Section 10

Metals: Electron Dynamics and Fermi Surfaces

Electron dynamics

The next important subject we address is electron dynamics in metals. Our consideration will be based on a semiclassical model. The term "semiclassical" comes from the fact that within this model the electronic structure is described quantum-mechanically but electron dynamics itself is considered in a classical way, i.e. using classical equations of motion. Within the semiclassical model we assume that we know the electronic structure of metal, which determines the energy band as a function of the wave vector. The aim of the model is to relate the band structure to the transport properties as a response to the applied electric field.

Given the functions $E_n(\mathbf{k})$ the semiclassical model associates with each electron a position, a wave vector and a band index n. In the presence of applied fields the position, the wave vector, and the index are taken to evolve according to the following rules:

(1) The band index is a constant of the motion. The semiclassical model ignores the possibility of interband transitions. This implies that within this model it assumed that the applied electric field is small.

(2) The time evolution of the position and the wave vector of an electron with band index n are determined by the equations of motion:

$$\frac{d\mathbf{r}}{dt} = \mathbf{v}_n(\mathbf{k}) = \frac{1}{\hbar}\frac{dE_n(\mathbf{k})}{d\mathbf{k}} \tag{1}$$

$$\hbar\frac{d\mathbf{k}}{dt} = \mathbf{F}(\mathbf{r},t) = -e\mathbf{E}(\mathbf{r},t) \tag{2}$$

Strictly speaking Eq.(2) has to be proved. It is identical to the Newton's second law if we assume that the electron momentum is equal to $\hbar\mathbf{k}$. The fact that electrons belong to particular bands makes their movement in the applied electric field different from that of free electrons. For example, if the applied electric field is independent of time, according to Eq.(2) the wave vector of the electron increases uniformly with time.

$$\mathbf{k}(t) = \mathbf{k}(0) - \frac{e\mathbf{E}t}{\hbar} \tag{3}$$

Since velocity and energy are periodic in the reciprocal lattice, the velocity and the energy will be oscillatory. This is in striking contrast to the free electron case, where **v** is proportional to **k** and grows linearly in time.

The k dependence (and, to within a scale factor, the t dependence) of the velocity is illustrated in Fig.2, where both $E(k)$ and v(k) are plotted in one dimension. Although the velocity is linear in k near the band minimum, it reaches a maximum as the zone boundary is approached, and then drops back down, going to zero at the zone edge. In the region between the maximum of v and the zone edge the velocity actually decreases with increasing k, so that the acceleration of the electron is opposite to the externally applied electric force!

This extraordinary behavior is a consequence of the additional force exerted by the periodic potential, which is included in the functional form of $E(k)$. As an electron approaches a Bragg plane, the external electric field moves it in the opposite direction due to the Bragg-reflection.

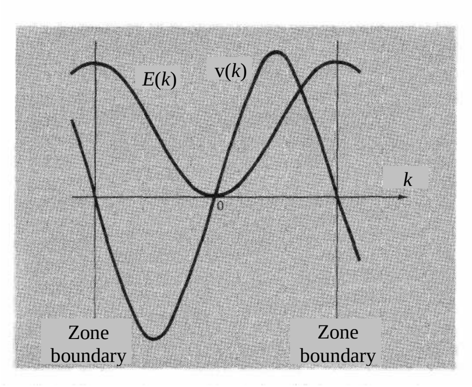

Fig.2. $E(k)$ and $\mathrm{v}(k)$ vs. k in one dimension (or three dimensions, in a direction parallel to a reciprocal lattice vector that determines one of the first-zone faces.)

Effective mass

When discussing electron dynamics in solids it is often convenient to introduce the concept of effective mass. If we differentiate Eq. (1) with respect to time we find that

$$\frac{d\mathbf{v}}{dt} = \frac{1}{\hbar}\frac{d^2E}{d\mathbf{k}dt} = \frac{1}{\hbar}\frac{d^2E}{d\mathbf{k}^2}\frac{d\mathbf{k}}{dt}, \tag{4}$$

Where the second derivative with respect to a vector should be understood as a tensor. Using Eq. (2) we find that

$$\frac{d\mathbf{v}}{dt} = \frac{1}{\hbar^2}\frac{d^2E}{d\mathbf{k}^2}\mathbf{F}, \tag{5}$$

In one dimensional case this reduces to

$$\frac{d\mathrm{v}}{dt} = \frac{1}{\hbar^2}\frac{d^2E}{dk^2}F. \tag{6}$$

This has the same form as the Newton's second law, provided that we defined an effective mass by the relation:

$$\frac{1}{m^*} = \frac{1}{\hbar^2}\frac{d^2E}{dk^2}. \tag{7}$$

The mass m^* is inversely proportional to the curvature of the band; where the curvature is large - that is, d^2E/dk^2 is large - the mass is small; a small curvature implies a large mass (Fig. 3).

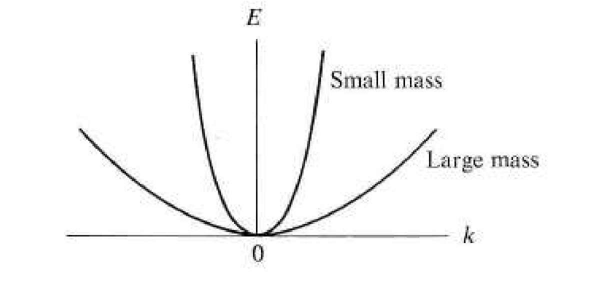

Fig. 3 The inverse relationship between the mass and the curvature of the energy band.

In a general case the effective mass is a tensor which is defined by

$$\left(\frac{1}{m^*}\right)_{\mu\nu} = \frac{1}{\hbar^2}\frac{d^2E}{dk_\mu dk_\nu}, \qquad (8)$$

where k_μ and k_ν are Cartesian coordinates.

The effective mass can be different depending on the directions on the crystal.

Current density

The current density within a free electron model was defined as $\mathbf{j} = -en\mathbf{v}$, where *n* is the number of valence electrons per unit volume, and **v** is the velocity of electrons. This expression can generalized to the case of Bloch electrons. In this case the velocity depends of the wave vector and we need to sum up over **k** vectors for which there are occupied states available:

$$\mathbf{j} = \frac{-e}{V}\sum_{\mathbf{k},occupied} \mathbf{v}(\mathbf{k}) \qquad (9)$$

Here the sum is performed within the extended zone scheme and V is the volume of the solid. It is often convenient to replace the summation by the integration. Because the volume of **k**-space per allowed **k** value is $\Delta\mathbf{k} = 8\pi^3/V$, we can write the sum over **k** as

$$\sum_{\mathbf{k}} = \frac{V}{8\pi^3}\int d\mathbf{k}\,. \qquad (10)$$

Taking into account the spin degeneracy we obtain for the current density:

$$\mathbf{j} = -e\int_{occupied}\frac{d\mathbf{k}}{4\pi^3}\mathbf{v}(\mathbf{k})\,. \qquad (11)$$

Using this expression we show now that *completely filled bands do not contribute to the current*. For the filled bands Eq. (11) should be replaces by

$$\mathbf{j} = -e\int_{zone}\frac{d\mathbf{k}}{4\pi^3}\frac{dE(\mathbf{k})}{d\mathbf{k}}, \qquad (12)$$

This vanishes as a consequence of the theorem that the integral over any primitive cell of the gradient of a periodic function must vanish.

Prove:

Let *f*(**r**) be any function with the periodicity of the lattice. The integral over the primitive cell

$$I(\mathbf{r}') = \int_{cell} d\mathbf{r} f(\mathbf{r}+\mathbf{r}'), \qquad (13)$$

is independent of $\mathbf{r}'$. Therefore,

$$0 = \frac{dI(\mathbf{r}')}{d\mathbf{r}'} = \int_{cell} d\mathbf{r}\frac{df(\mathbf{r}+\mathbf{r}')}{d\mathbf{r}'} = \int_{cell} d\mathbf{r}\frac{df(\mathbf{r}+\mathbf{r}')}{d\mathbf{r}}\,. \qquad (14)$$

At point $\mathbf{r}' = 0$ this results in

$$\int_{cell} d\mathbf{r}\frac{df(\mathbf{r})}{d\mathbf{r}} = 0\,. \qquad (15)$$

Since the Brillouin zone is a primitive cell in the reciprocal space the integral (12) vanishes. This implied that filled bands do not contribute to the current. Only partially filled bands need be considered in calculating the electronic properties of a solid. This explains why the Drude's theory assumption is often successful: in many cases those bands derived from the atomic valence electrons are the only ones that are partially filled.

Hole

One of the most impressive achievements of the semiclassical model is its explanation for phenomena that free electron theory can account for only if the carriers have a positive charge. We now introduce the concept of a hole.

The contribution of all the electrons in a given band to the current density is given by Eq. (11), where the integral is over all occupied levels in the band. By exploiting the fact that a completely filled band carries no current,

$$0 = \int_{zone} \frac{d\mathbf{k}}{4\pi^3} \mathbf{v}(\mathbf{k}) = \int_{occupied} \frac{d\mathbf{k}}{4\pi^3} \mathbf{v}(\mathbf{k}) + \int_{unoccupied} \frac{d\mathbf{k}}{4\pi^3} \mathbf{v}(\mathbf{k}) . \qquad (16)$$

we can equally well write Eq. (11), in the form:

$$\mathbf{j} = +e \int_{unoccupied} \frac{d\mathbf{k}}{4\pi^3} \mathbf{v}(\mathbf{k}) . \qquad (17)$$

Thus *the current produced by electrons occupying a specified set of levels in a band is precisely the same as the current that would be produced if the specified levels were unoccupied and all other levels in the band were occupied but with particles of charge +e* (*opposite to the electronic charge*).

Thus, even though the only charge carriers are electrons, we may, whenever it is convenient, consider the current to be carried entirely by fictitious particles of positive charge that fill all those levels in the band that are unoccupied by electrons. The fictitious particles are called *holes*.

It must be emphasized that pictures cannot be mixed within a given band. If one wishes to regard electrons as carrying the current, then the unoccupied levels make no contribution; if one wishes to regard the holes as carrying the current, then the electrons make no contribution. One may, however, regard some bands using the electron picture and other bands using the hole picture, as suits one's convenience.

Normally it is convenient to consider transport of the holes for the bands which are almost occupied, so that only a few electrons are missing. This happens in semiconductors in which a few electrons are excited from the valence to the conduction bands.

Similar to electrons we can introduce the effective mass for the holes. It has a negative sign.

Fermi surface

The ground state of N Bloch electrons is constructed is constructed in a similar fashion as that for free electrons, i.e. by occupying all one-electron energy levels with band energies $E_n(\mathbf{k})$ less than E_F, where E_F is determined by requiring the total number of levels with energies less than E_F to be equal to the total number of electrons. The wave vector **k** must be confined to a single primitive cell of the reciprocal lattice. When the lowest of these levels are filled by a specified number of electrons, two quite distinct types of configuration can result:

1. A certain number of bands may be completely filled, all others remaining empty. Because the number of levels in a band is equal to the number of primitive cells in the crystal (and because each level

can accommodate two electrons (one of each spin), a configuration with a band gap can arise only if the number of electrons per primitive cell is even.

2. A number of bands may be partially filled. When this occurs, the energy of the highest occupied level, the Fermi energy E_F, lies within the energy range of one or more bands. For each partially filled band there will be a surface in **k**-space separating the occupied from the unoccupied levels. The set of all such surfaces is known as the Fermi surface, and is the generalization to Bloch electrons of the free electron Fermi sphere. The parts of the Fermi surface arising from individual partially filled bands are known as branches of the Fermi surface.

Analytically, the branch of the Fermi surface in the n-th band is that surface in **k**-space determined by

$$E_n(\mathbf{k}) = E_F \tag{18}$$

Thus the Fermi surface is a constant energy surface (surfaces) in **k**-space.

Since the $E_n(\mathbf{k})$ are periodic in the reciprocal lattice, the complete solution to Eq.(18) for each n is a **k**-space surface with the periodicity of the reciprocal lattice. When a branch of the Fermi surface is represented by the full periodic structure, it is said to be described in a *repeated zone scheme*. Often, however, it is preferable to take just enough of each branch of the Fermi surface so that every physically distinct level is represented by just one point of the surface. This is achieved by representing each branch by that portion of the full periodic surface contained within a single primitive cell of the reciprocal lattice. Such a representation is described as a *reduced zone scheme*. The primitive cell chosen is often, but not always, the first Brillouin zone.

Brillouin zones

We consider now an example of building of a Fermi surface. We start from considering the Fermi surface for free electrons and then investigate the influence of the crystal potential. The Fermi surface for free electrons is a sphere centered at k = 0. To construct the Fermi surface in the reduced-zone scheme, one can translate all the pieces of the sphere into the first zone through reciprocal lattice vectors. This procedure is made systematic through the geometrical notion of the higher Brillouin zones.

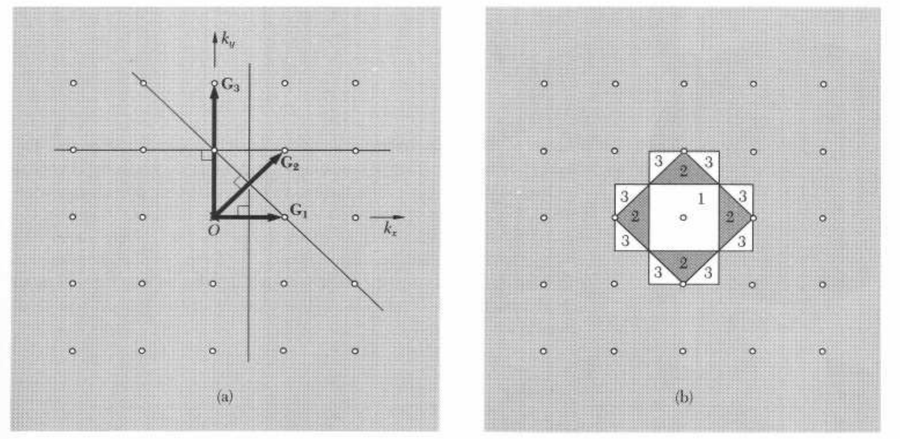

Fig. 4 (a) Construction in **k** space of the first three Brillouin zones of a square lattice. The three shortest forms of the reciprocal lattice vectors are indicated as $\mathbf{G}_1$, $\mathbf{G}_2$, and $\mathbf{G}_3$. The lines drawn are perpendicular bisectors of these **G**'s. (b) On constructing all lines equivalent by symmetry to the three lines in (a) we obtain the regions in **k** space which form the first three Brillouin zones. The numbers denote the zone to which the regions belong; the numbers here are ordered according to the length of vector **G** involved in the construction of the outer boundary of the region.

We illustrate this construction for the two dimensional cubic lattice shown in Fig.4. Recall that the boundaries of the Brillouin zones are planes normal to **G** at the midpoint of **G**. The first Brillouin zone of the square lattice is the area enclosed by the perpendicular bisectors of $\mathbf{G}_1$ and of the three reciprocal lattice vectors equivalent by symmetry to $\mathbf{G}_1$ in Fig. 4a. These four reciprocal lattice vectors are $\pm(2\pi/a)\hat{\mathbf{k}}_x$ and $\pm(2\pi/a)\hat{\mathbf{k}}_y$.

The second zone is constructed from $\mathbf{G}_2$ and the three vectors equivalent to it by symmetry, and similarly for the third zone. The pieces of the second and third zones are drawn in Fig. 4b.

In general, the *first Brillouin zone* is the set of points in k-space that can be reached from the origin without crossing *any* Bragg plane. The *second Brillouin zone* is the set of points that can be reached from the first zone by crossing only one Bragg plane. The (n+1)-th *Brillouin zone* is the set of points not in the (n–l)-th zone that can be reached from the n-th zone by crossing only one Bragg plane.

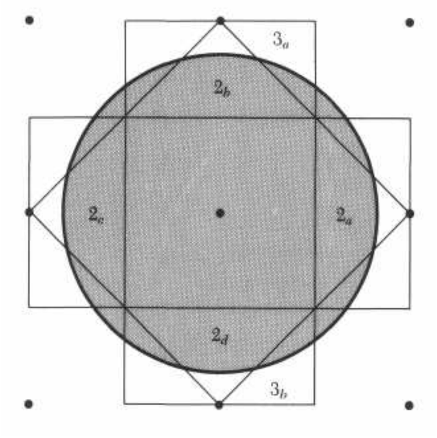

Fig.5 Brillouin zones of a square lattice in two dimensions. The circle shown is a surface of constant energy for free electrons; it will be the Fermi surface for some particular value of the electron concentration. The total area of the filled region in **k** space depends only on the electron concentration and is independent of the interaction of the electrons with the lattice. The shape of the Fermi surface depends on the lattice interaction, and the shape will not be an exact circle in an actual lattice.

The free electron Fermi surface for an arbitrary electron concentration is shown in Fig. 5. Now we perform a transformation to the reduced zone scheme as is shown in Figs.6 and 7. We take the triangle labeled 2_a and move it by a reciprocal lattice vector $\mathbf{G} = -(2\pi/a)\hat{\mathbf{k}}_x$ such that the triangle reappears in the area of the first Brillouin zone (Fig. 6). Other reciprocal lattice vectors will shift the triangles 2_b, 2_c, 2_d to other parts of the first zone, completing the mapping of the second zone into the reduced zone scheme. The parts of the Fermi surface falling in the second zone are now connected, as shown in Fig. 7.

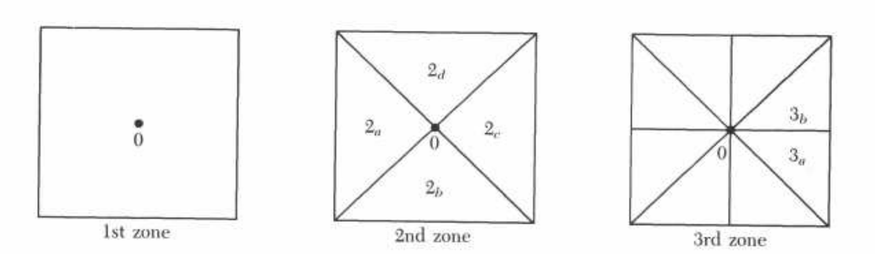

Fig.6 Mapping of the first, second, and third Brillouin zones in the reduced zone scheme. The sections of the second zone in Fig. 4 are put together into a square by translation through an appropriate reciprocal lattice vector. A different **G** is needed for each piece of a zone.

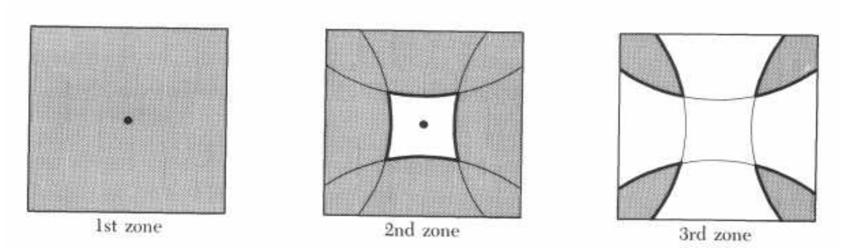

Fig.7 The free electron Fermi surfaces of Fig.5, as viewed in the reduced zone scheme. The shaded areas represent occupied electron states. Parts of the Fermi surface fall in the second, third and fourth zones. The fourth zone is not shown. The first zone is entirely occupied.

Construction of Brillouin zones and Fermi surfaces in three-dimensions is more complicated. Fig.8 shows the first three Brillouin zones for bcc and fcc structures.

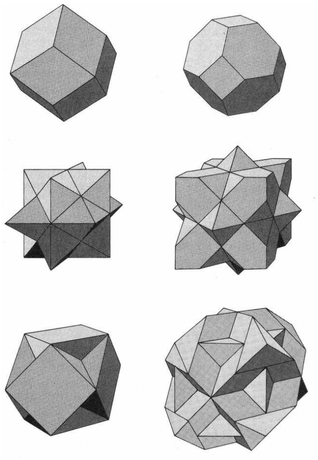

Fig.8 Surfaces of the first, second, and third Brillouin zones for (a) body-centered cubic and (b) face-centered cubic crystals. (Only the *exterior* surfaces are shown. The *interior* surface of the *n*th zone is identical to the exterior surface of the (*n*–l)-th zone.) Evidently the surfaces bounding the zones become increasingly complex as the zone number increases.

The free electron Fermi surfaces for fcc cubic metals of valence 2 and 3 are shown in Fig.9.

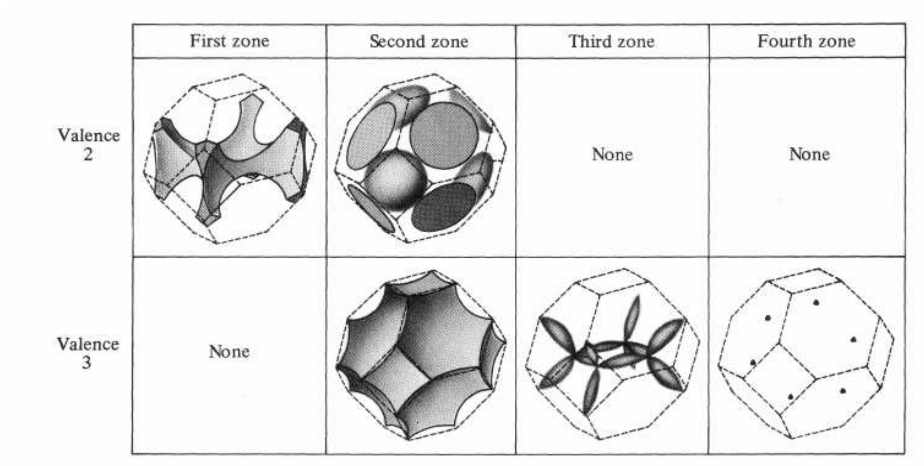

Fig.9 The free electron Fermi surfaces for face-centered cubic metals of valence 2 and 3. (For valence 1 the surface lies entirely within the interior of the first zone and therefore remains a sphere to lowest order) All branches of the Fermi surface are shown. The primitive cells in which they are displayed have the shape and orientation of the first Brillouin zone.

Effect of a crystal potential

How do we go from Fermi surfaces for free electrons to Fermi surfaces in the presence of a weak crystal potential? We can make approximate constructions freehand by the use of four facts:

(i) The interaction of the electron with the periodic potential of the crystal causes energy gaps at the zone boundaries.

(ii) Almost always the Fermi surface will intersect zone boundaries perpendicularly. Using the equation for the energy near the zone boundary it is easy to show that $\frac{dE}{d\mathbf{k}} = \frac{\hbar^2}{m}(\mathbf{k} - \frac{1}{2}\mathbf{G})$, which implies that on the Bragg plane the gradient of energy is parallel to the Bragg plane. Since the gradient is perpendicular to the surfaces on which function is constant, the constant energy surfaces at the Bragg plane are perpendicular to the plane.

(iii) The crystal potential will round out sharp corners in the Fermi surfaces.

(iv) The total volume enclosed by the Fermi surface depends only on the electron concentration and is independent of the details of the lattice interaction.

(v) If a branch of the Fermi surface consists of very small pieces of surface (surrounding either occupied or unoccupied levels, known as "pockets of electrons" or "pockets of holes"), then a weak periodic potential may cause these to disappear. In addition, if the free electron Fermi surface has parts with a very narrow cross section, a weak periodic potential may cause it to become disconnected at such points.

Below we give a few examples for real metals.

Alkali metals

The radius of the Fermi sphere in bcc alkali metals is less than the shortest distance from the center of the zone to a zone face and therefore the Fermi sphere lies entirely within the first Brillouin zone. The crystal potential does not distort much the free electron Fermi surface and it remains very similar to a sphere.

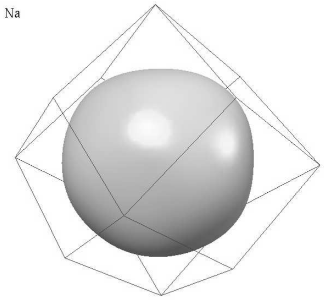

Fig.10 Fermi surface of sodium.

The noble metals

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 [111] directions, where it reaches 0.903 of the distance from the origin to the center of the hexagonal face. For all three noble metals therefore their Fermi surfaces are closely related to the free electron sphere. However, in the [111] directions contact is actually made with the zone faces, and the measured Fermi surfaces have the shape shown in Fig.11. Eight "necks" reach out to touch the eight hexagonal faces of the zone, but otherwise the surface is not grossly distorted from spherical.

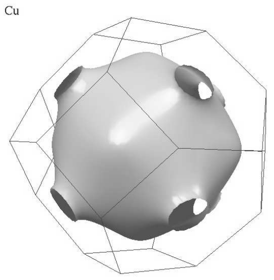

Fig. 11 In the three noble metals the free electron sphere bulges out in the [111] directions to make contact with the hexagonal zone faces.

The cubic divalent metals

With two electrons per primitive cell, calcium, strontium, and barium could, in principle, be insulators. In the free electron model, the Fermi sphere has the same volume as the first zone and therefore intersects the zone faces. The free electron Fermi surface is thus a fairly complex structure in the first zone, and pockets of electrons in the second. The question is whether the effective lattice potential is strong enough to shrink the second-zone pockets down to zero volume, thereby filling up all the unoccupied levels in the first zone. Evidently this is not the case, since the group II elements are all metals. Calculations show that the first Brillouin zone is completely filled and a small number of electrons in the second zone determine the non-zero conductance.

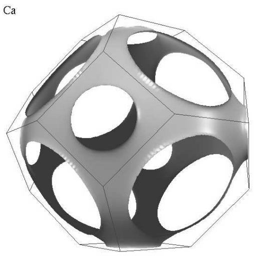

Fig.12 Fermi surface of calcium

Trivalent metals

The Fermi surface of aluminum is close to that of the free electron surface for fcc cubic monoatomic lattice with three conduction electrons per atom. The first Brillouin zone is filled and the Fermi surface of free electrons is entirely contained in the second, third and fourth Brillouin zones. When displayed in a reduced-zone scheme the second-zone surface is a closed structure containing unoccupied levels, while the third-zone surface is a complex structure of narrow tubes (Fig.9). The amount of surface in the fourth zone is very small, enclosing tiny pockets of occupied levels.

The effect of a weak periodic potential is to eliminate the fourth-zone pockets of electrons, and reduce the third-zone surface to a set of disconnected "rings" (Fig.13).

Aluminum provides a striking illustration of the theory of Hall coefficients. The high-field Hall coefficient should be $R_H = -1/\left(n_e - n_h\right)e$, where n_e and n_h are the number of levels per unit volume enclosed by the particle-like and hole-like branches of the Fermi surface. Since the first zone of aluminum is completely filled and accommodates two electrons per atom, one of the three valence electrons per atom remains to occupy second- and third-zone levels. Thus

$$n_e^{\mathrm{II}} + n_e^{\mathrm{III}} = \frac{n}{3} \tag{19}$$

where n is the free electron carrier density appropriate to valence 3. On the other hand, since the total number of levels in any zone is enough to hold two electrons per atom, we also have

$$n_e^{\mathrm{II}} + n_h^{\mathrm{II}} = 2\frac{n}{3} \tag{20}$$

Subtracting (20) from (19) gives

$$n_e^{\mathrm{III}} - n_h^{\mathrm{II}} = -\frac{n}{3} \tag{21}$$

Thus the high-field Hall coefficient should have a positive sign and yield an effective density of carriers a third of the free electron value. This is precisely what is observed.

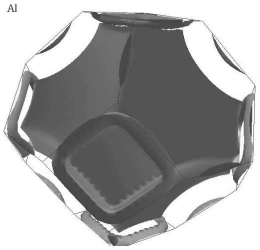

Fig.13 Fermi surface of aluminum