely filled - takes $2N$ states

\Rightarrow N electrons remain to go into 2nd and 3rd bands

If n is the electron density, then $n = \frac{3N}{V}$

$$N_e^{\text{II}} + N_e^{\text{III}} = N$$

electrons in band II + band III

$$N_e^{\text{II}} + N_h^{\text{II}} = 2N$$

occupied + unoccupied states

is $2N$

subtract

$$N_e^{\text{III}} - N_h^{\text{II}} = -N$$

in terms of densities, $n_e^{\text{III}} - n_h^{\text{II}} = -\frac{N}{V} = -\frac{n}{3}$

We will see that one can interpret transport properties of a partially filled band as if it was $-e$ charged electrons in the occupied states OR as $+e$ charged holes in the unoccupied states

So we interpret above as density n_e^{III} of electrons in band 3 and density n_h^{II} of holes in band 2. As in HW #1, this will behave like a system with

$$n_{\text{eff}} = n_e^{\text{III}} - n_h^{\text{II}} = -\frac{n}{3}$$

electrons, and have Hall coefficient

$$R_H = \frac{1}{n_{\text{eff}} e c} \quad \text{with } n_{\text{eff}} = -\frac{n}{3}$$

If we compute the free electron

$\frac{-1}{m_e c R_H}$, with n the total electron density

we then get, with $R_H = \frac{-1}{m_{\text{eff}} e c} = \frac{3}{m_e c}$

$$\text{then } \frac{-1}{m_e c R_H} = \frac{-1}{m_e c} \frac{m_e c}{3} = -\frac{1}{3}$$

Measurement of $\frac{-1}{m_e c R_H^{\text{exp}}} = -0.3$

so pretty good agreement! Band structure explains both the magnitude of $\frac{-1}{m_e c R_H}$ being $\frac{1}{3}$ of what we expect,

as well as the sign being opposite of what we expect!

A crucial reason, as we will soon see, why the above works is because the geometry of the Fermi surface in both 2nd and 3rd bands are closed. If the Fermi surface included open orbits, the situation gets much more complicated.

Tetravalent

$Z=4$

free Fermi sphere has branches in 2nd, 3rd, 4th BZ
But potential eliminates the pockets in 4th BZ

lead Pb

Tin Sn

For N ions there are $4N$ electrons

$2N$ electrons fill 1st band

$2N$ electrons are in 2nd and 3rd bands

electron density is $n = \frac{4N}{V}$

$$N_e^{II} + N_e^{III} = 2N$$

$$N_e^{II} + N_h^{II} = 2N$$

since $2N$ states in each band

$$\frac{N_e^{III}}{V} - \frac{N_h^{II}}{V} = 0 \Rightarrow m_e^{III} - m_h^{II} = m_{eff} = 0$$

But orbits of band \neq electrons contain open orbits \Rightarrow Hall effect more complicated

$Z=5$ Semi Metals

As, Sb, Bi are

BL with 2pt basis

$\Rightarrow 10N$ electrons ($N = \# \text{BL sites}$)

\Rightarrow free Fermi sphere has vol
5x vol 1st BZ

Free electron Fermi sphere
almost fills low lying bands,
leaves small pockets of holes
and small packets of electrons

\Rightarrow very low carrier density

Graphite $\sim 10^{17}/\text{cm}^3$, Bi $\sim 10^{18}/\text{cm}^3$

Sb $\sim 10^{19}/\text{cm}^3$, As $\sim 10^{20}/\text{cm}^3$

compared to more usual metals with $\sim 10^{22}/\text{cm}^3$

low carrier density \Rightarrow small $g(E_F)$

Transition Metals
Rare Earth metals