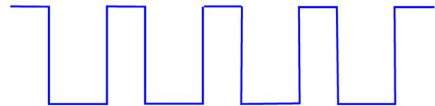# NEARLY FREE ELECTRON MODEL (Contd)

Lecture 19

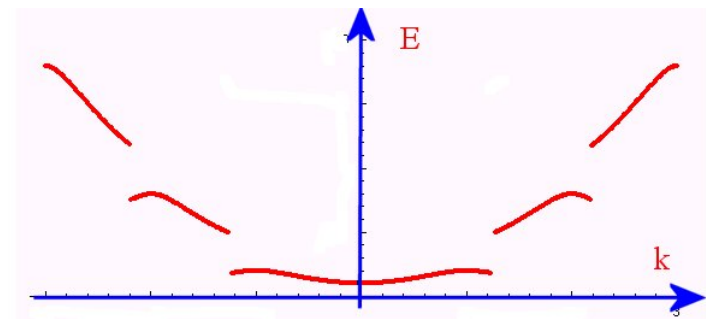### *A.H. Harker*
Physics and Astronomy
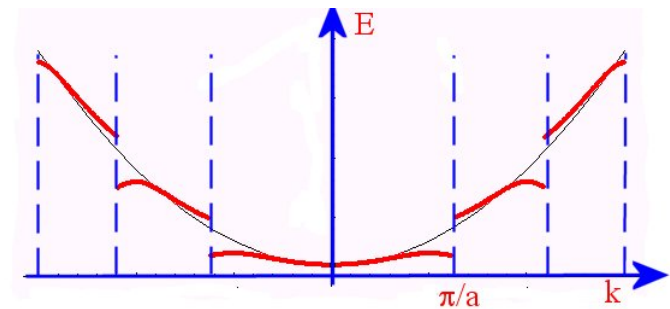#### *UCL*

7.3 An exactly-soluble model

We know from second-year quantum mechanics that square well potentials are quite easy to deal with. The Kronig-Penney model is based on this.

For details of the calculation, see for example Kittel *Introduction to Solid State Physics*.

We can seen the gaps in the energy spectrum – regions of energy in which there are no allowed states.

The free electron approximation remains a good approximation well away from the edges of the Brillouin zone – only wave-vectors close to a multiple of π/a are mixed together and have their energies altered by the periodic potential.

Translational symmetry is not essential for producing a band gap – amorphous solids also have band gaps.
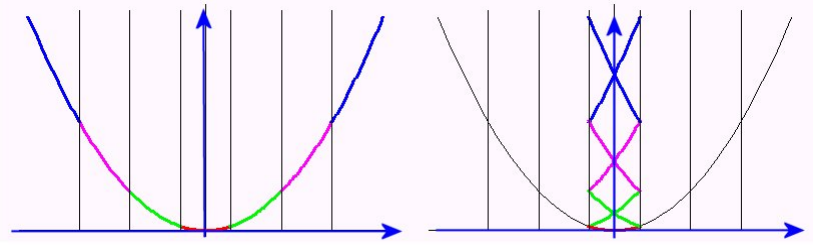
7.4 Sketching energy bands

7.4.1 The empty lattice

Imagine first that the periodic crystal potential is vanishingly small. Then we want to impose periodic structure without distorting the free electron dispersion curves.We now have

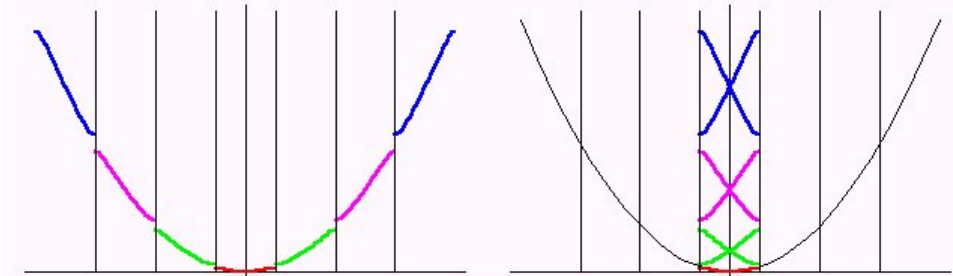$$E(k) = E(k + G),$$

where G is a reciprocal lattice vector.

We can use the *extended zone scheme* (left) or displace all the segments of the dispersion curve back into the first Brillouin zone (right).

7.4.2 The nearly free electron

Modify the free electron picture by opening up small gaps near the zone boundaries.

7.5 Consequences of the energy gap

7.5.1 Density of states

The number of allowed k values in a Brillouin zone is equal to the number of unit cells in the crystal. *Proof:* in one dimension, with periodic boundary conditions,

$$g(k) = \frac{L}{2\pi},$$

where L is the length of the crystal, so the number of states in a Brillouin zone is

$$N = \int_{-\pi/a}^{\pi/a} g(k)\mathrm{d}k = \frac{L}{2\pi} \int_{-\pi/a}^{\pi/a} \mathrm{d}k = \frac{L}{a},$$

but a was the size of the real space unit cell, so N is the number of unit cells in the crystal. The same argument holds in two or three dimensions. Note that we get the number of unit cells – only for a monatomic unit cell is this the same as the number of atoms.

So, taking spin degeneracy into account, a Brillouin zone contains $2N$ allowed electron states.
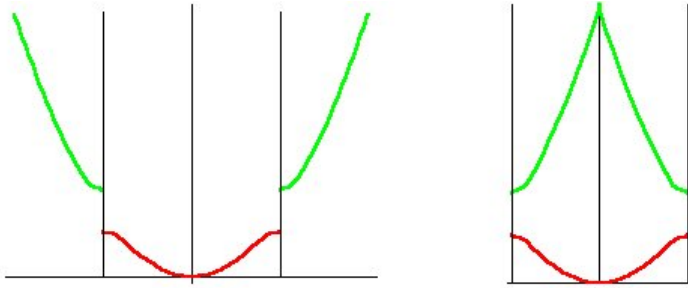
7.5.2 States in one dimension
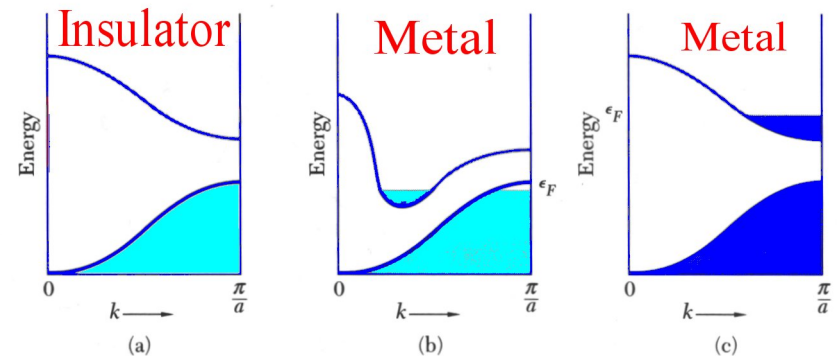
In the insulator, there is an energy gap between the occupied and unoccupied states. For a metal, there may be overlap (b) or not (c).

Draw the dispersion relation with slight distortions near the zone boundary

in either the extended zone scheme (left) or the reduced zone scheme (right). Note that states further from the origin in the extended zone scheme can also be represented as higher bands in the reduced zone scheme.

For free electrons, the constant energy surfaces are circular.

For a monovalent element, the volume of the Fermi surface is half that of the Brillouin zone:
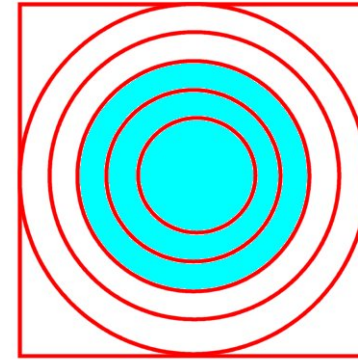
so that it is free to be displaced by an electric field – a free-electron-like *metallic* system.
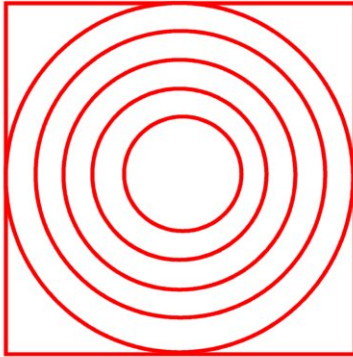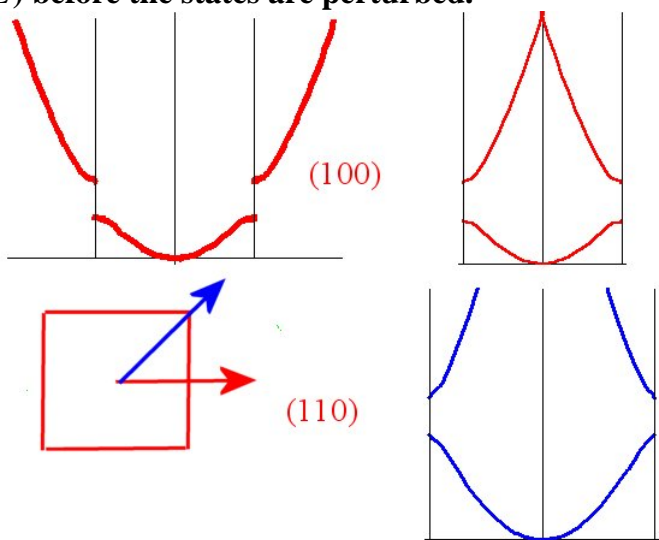
With the crystal potential, the energy inside the first Brillouin zone is *lower* close to the zone boundary. So the Fermi surface is extended *towards* the zone boundary as it gets close.
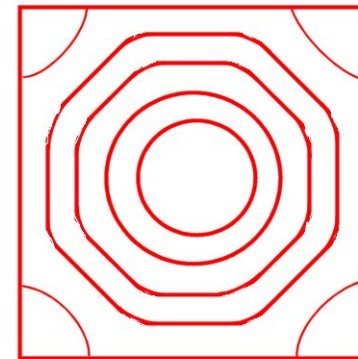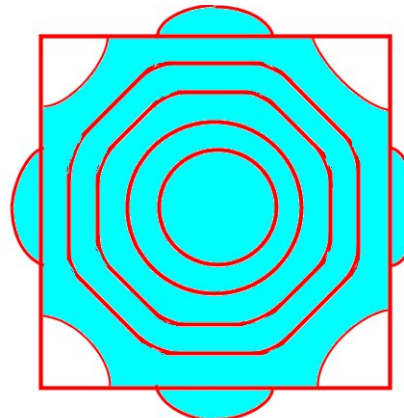
Depending on the direction in the Brillouin zone, we may go to larger k (larger E) before the states are perturbed.
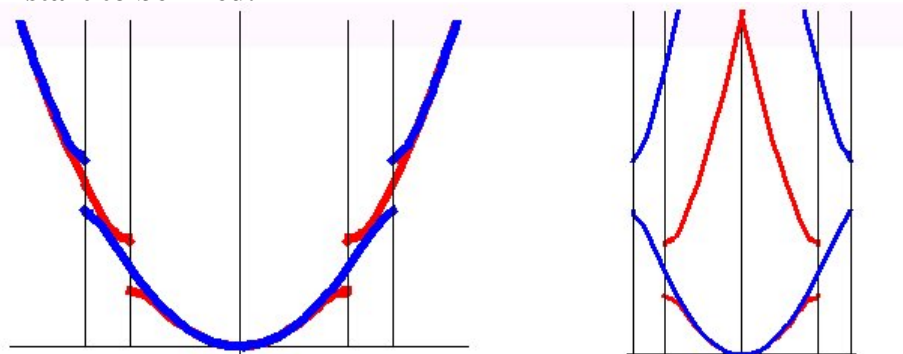

(100)

(110)

If the gap is small, the filled states will be in both the first and second zones.
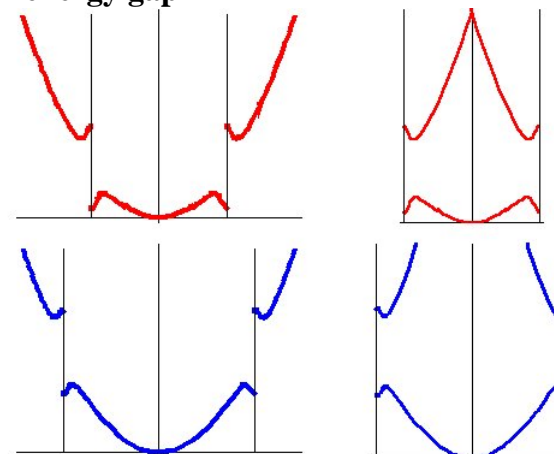

This will be a metal.

Consider a divalent metal in two dimensions. The area of k-space needed to accommodate all the electrons is equal to the area of the first Brillouin zone. We can see that the red states in the second band will start to be filled.
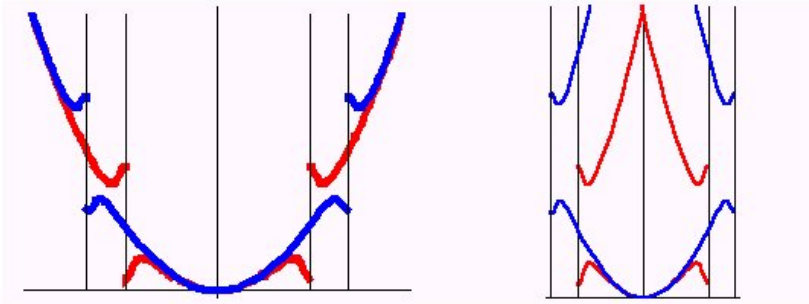
Take a larger energy gap

Superpose the curves

For a large gap, the whole of the first zone will be filled. This gives an insulator because if we apply a field to increase an electron's k vector, electrons at the zone boundary will be Bragg reflected back to the other side of the zone – there will be no nett drift velocity. We only get current if we can excite some electrons into a higher energy band.

An insulator.

Bragg reflection is a natural consequence of the periodic nature of the energy in k-space, and the fact that
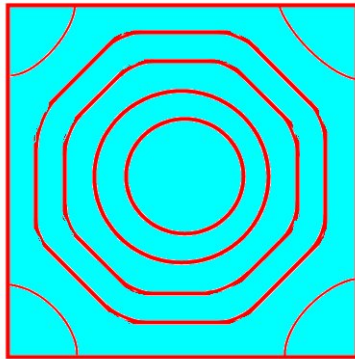
$$\text{group velocity} = \frac{\mathrm{d}\omega}{\mathrm{d}k} = \frac{1}{\hbar}\frac{\mathrm{d}E}{\mathrm{d}k}.$$
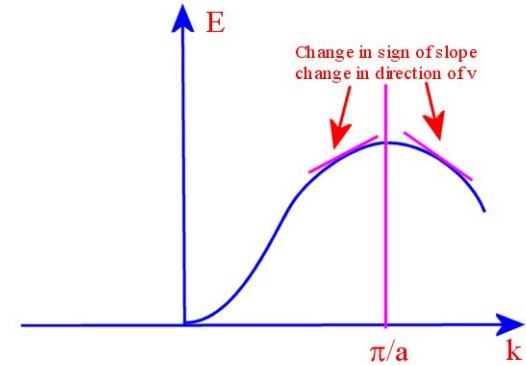
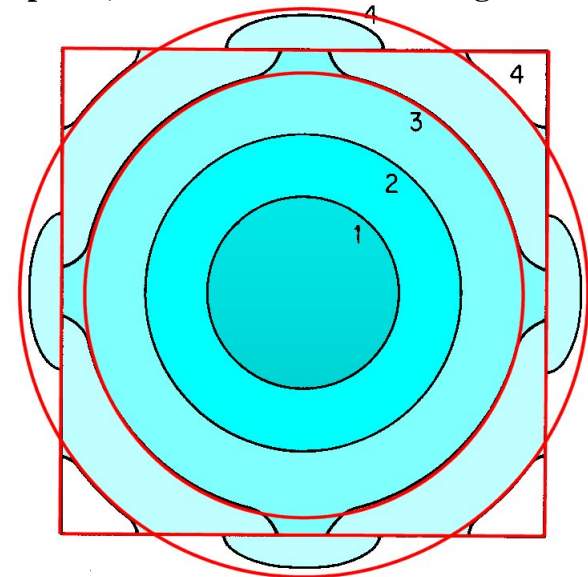On crossing the zone boundary, the phase velocity changes direction: the electron is reflected.

7.5.3 Sketching a nearly free electron Fermi surface

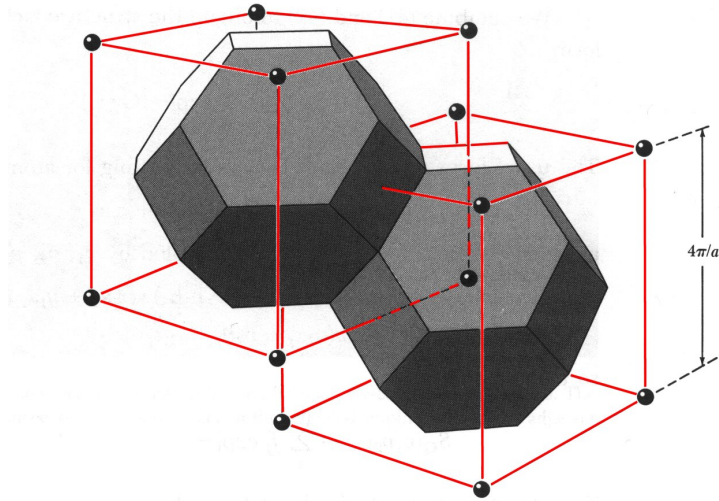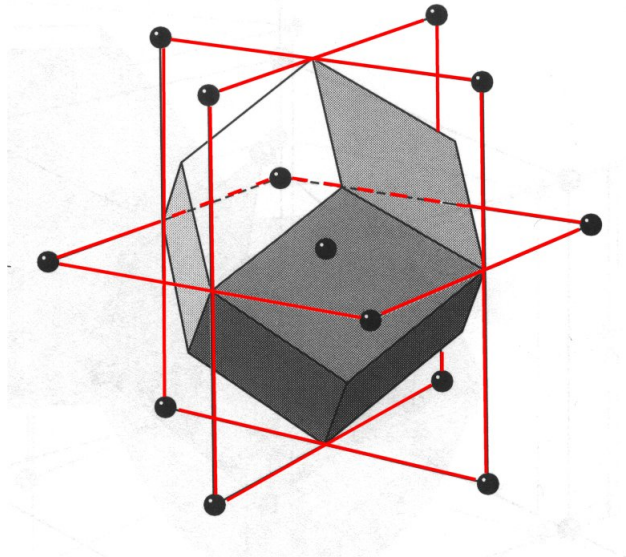**Start with the sphere, and distort it near the edges of the zone.**

7.5.4 Typical Fermi surfaces in 3D

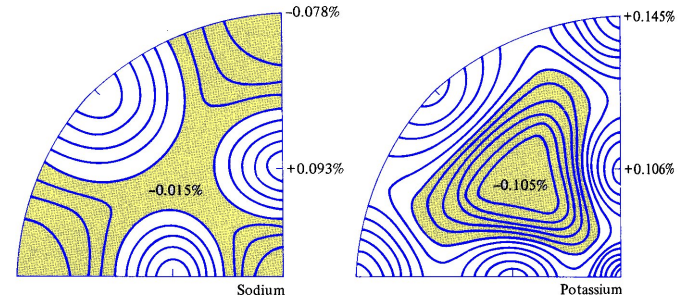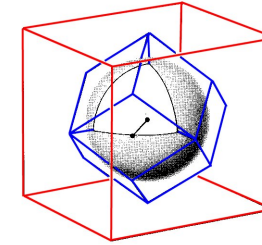**The Brillouin zone is taken as the reciprocal space Wigner-Seitz cell.**
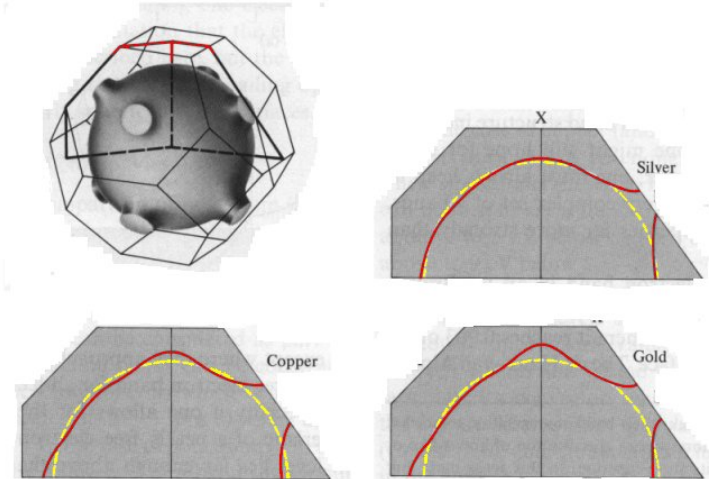

$4\pi/a$

FCC lattice, BCC reciprocal lattice
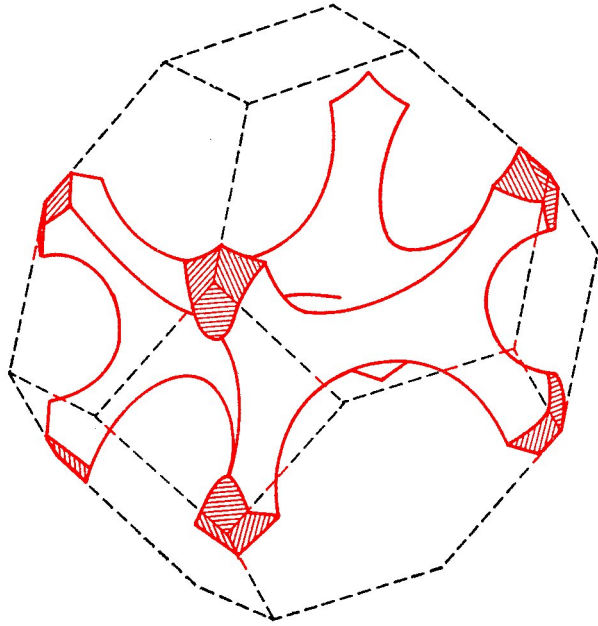

BCC lattice, FCC reciprocal lattice

The alkali metals are only slightly distorted from spheres.

~0.078%   +0.145%

+0.093%   +0.106%

−0.015%   −0.105%

Sodium   Potassium

The noble metals are connected in k-space.

X

Silver

Copper   Gold

For polyvalent materials, the Fermi surfaces get more complicated.

7.5.5 Effects of fields on electrons in bands

Electric field: a simple picture will show how the Fermi surface in a partly-filled zone will be shifted:

A nett current flow (really arising from $\langle v \rangle$, not $\langle k \rangle$, so a conductor.
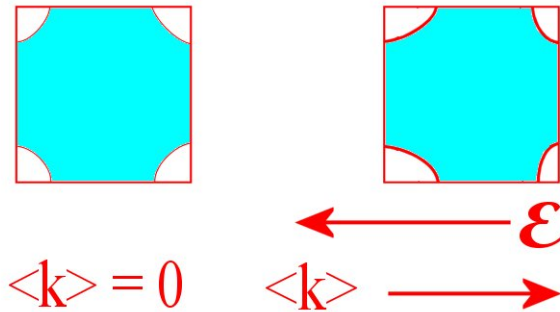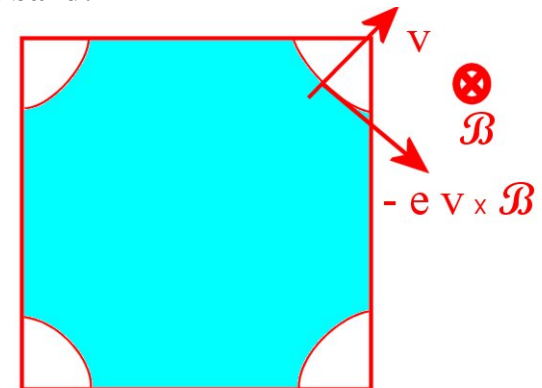
Magnetic field:

$$\hbar \frac{d\mathbf{k}}{dt} = -e\mathbf{v} \times \mathcal{B}.$$
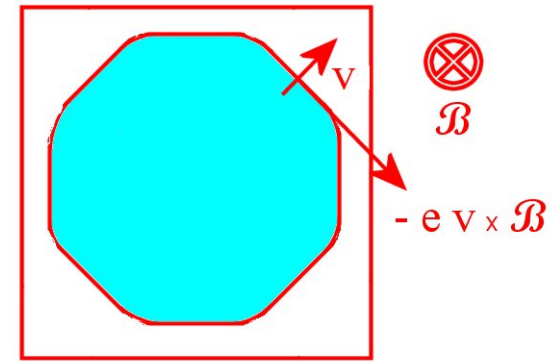
The change in k is perpendicular to both v and $\mathcal{B}$ – the electron stays on the constant energy surface.
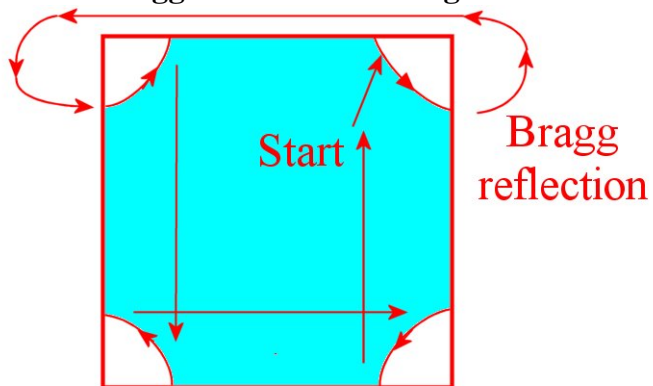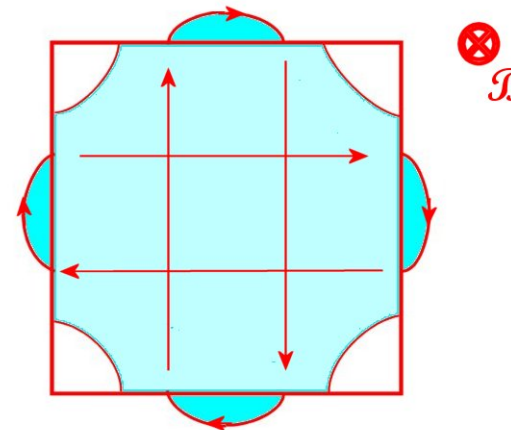
Near the top of a band:

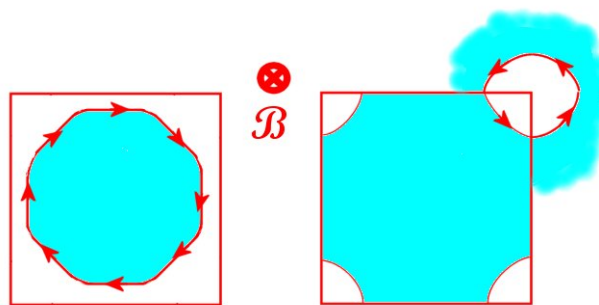**The electrons are Bragg reflected at the edges of the Brillouin zone.**

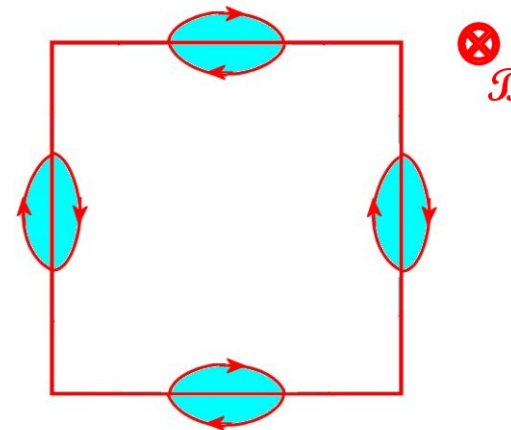**What about the electrons in the second zone in a metallic system?**

Redrawing, using the periodic nature of the system:

The electrons orbit, in k-space, the opposite way round occupied or unoccupied states. The behaviour looks like that of an oppositely charged particle – a _hole_.

This is electron-like behaviour.
There can be a balance between electron-like and hole-like behaviour – hence the strange Hall coefficients of the polyvalent metals.