§ 5.1.2 Free electrons in empty periodical lattice.

This material can be considered as the next stage of complication. We have again the set of free non interacting electrons but now we take into account the periodicity properties of crystal. Mathematically, this property means that there is a vector of the crystal translations:

$$\vec{R}=n_1 \cdot \vec{a}_1+n_2 \cdot \vec{a}_2+n_3 \cdot \vec{a}_3 \quad \text{, here} \quad \vec{a}_i \quad \text{is a set of basis vectors and } n_i \in Z$$

NB ! n_i can be interpreted as the coordinates of different elementary cells. $\qquad$ (1)

so that for any physical quantity: $A(\vec{r})=A(\vec{r}+\vec{R})$, for example for density of probability we have the next expression.

$$\varphi(\vec{r})^2=\varphi(\vec{r}+\vec{R})^2 \tag{2}$$

The wave function φ (r) and energy for free electrons (see previous lecture) are looks like so:

$$\varphi(\vec{r})=A e^{i\vec{k}\cdot\vec{r}}, \quad E=\frac{\hbar^2 k^2}{2m}=\frac{p^2}{2m}, \text{ here } \vec{k}=(k_x,k_y,k_z) \text{ is a wave vector and momentum } \vec{p}=\hbar\vec{k}. \tag{3}$$

But the periodicity property of a crystal modifies the wave function (despite the independence of the electrons). Bloch showed that in periodic structures, the wave function of an electron can usually be represented in the following form:

$$\varphi(\vec{r})=u(\vec{r})e^{i\vec{k}\cdot\vec{r}}, \quad \text{here} \quad u(\vec{r})=u(\vec{r}+\vec{R}) \quad \text{is a periodical part of total wavefunction.} \tag{4}$$

In this case wave function automatically satisfied to condition (2).

Mathematically the periodicity of crystal means that any physical quantity **A** of crystal can be represented as a Fourier series:

$$A(\vec{r})=\sum_g V_g \cdot e^{i\vec{r}\vec{b}_g} \text{ here } V_g \text{ is a Fourier image of the } \mathbf{A} \text{ quantity} \tag{5}$$

What about vector $\vec{b}_g$? This is a vector of translations for reciprocal space (it means that lattice must be periodical not only in real space but in reciprocal space too) . This vector looks like so:

$$\vec{b}_g=g_1 \cdot \vec{b}_1+g_2 \cdot \vec{b}_2+g_3 \cdot \vec{b}_3 \quad \text{, here} \quad \vec{b}_i \quad \text{is a set of basis vectors in reciprocal space and } g_i \in Z \tag{6}$$

The relation between basis vectors $\vec{a}_i$ and $\vec{b}_i$ is:

$$b_1=\frac{2\pi}{V_0}\vec{a}_2 \times \vec{a}_3 \;\;, \;\; b_2=\frac{2\pi}{V_0}\vec{a}_3 \times \vec{a}_1 \;\;, \;\; b_3=\frac{2\pi}{V_0}\vec{a}_1 \times \vec{a}_2 \quad \text{and} \quad V_0=\vec{a}_1(\vec{a}_2 \times \vec{a}_3) \text{ - volume of elemen-} \tag{7}$$

tary cell.

The practical calculations we will do for Face Centered Crystal(FCC). Elementary cell and basis vectors for primitive cell presented on figure 1.
The basis vectors for primitive cell in this case are: $a_1=a(1/2,1/2,0)$, $a_2=a(1/2,0,1/2)$, $a_3=a(0,1/2,1/2)$.

Using (7) we have for $V_0 = a^3/4$ and basis vectors for reciprocal lattice

$$\vec{b}_1 = \frac{2\pi}{a}(1,1,-1), \vec{b}_2 = \frac{2\pi}{a}(1,-1,1), \vec{b}_3 = \frac{2\pi}{a}(-1,1,1) \tag{8}$$
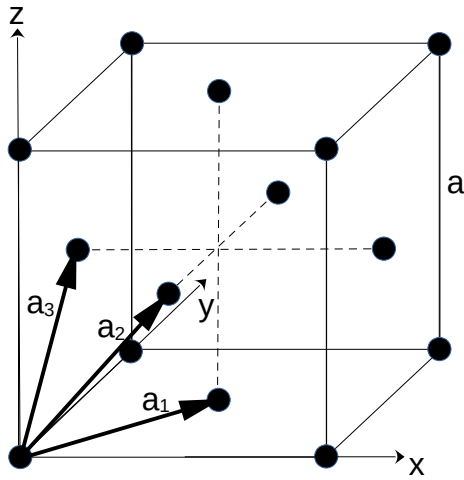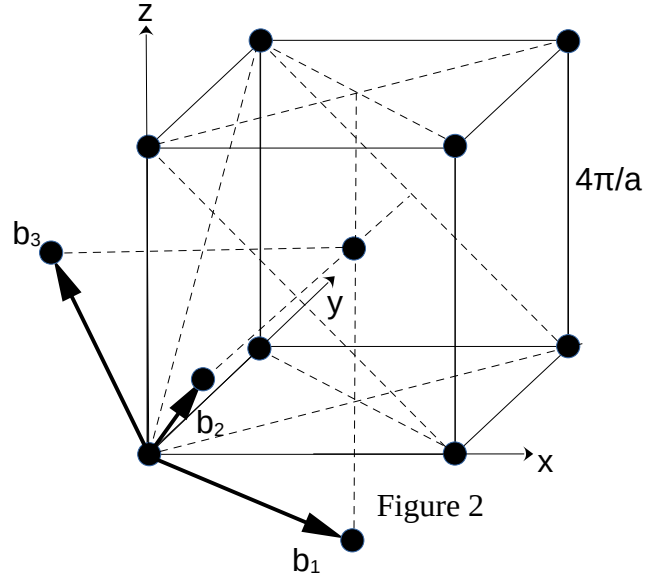

Figure 1

Figure 2

As you see on Figure 2 for FCC in real space the basis vector form the Base Centered Crystal (BCC) in reciprocal space. Now we are ready to write the wavefunction satisfied to Bloch theorem (4):

$$\varphi_g(\vec{r}, \vec{k}) = A e^{i\vec{r}\cdot(\vec{k}+\vec{b}_g)} \tag{9}$$

Wave function substitution to Schrodinger equation :

$$-\frac{\hbar^2}{2m}\hat{\Delta}\cdot\varphi = E\cdot\varphi \tag{10}$$

gives the expression for energy:

$$E_g(\vec{k}) = \frac{\hbar^2(\vec{k}+\vec{b}_g)^2}{2m} \tag{11}$$

In (9) and (11) g-parameter according to the expression (6) include the combination of the three integer numbers $g \equiv g_1, g_2, g_3$. Now we have almost a full set of expression to calculate wavefunction and electron energy (6,7,9,11). The last problem related to calculation of wave vector $\vec{k}$. To get corresponding formula we can use the periodic boundary conditions of lattice (analogically to atoms vibrations). If vector $\vec{R}_L = L_1\vec{a}_1 + L_2\vec{a}_2 + L_3\vec{a}_3$, here L_1, L_2, L_3 gives the position of elementary cells located on crystal surface in direction of basis vectors $\vec{a}_1, \vec{a}_2, \vec{a}_3$, then

$$e^{i\vec{r}(\vec{k}+\vec{b}_g)} = e^{i(\vec{r}+\vec{R}_L)(\vec{k}+\vec{b}_g)} \Rightarrow e^{i\vec{R}_L\vec{k}} = 1 \tag{12}$$

In Cartesian coordinates generally $\vec{R}_L = (L_1 a_{1x} + L_2 a_{2x} + L_3 a_{3x}, L_1 a_{1y} + L_2 a_{2y} + L_3 a_{3y}, L_1 a_{1z} + L_2 a_{2z} + L_3 a_{3z})$ and for FCC lattice $\vec{R}_L = a/2(L_1+L_2, L_1+L_3, L_2+L_3)$. Substitution to (12) gives:

$$k_x = \frac{4\pi}{a(L_1+L_2)}n_x,\ k_y = \frac{4\pi}{a(L_1+L_3)}n_y,\ k_z = \frac{4\pi}{a(L_2+L_3)}n_z$$

$$\text{If we assume that } L_\alpha = L \text{ then } \quad k_\alpha = \frac{2\pi}{aL}n_\alpha \tag{13}$$

and the total volume of crystal is equal to $V = a^3 L^3/4$.

Due to the periodicity of the properties of the crystal in the reciprocal lattice we have the next additional condition for electron energy $E_g(\vec{k}) = E_g(\vec{k}+\vec{b}_g)$. It means that make sense to take into the the account not all but only non equivalent values for wave vector $\vec{k}$. All this values located in so called Brillouin Zone (BZ). BZ is building in reciprocal lattice as Wigner-Seitz elementary cell (analogically as Wigner-Seitz is building in real space). For FCC crystal lattice BZ with symmetrical points and directions presented on Figure 3.
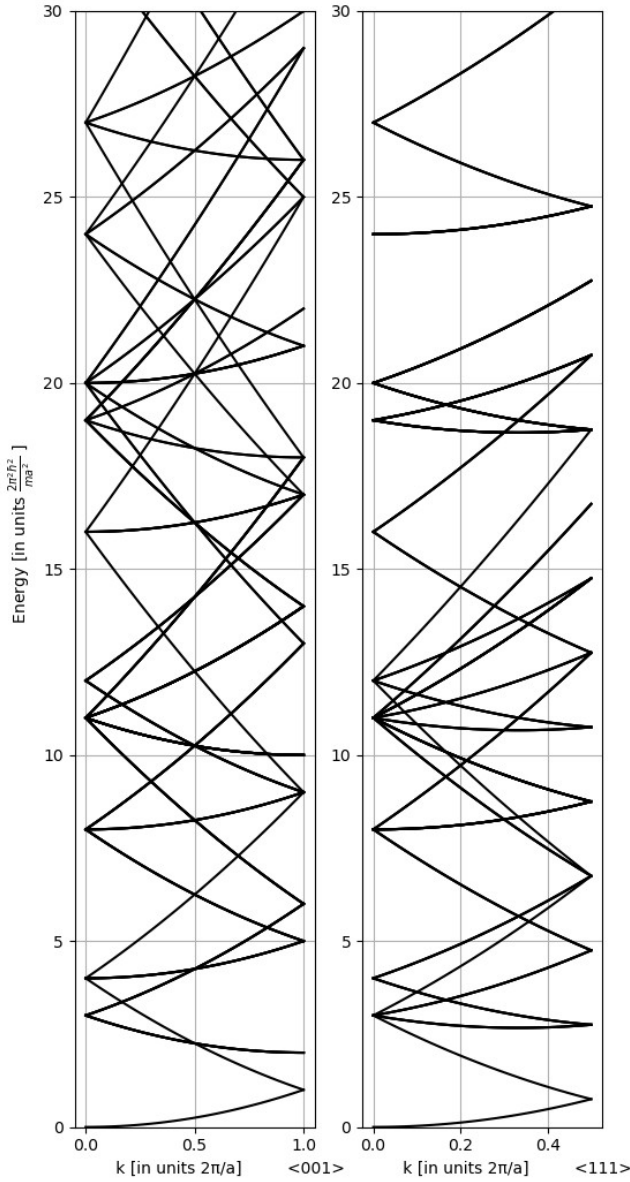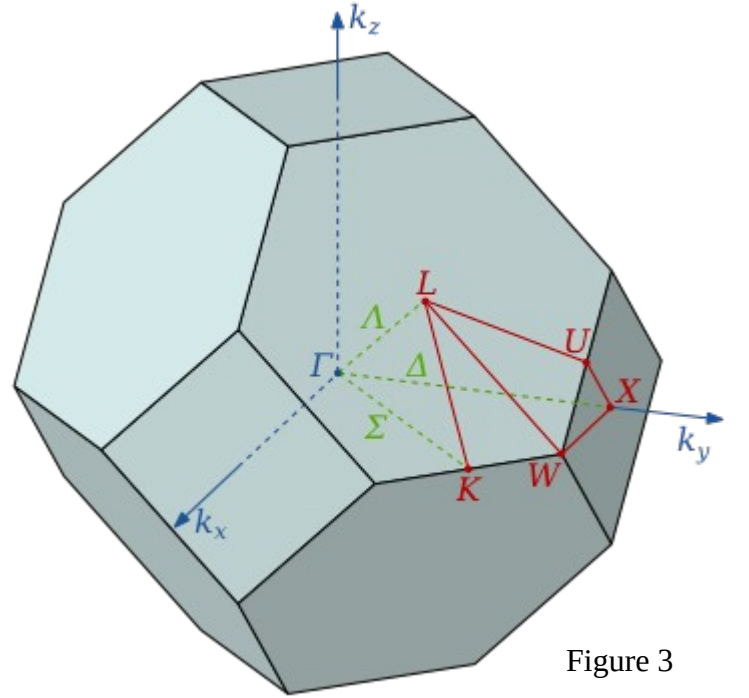

Figure 3

Figure 4

In our case (FCC lattice) for:

Γ-point $\quad \vec{k} = \frac{2\pi}{a}(0,0,0)$

X-point $\quad \vec{k} = \frac{2\pi}{a}(0,1,0)$

L-point $\quad \vec{k} = \frac{2\pi}{a}(1/2,1/2,1/2)$ $\tag{14}$

W-point $\quad \vec{k} = \frac{2\pi}{a}(1/2,1,0)$

K-point $\quad \vec{k} = \frac{2\pi}{a}(3/4,3/4,0)$.

Now we can draw the energy spectrum (energy band structure) for electrons by using (11) $E_g(\vec{k}) = \frac{\hbar^2(\vec{k}+\vec{b}_g)^2}{2m}$. We do this calculations only for directions <100> $\Gamma{\rightarrow}X$ and <111>$\Gamma{\rightarrow}L$.

By using (6) we get:

$$E_{g_1,g_2,g_3}(k_x,k_y,k_z)=\frac{\hbar^2}{2m}[(k_x+g_1 b_{1x}+g_2 b_{2x}+g_3 b_{3x})^2+(k_y+g_1 b_{1y}+g_2 b_{2y}+g_3 b_{3y})^2+(k_z+g_1 b_{1z}+g_2 b_{2z}+g_3 b_{3z})^2]$$

Application to FCC gives (we present in form $\vec{k}=\frac{2\pi}{a}\vec{K}_d$, here $\vec{K}_d$ − dimensionless wavevector :

$$E_{g_1,g_2,g_3}(k_x,k_y,k_z)=\frac{2\pi^2\hbar^2}{m}[(K_{dx}+g_1+g_2-g_3)^2+(K_{dy}+g_1-g_2+g_3)^2+(K_{dz}-g_1+g_2+g_3)^2] \tag{15}$$

Results of calculations presented on Figure 4. As you can see, we got a set of different energy bands for different combinations of g_1, g_2, g_3 (in our calculations taken only values [-2,-1,0,1,2]). This combination can be interpreted as the number of the corresponding energy band. Make sense to substitute three parameters by only one parameter g – is a number of the corresponding combination of g_1, g_2, g_3.
For example in <001> direction energy dependence on wavevector is looks like so:

$$E_{g_1,g_2,g_3}(k_x,k_y,k_z)=\frac{2\pi^2\hbar^2}{m}[(g_1+g_2-g_3)^2+(g_1-g_2+g_3)^2+(K_{dz}-g_1+g_2+g_3)^2] \quad \text{here } K_{dz}\in[0,1] \tag{16}$$

In Γ-point (see Figure 4) the calculated energy and corresponding combinations for g_1, g_2, g_3 presented in Table 1

The lowest energy with energy 0 is not degenerate. The first excited level (energy 3) is 8 times degenerate, and the second excited level (energy 4) is 6 times degenerate and etc.

There is a very important function that characterizes the energy spectrum of electrons in periodic lattices, the so-called density of states (DOS) function g(E). The physical meanings of this function is simple, g(E)dE gives the number of states in region of energies from E to E+dE.

In practical numerical simulation of real crystals the following expression is using:

$$g(E)=\sum_{\vec{k},g}\delta(E-E_g(\vec{k})) \tag{17}$$

Energy in units $2\pi^2 h^2/ma^2$	g_1	g_2	g_3
0	0	0	0
3	0	0	1
3	0	0	-1
3	0	1	0
3	0	-1	0
3	0	1	0
3	-1	0	0
3	1	1	1
3	-1	-1	-1
4	0	1	1
4	0	-1	-1
4	1	0	1
4	-1	0	-1
4	1	1	0
4	-1	-1	0

Table 1

The summation must be performed over some (take only actual) energy bands and over all wave vectors located inside the BZ (for an FCC crystal, see Fig. 3).
There is some problems with numerical summation over wave vector. For example in Γ→X direction $k_y=\frac{2\pi}{aL}n_y$, here L is equal to Avogadro number it means that integer number $n_y\in[-L,+L]$ and direct exact summation over wave vectors is impossible. The problem can be solved by next way. If we have exactly calculated DOS function so:

$$\sum_{g,\vec{k}} g_{exact}(E_g(\vec{k}))=N_k^{BZ}N_{bands}, here$$

$$N_k^{BZ}-\text{exact number of wave vectors}(\text{this number is around }10^{70}),$$
$$N_{bands}-\text{number of energy bands taken into the considiration}$$
$$\tag{18}$$

But not needs to take into account all k-points but only part of it. In this case calculated DOS is not exact but sufficiently accurate. For limited number of k-points we have:

$$\sum_{g,\vec{k}} g_{\text{approx}}(E_g(\vec{k})) = C N_k N_{bands}, here$$

$N_k <<< N_k^{BZ} - number\ of\ k-points,$

$N_{bands} - number\ of\ energy\ bands\ taken\ into\ the\ considiration$

$C - additional\ normalizing\ constant\ which\ can\ be\ obtained\ from\ calculations.$

(19)

It is clear that $g_{\text{approx}}(E)/(C N_k) = g_{\text{exact}}(E)/N_k^{BZ}$. It is important to emphasize that in practical calculations, not g(E), but g(E)/N_k appears. The fact is that N_k equal to number of elementary cells and $N_k V_0$ gives the total volume of crystal.

It makes sense to note that, despite the simplicity of this model, it reflects the most important property of periodic structures - the band nature of the electron energy and its periodicity. This approach can be used as a start point (zero approximation) for further more realistic calculations the properties of crystals.

The addition of a periodic potential for electrons only leads to some correction of the band structure of electron energy (picture on Figure 4. for FCC crystal).