Solids

1. Binding types
2. Crystal lattices
3. Lattice vibrations
4. Electrons in crystal lattices

Electrons in crystal lattices

- Electrical conductivity and Ohm's law
- Drude model
- Sommerfeld model
- Bloch waves
- Energy bands and Fermi surfaces
- Photoemission Spectroscopy
- Semiclassical Electron Dynamics
- Semiconductors
- Ferromagnetism
- Superconductivity

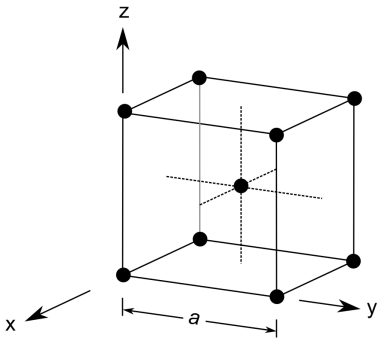
Sodium

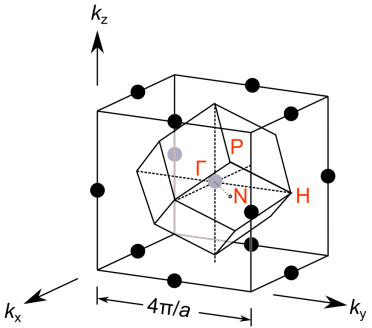
Energy bands and Fermi surfaces 2

- Quasi-free electrons in the sc-lattice
- Sodium
- Copper
- Zinc

Sodium 1

- Sodium atoms form a bcc lattice (and the reciprocal lattice is an fcc lattice)





- The shortest distance between the center and the boundaries of the 1st Brillouin zone is between the Γ and the N point with $\frac{1}{2}\sqrt{2}\frac{2\pi}{a} = \frac{4.44}{a}$

Sodium 1

Comment

Metallic sodium is considered as the first realistic example.

Sodium crystallizes in a bcc lattice.

The left figure shows the cubic unit cell.

The right figure shows the 1st Brillouin zone.

The reciprocal lattice of sodium is an fcc lattice.

The shortest distance between the Γ point and the surface of the 1st Brillouin zone is the distance Γ-N with about 4.44/*a*.

Sodium 2

- The electron configuration of the free sodium atom is $[\mathrm{Ne}]3s^1$
- The periodic variation of the potential energy of the 3s electron is small
- Since the cubic cell of the bcc lattice contains 2 sodium atoms, the electron density is $2/a^3$ and the Fermi wave number is

$$k_F^3 = 3\pi^2 \frac{N}{V} = 3\pi^2 \frac{2}{a^3} \rightarrow k_F = \frac{3.9}{a} < \frac{4.44}{a}$$

- The Fermi sphere of the 3s electrons is well enclosed in the 1st Brillouin zone

Sodium 2

Comment

The 3s electron of the sodium atom is the conduction electron.

The variation in the potential energy of the 3s electron is small and the quasi-free electron approximation is not that bad.

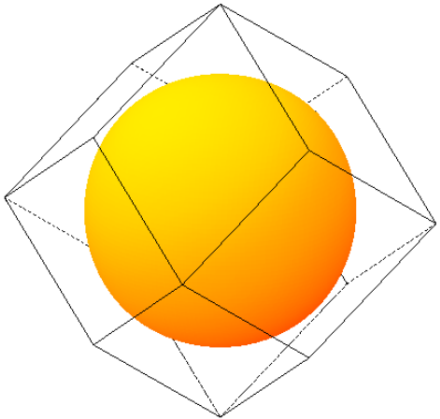
The Fermi wave number can be calculated with the electron density.

The Fermi sphere is enclosed by the 1^{st} Brillouin zone.

The following figure shows the Fermi sphere within the 1^{st} Brillouin zone of sodium.

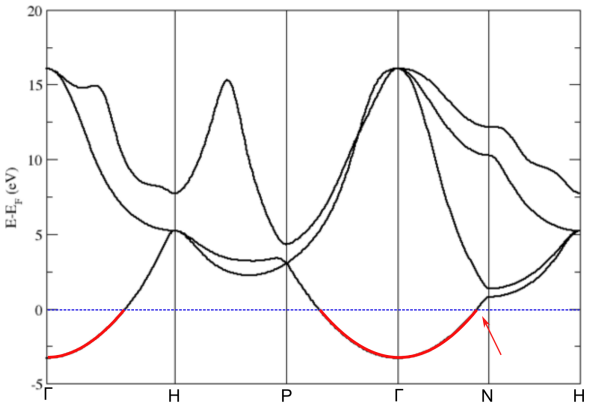
Sodium 3

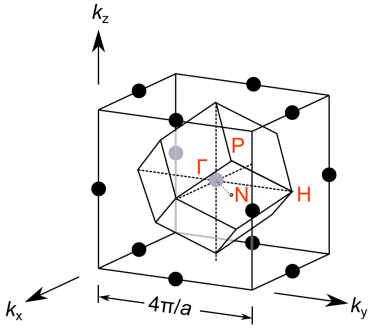
Fermi sphere and 1st Brillouin zone of sodium



Sodium 4

band structure of metallic sodium





Sodium 4 Comment 1

The figure on the left shows the band structure of metallic sodium along the indicated directions within the 1st Brillouin zone.

The right figure shows the 1st Brillouin zone of the bcc lattice with the symmetry points.

The band structure of sodium is very close to the band structure of the quasi-free electron approximation.

The figure shows that even the free electron approximation in three dimensions leads to an astonishingly complex band structure, although it results from the parabolas of the kinetic energy of a quasi-free electron.

The properties of metallic sodium are determined by the electrons on the Fermi surface.

Sodium 4

Comment 2

The thermal energy at room temperature (300 K) is only $k_B T \approx 26$ mK and is much smaller than the Fermi energy ($E_F = 3.24$ eV).

The red lines indicate the occupied k states.

The occupied k states are enclosed by the Fermi surface, which is a sphere in a good approximation.

As expected, the N point of the 1^{st} Brillouin zone has the smallest distance to the Fermi surface (indicated by the small arrow).

Copper

Energy bands and Fermi surfaces 3

- Quasi-free electrons in the sc-lattice
- Sodium
- Copper
- Zinc

Copper 1

band structure of Copper

- The electron configuration of metallic copper is $[\mathrm{Ar}]4s^1 3d^{10}$
- The energy levels of the 4s and 3d orbitals are close to each other
- The 4s electron is the conduction electron
- Since the cubic cell of the fcc lattice contains 4 copper atoms, the density of the 4s electrons is $4/a^3$ and the Fermi wave number is

$$k_F^3 = 3\pi^2 \frac{N}{V} = 3\pi^2 \frac{4}{a^3} \rightarrow k_F = \frac{4.9}{a}$$

Copper 1

Comment

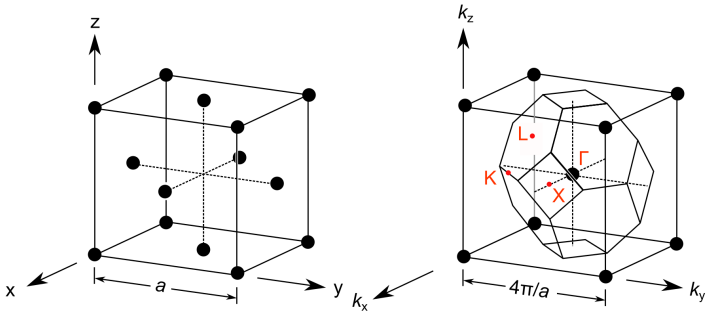
The electron configuration of copper is $[\mathrm{Ar}]4s^1 3d^{10}$.

Metallic copper forms an fcc lattice with a lattice parameter of the cubic unit cell of $a = 3.61 \cdot 10^{-10}$ m .

The 4s electron is the conduction electron for which the Fermi wave number $k_\mathrm{F} = 4.9/a$ results.

Copper 2

cubic unit cell and 1st Brillouin zone of copper



- The distance between the Γ point and X is $2\pi/a \approx 6.2/a$
- The distance between the Γ point and L is $\frac{1}{2}\frac{2\pi}{a}\sqrt{3} \approx 5.4/a$
- The Fermi sphere of the 4s electrons is enclosed by the 1st Brillouin zone

Copper 2

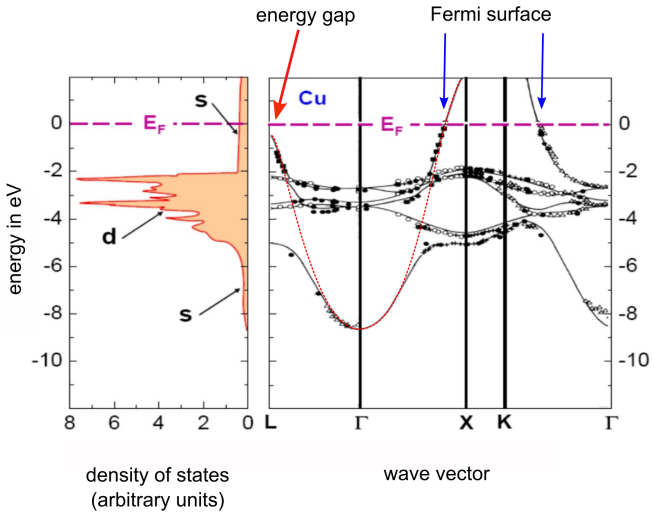
Comment

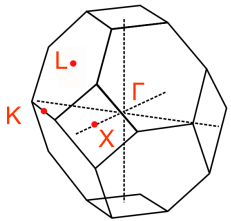
The left figure shows the cubic fcc unit cell of copper and the right figure the 1st Brillouin zone.

The distance between the L point on the hexagonal surface of the 1st Brillouin zone and the Γ point is with $5.4/a$ the smallest between the surface of the 1st Brillouin zone and the Γ point.

The Fermi surface of the 4s electrons lies within the 1st Brillouin zone.

Copper 3


energy gap
Fermi surface
Cu
s
d
s
E_F
E_F
energy in eV
0
-2
-4
-6
-8
-10
8 6 4 2 0
L Γ X K Γ
density of states
(arbitrary units)
wave vector


L
Γ
K
X

Copper 3 Comment 1

The left part of the figure shows the density of states of the electrons that occupy the 3d orbitals and the 4s orbital.

The electrons of the 4s and the 3d orbitals share the same energy range.

The middle part of the figure shows the band structure of copper.

The 1st Brillouin zone is sketched at right to illustrate the directions in which the band structure was measured and calculated.

The 4s electrons show roughly the behavior of the free electrons.

For comparison I have drawn a red dotted parabola for the kinetic energy of the quasi-free 4s electrons.

Compared to the band of 4s electrons, the bands of 3d electrons are narrow.

Copper 3 Comment 2

This suggests that the mobility of the 3d electrons is rather low, i.e. it is more difficult for 3d electrons to gain kinetic energy with increasing momentum $\hbar\vec{k}$ than for 4s electrons.

Although the 3d electrons are not bound to the copper atoms, they cannot contribute to the conductivity of copper.

The energy of the 3d electrons is well below the Fermi energy of the 4s electrons.

There are five 3d bands and ten 3d electrons per copper atom.

For all five 3d bands, all *k*-states within the 1st Brillouin zone are occupied by two electrons and for every electron wave there is an electron wave that propagates in the opposite direction.

Due to the periodicity of the electron wave functions in the reciprocal lattice, this cannot be changed even by applying an electric field.

Copper 3 Comment 3

Since there are five comparatively narrow 3d bands, the density of states of the 3d electrons is concentrated in a small energy range and therefore large compared to the density of states of the 4s electrons.

The energy band of the 4s electrons must pass through the area of the 3d energy bands.

This leads to avoided level crossings and there are no electron states on the idealized parabola in this energy range.

The 4s electrons with the highest energy define the Fermi surface.

The occupied *k* states reach the Fermi energy near the X and K points

I have marked these points in the band structure with blue arrows.

Copper 3

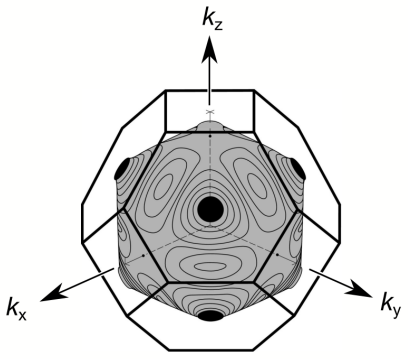
Comment 4

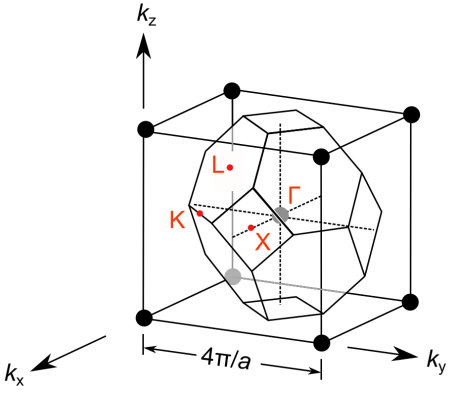
The Fermi surface is slightly closer to the X point than to the K point. (The distance Γ-K is $\frac{3\pi}{\sqrt{2}a} \approx 6.66/a$)

The band structure in the area of the L point is remarkable.

The energy of the *k* states of the 4s electron is smaller than the Fermi energy, i.e. all *k* states up to the border of the 1^{st} Brillouin zone are occupied with electrons.

Copper 4





Copper 4

Comment 1

The left figure shows the Fermi surface of copper and the right figure again the 1st Brillouin zone of the fcc lattice.

The Fermi surface is almost spherical with the remarkable deviations at the L points.

The energy of the *k* states within the black circles at the L points is smaller than the Fermi energy.

Only at the edge of the black circles does the energy of the *k* states reach the Fermi energy.

The Fermi surface is shown in gray.

Copper 4

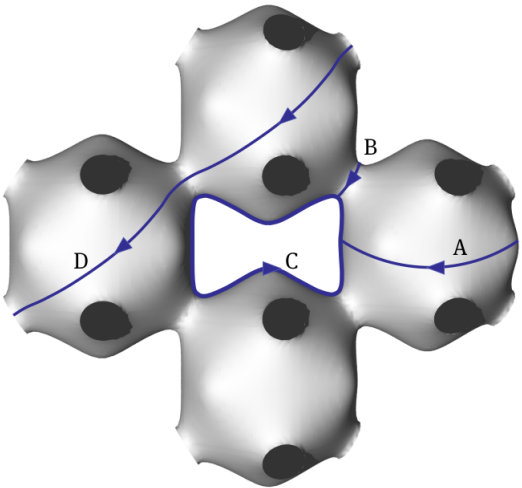
Comment 2

The contour lines around the L point indicate that the Fermi surface rises above the level of a spherical Fermi surface.

The contour lines in the area of the K point indicate that the Fermi surface is slightly below the level of a spherical Fermi surface.

Copper 5

Fermi surface of copper in the periodic zone scheme



Copper 5 Comment

The figure shows the Fermi surface of copper in the periodic zone scheme.

The blue lines indicate “electron” orbits when a magnetic field is applied. They will be explained later.

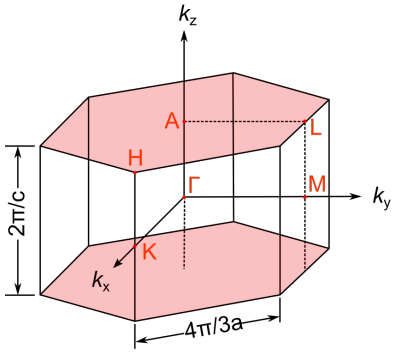
“Electron” here does not mean the elementary particles that occupy the wave functions of the Schrödinger equation, i.e. the *k* states, but rather excited states of the conduction electrons that can scatter and react to applied electric and magnetic fields. This also needs to be explained in more detail later.

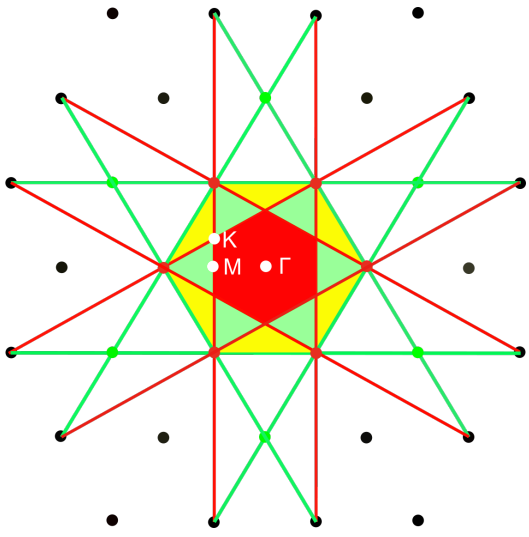
Zinc

Energy bands and Fermi surfaces 4

- Quasi-free electrons in the sc-lattice
- Sodium
- Copper
- Zinc

Zinc 1: Brillouin zones of zinc





Zinc 1

Comment

Before discussing the band structure and Fermi surfaces of zinc, it is helpful to take a look at the Brillouin zones of the hexagonal crystal lattice.

The left figure shows the 1st Brillouin zone of zinc with its characteristic points.

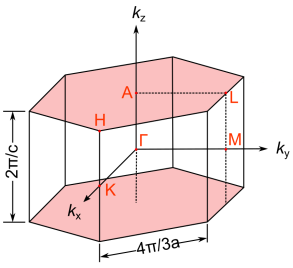
The right figure shows the 1st Brillouin zone (red), 2nd Brillouin zone (green) and 3rd Brillouin zone (yellow) in the hexagonal plane of the lattice.

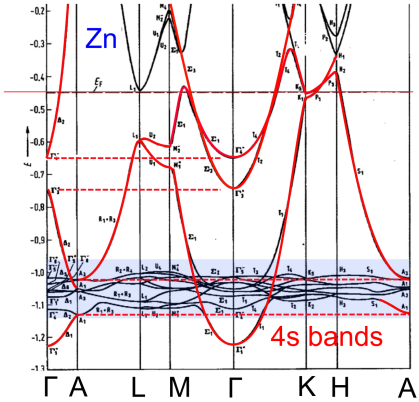
Along the hexagonal axis of symmetry, the first Bragg plane intersects the k_z axis at point A.

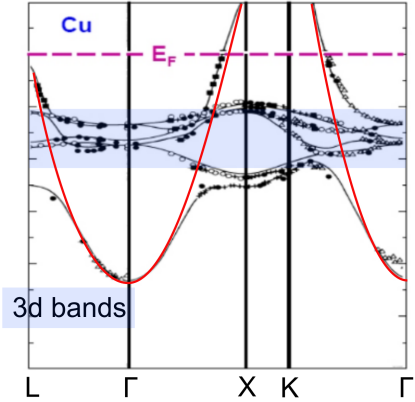
The second Bragg plane intersects k_z at the Γ point because it is halfway to the 2nd Γ point.

Zinc 2

The electron configuration of zinc is $[Ar]4s^2 3d^{10}$



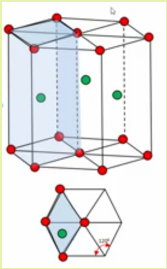




Zinc 2

Comment 1

Zinc crystallizes in an hcp lattice that is slightly stretched along the c axis compared to the hexagonal closest packing and there are two zinc atoms per primitive unit cell (compare the following figure).



The Fermi wave number of the 4s electrons can be calculated using the electron configuration of zinc.

Zinc 2

Comment 2

The figure on the left shows the 1st Brillouin zone of the hexagonal lattice.

$a = 0.266\,\text{nm}$ and $c = 0.495\,\text{nm}$ denote the lattice constants.

The middle panel shows the band structure of zinc.

For comparison, the figure on the right shows the band structure of copper again.

In contrast to copper, zinc has an extra electron.

Zinc 2

Comment 3

In both band structures, the narrow 3d bands crossing the 4s band can be seen at low energies.

The parabolic segments of the kinetic energy of the 4s electrons are marked in red ($E_{kin} = \frac{\hbar^2 \vec{k}^2}{2m}$).

In zinc, the 4s bands are occupied to a higher energy than in copper, since there are four electrons in the primitive unit cell, instead of only one in copper.

The 1st Brillouin zone shows that the Bragg planes have smaller distances along the z-direction than in the directions perpendicular to it.

Zinc 2

Comment 4

As a result, the 4s band is split into three sub-bands along the path Γ-A in the energy range under consideration.

The first band gap at the A point is in the energy range of the 3d bands, which is confusing because of the interaction between the 4s and 3d electrons.

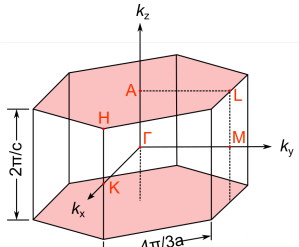
The second band gap at the Γ point can be clearly seen.

Perpendicular to the z-direction, the Bragg planes have larger distances, so that the energy between the band gaps is larger.

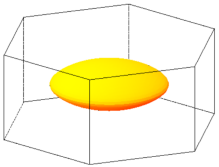
This circumstance introduces a new feature of the band structure that has not occurred before.

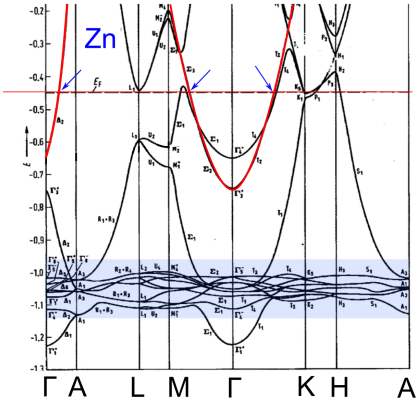
In addition to the energy splittings at the Γ point and the Bragg planes, there are now avoided level crossing within the 1^{st} Brillouin zone.

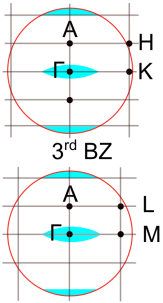
Zinc 3: Fermi surfaces of zinc



Fermi surface of the 3rd Brillouin Zone







Zinc 3

Comment

The left side of the figure shows the 1st Brillouin zone of the hexagonal lattice and below it the Fermi surface of the 3rd Brillouin zone, which has been shifted back into the 1st Brillouin zone.

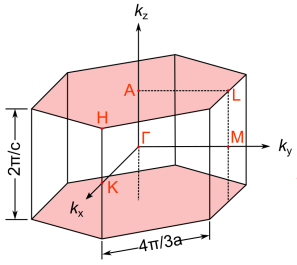
The right side shows the construction of the Fermi surface.

The radius of the Fermi sphere takes into account that there are four 4s electrons in the primitive unit cell of zinc (There are two zinc atoms per primitive unit cell of the quasi hcp-lattice).

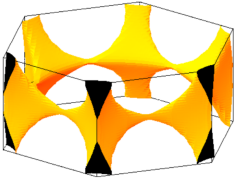
The energy bands that contribute to the Fermi surface are marked in red.

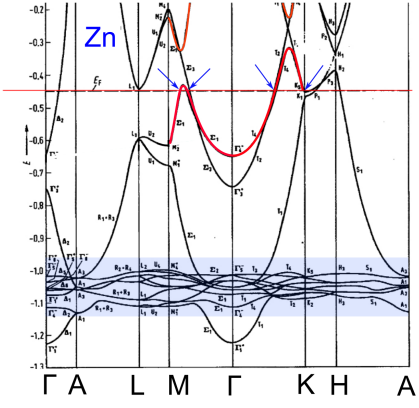
The Fermi energies of these bands are marked with blue arrows and the Fermi surface envelops occupied electron states.

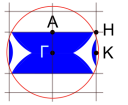
Zinc 4: Fermi surfaces of zinc

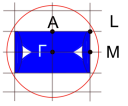


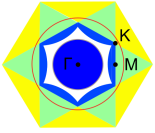
Fermi surface of the 2nd BZ











Zinc 4 Comment 1

The figures on the left show the 1st Brillouin zone of a hexagonal crystal lattice at the top and below the Fermi surface of the second energy band.

The Fermi surface envelops the unoccupied electron states.

This Fermi surface results when the areas of the Fermi sphere that are in the 2nd Brillouin zone are shifted into the 1st Brillouin zone.

These operations are shown in the figures on the right.

The top figure shows the A-Γ-K plane.

The blue areas denote the occupied electronic states.

Zinc 4 Comment 2

The white areas in the 1st Brillouin zone are the unoccupied electron states.

The displacements take place along the Γ-A-direction (large sections of the Fermi sphere) and along the Γ-K-direction (small sections of the Fermi sphere).

The middle figure shows the A-Γ-M plane.

Since the distance Γ-M is smaller than the distance Γ-K, the segments of the Fermi sphere shifted in the Γ-M direction are larger than in the A-Γ-K plane.

Therefore, the areas of unoccupied electron states in the A- Γ-M plane are smaller than in the A -Γ-K plane (Compare the spatial representation of the Fermi surface on the left.).

Zinc 4 Comment 3

The bottom figure shows the K-Γ-M plane, which is perpendicular to the hexagonal axis of the crystal lattice.

The blue circular area in the middle of the 1st Brillouin zone results from the displacements of the 2nd Brillouin zone into the 1st Brillouin zone along the Γ-A direction.

The blue segments at the edge of the 1st Brillouin zone arise when the areas of the Fermi sphere that lie in the areas of the 2nd Brillouin zone (marked in green) are shifted into the 1st Brillouin zone.

The blue arrows in the middle figure mark the points at which the band energy is equal to the Fermi energy, and it can be concluded that the area of unoccupied *k* states in the Γ-K direction is larger than in the Γ-M direction.

Zinc 4

Comment 4

With these simple constructions it can be visualized, at least qualitatively, how the complicated Fermi surface of the 2nd-band comes about in a hexagonal crystal lattice.

The *k* states of the first band fill the complete 1st Brillouin zone of the hexagonal lattice.

In addition to the two Fermi surfaces just discussed, there are other Fermi surfaces that enclose smaller areas of the reciprocal lattice.

Revision

Summary in Questions

1. Sketch the band structure of quasi-free electrons in a simple cubic crystal lattice for the path Γ-X-M-Γ for the 1st and 2nd energy bands.
2. Compare your sketch to the band structure of sodium for the path Γ-H-P-Γ.
3. Sodium crystallizes in bcc lattice. Calculate the distance between P and Γ of the 1st Brillouin zone ($\frac{1}{2}\sqrt{3}\frac{2\pi}{a}$).