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Leszek Bryja, Joanna Jadczyk

THEORY OF CONDENSED MATTER

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Preface

This textbook have its origin in courses on *Solid State Physics* taught first in Polish in years 2001-2012 at Wroclaw University of Technology for students from varies faculties: Physics, Chemistry and Engineering with different background in physics. The same concern students attending course *Theory of Condensed Matter* on the second level study. The composition of the students in the course of is typically 70% from the Physics (continuation of the first level study) and the rest are from Technical Physics and from other countries. As a consequence of the this there was a necessity to have a textbook which gives a concise account of main elements of physics of solid states valuable for variety of students. One problem encountered in teaching physics of condensed matter was the lack of adequate textbook which can be realised in one semester. There are many very good textbook on this subject but to commodious to be taught in one semester. The object of this book is to present the basic properties of condensed matter in a very short manner. In this textbook the fundamental aspects of theory of condensed matter in presented in the order: crystal structures, lattice vibrations, electronic properties and electron and hole concentrations in solids. Bibliography at the end of the book should be helpful for the reader who needs extended knowledge in a special area of condensed matter. It is designed to be of the interest to graduate students of physics, chemistry and engineering. It is hoped that it will also serve as a review for young scientist working in different areas of study who need to be familiar with basics of condensed matter.

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Leszek Bryja
Joanna Jadczyk

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1. Introduction. Symmetry in crystals

Direct lattice

Most of solids states have a crystal structure. In crystallography the first idea of mathematical description of crystal is to introduce a point group, called direct lattice with set of points defined as:

$$\bar{R} = n_1\bar{a}_1 + n_2\bar{a}_2 + n_3\bar{a}_3, \quad (1.1)$$

where \bar{a}_1 , \bar{a}_2 and \bar{a}_3 are primitive lattice vectors and n_1 , n_2 and n_3 are integral numbers.

The direct lattice is immersed in a real 3 dimensional space:

$$\bar{r} = r_1\bar{a}_1 + r_2\bar{a}_2 + r_3\bar{a}_3, \quad (1.2)$$

where r_1 , r_2 and r_3 are real numbers.

Miller's indices

A plane formed by lattice points:

$$n_1a_1, 0, 0 \quad 0, n_2a_2, 0 \quad 0, 0, n_3a_3, \quad (1.3)$$

can be represented by a formula:

$$\frac{x}{n_1a_1} + \frac{y}{n_2a_2} + \frac{z}{n_3a_3} = 1. \quad (1.4)$$

Product of n_1 , n_2 and n_3 is equal to:

$$n_1n_2n_3 = m \cdot p, \quad (1.5)$$

where m is the minimal common multiple of n_1 , n_2 and n_3 .

We can define a set of numbers:

$$h = \frac{m}{n_1} \quad k = \frac{m}{n_2} \quad l = \frac{m}{n_3}, \quad (1.6)$$

called Miller's indices.

Equation representing a set of parallel lattice planes can then be expressed in a form:

$$h \frac{x}{a_1} + k \frac{y}{a_2} + l \frac{z}{a_3} = p \quad p = 0, \pm 1, \pm 2, \dots \quad (1.7)$$

For simplicity we describe a set of such planes by h, k, l .

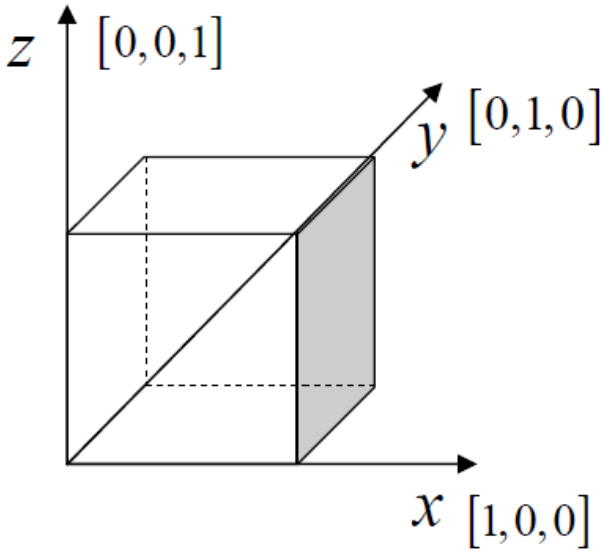


Fig. 1.2. The primary lattice axis.

A vector defined as:

$$\vec{R} = h\vec{a}_1 + k\vec{a}_2 + l\vec{a}_3 \quad (1.8)$$

is called a lattice axis and is represented by h, k, l . The primary lattice axis is presented in the Fig. 1.2.

Reciprocal lattice

For a given direct lattice we can define a reciprocal lattice with primitive reciprocal lattice vectors \vec{b}_i^* satisfying a condition:

$$\bar{b}_i \bar{a}_j = \delta_{ij}. \quad (1.10)$$

The set of vectors satisfying above condition can be chosen in different ways. The most common base of reciprocal vectors \bar{b}_i is given in a form:

$$\bar{b}_1 = \frac{\bar{a}_2 \times \bar{a}_3}{\bar{a}_1 \times \bar{a}_2 \cdot \bar{a}_3} \quad \bar{b}_2 = \frac{\bar{a}_3 \times \bar{a}_1}{\bar{a}_1 \times \bar{a}_2 \cdot \bar{a}_3} \quad \bar{b}_3 = \frac{\bar{a}_1 \times \bar{a}_2}{\bar{a}_1 \times \bar{a}_2 \cdot \bar{a}_3}. \quad (1.11)$$

The reciprocal lattice space is defined as a set of points:

$$\bar{R}^* = m_1 \bar{b}_1 + m_2 \bar{b}_2 + m_3 \bar{b}_3, \quad (1.12)$$

where m_1, m_2 and m_3 are integral numbers.

The reciprocal lattice is immersed in a real 3 dimensional space:

$$\bar{r}^* = r_1 \bar{b}_1 + r_2 \bar{b}_2 + r_3 \bar{b}_3. \quad (1.13)$$

The vector h, k, l in the reciprocal lattice is perpendicular to the plane h, k, l in the direct lattice and vice versa.

The distance between planes h, k, l in the direct lattice is equal to the invert length of vector $R_{h,k,l}^*$ in a reciprocal lattice:

$$d_{(h,k,l)} = \frac{1}{R_{[h,k,l]}^*}. \quad (1.14)$$

2. Vibrations of the crystal lattice. Part I - acoustic phonons

Acoustic vibrations

The vibrations of atoms in crystal in a harmonic approximation. Semi-classical picture.

Let us consider a one dimensional crystal with the lattice constant a and an atoms mass equal to m (Fig. 2.1)

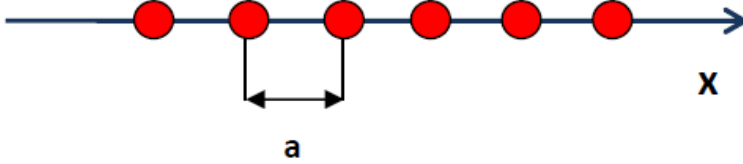


Fig. 2.1. A one dimensional crystal with the lattice constant a and an atom mass m .

Newton 2nd law for n -th atom in one dimensional crystal with lattice constant is:

$$m\ddot{\xi}_n = \kappa \xi_{n+1} - \xi_n - \kappa \xi_n - \xi_{n-1} , \quad (2.1)$$

where m is a mass of atom, ξ_n is a displacement of an atom n from its equilibrium position and κ a force constant a string. We are looking for the solution in a form of a wave function:

$$\xi_n = \zeta e^{i(qna - \omega t)} . \quad (2.2)$$

Inserting (3.2) into (3.1) we obtain:

$$-m\omega^2 = \kappa e^{iqa} + e^{-iqa} - 2\kappa = 2\kappa \cos qa - 1 . \quad (2.3)$$

After simple calculations we obtain:

$$\omega = \sqrt{\frac{4\kappa}{m}} \left| \sin \frac{qa}{2} \right| . \quad (2.4)$$

When $q \rightarrow 0$ we obtain:

$$\omega = \sqrt{\frac{\kappa}{m}} qa. \quad (2.5)$$

Velocity of sound in a crystal equals:

$$u = \frac{\omega}{q} \underset{q \rightarrow 0}{=} \sqrt{\frac{\kappa}{m}} a = \sqrt{\frac{\kappa a}{m/a}}. \quad (2.6)$$

In three dimensions we have:

$$u = \frac{\omega}{q} \underset{q \rightarrow 0}{=} \sqrt{\frac{E}{\rho}}, \quad (2.7)$$

where E is the Young's modulus and ρ is a density of a material.

Such vibrations are called **acoustic vibrations**. The vibrations with the shortest wavelength are those in which the neighbour atoms are displaced in opposite directions, it is they have opposite amplitudes $\pm A$. It is related to the wavelength of the vibration:

$$\frac{\lambda_{\min}}{2} = a \rightarrow \lambda_{\min} = 2a. \quad (2.8)$$

It corresponds to the maximum wavelength vector:

$$q_{\max} = \frac{2\pi}{\lambda_{\min}} = \frac{\pi}{a}. \quad (2.9)$$

So the total dependence of vibrations of atoms in crystals is related to the variation of a wave vector from:

$$q = 0 - \pm \frac{\pi}{a} \quad (2.10)$$

The dependence of acoustic vibration in the whole wave vector zone is presented in the Fig. 2.2.

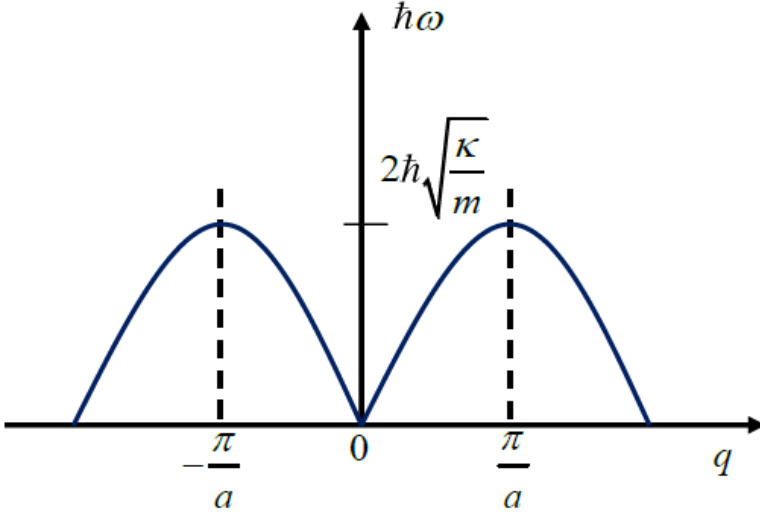


Fig. 2.2 Energy dispersion of acoustics phonons.

Quantization of vibrations. Energy quanta-phonon

The harmonic oscillations are well known problem in quantum mechanics. The vibrations total energy is given in a form:

$$E = \sum_q \left(n_q + \frac{1}{2} \right) \hbar\omega_q = E_0 + \sum_q n_q \hbar\omega_q, \quad (2.11)$$

where E_0 is a crystal lattice ground state at absolute zero temperature and n_q is the number quasi-particle with energy $\hbar\omega_q$ called phonons.

Phonons have also momentum:

$$\bar{p}_f = \hbar\bar{q}. \quad (2.12)$$

The total momentum of phonons equals:

$$\bar{p} = \sum_q n_q \hbar\bar{q}. \quad (2.13)$$

In the formalism of second quantization, phonons with wave vector \bar{q} are described by creation \bar{a}_q^+ and annihilation \bar{a}_q operators:

$$\begin{aligned}
 \bar{a}_q^+ |\dots, n_q, \dots\rangle &= \sqrt{n_q + 1} |\dots, n_{q+1}, \dots\rangle \\
 \bar{a}_q |\dots, n_q, \dots\rangle &= \sqrt{n_q} |\dots, n_{q-1}, \dots\rangle \\
 \bar{a}_q^+ \bar{a}_q |\dots, n_q, \dots\rangle &= |\dots, n_q, \dots\rangle \\
 \bar{a}_q^+ \bar{a}_q &= \bar{N}_q \\
 [\bar{a}_q, \bar{a}_q^+] &= \delta_{qq} \dots
 \end{aligned} \tag{2.14}$$

In this formalism the Hamiltonian and the energy of phonons are expressed in a form:

$$\begin{aligned}
 \hat{H} &= \sum_q \frac{\hbar \omega_q}{2} \bar{a}_q^+ \bar{a}_q + \bar{a}_q \bar{a}_q^+ \\
 E &= \sum_q \left(n_q + \frac{1}{2} \right) \hbar \omega_q
 \end{aligned} \tag{2.15}$$

3. Vibrations of the crystal lattice. Part II - optical phonons

Let's us regard a simplified problem of a crystal lattice vibration in one dimensional approximation with lattice constant equal to a . The vibrations of a crystal with two different base atoms, of mass m_1 and m_2 can be expressed in a form:

$$\begin{cases} m_1 \ddot{\xi}_{1n} = \kappa_2 (\xi_{2n} - \xi_{1n}) - \kappa_1 (\xi_{1n} - \xi_{2n-1}) \\ m_2 \ddot{\xi}_{2n} = \kappa_1 (\xi_{1n+1} - \xi_{2n}) - \kappa_2 (\xi_{2n} - \xi_{1n}) \end{cases} \quad (3.1)$$

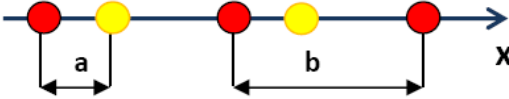


Fig.3.1 The scheme of crystal with two different base atoms.

Since the equation n is conjugated with equations $n-1$ and $n+1$ by variables ξ_{2n-1} and ξ_{1n+1} we are looking for the solution in a form of a wave function:

$$\begin{cases} \xi_{1n} = \zeta_1 e^{i qna - \omega t} \\ \xi_{2n} = \zeta_2 e^{i qna - \omega t} \end{cases}, \quad (3.2)$$

where ξ_{1n} and ξ_{2n} denote different amplitudes and phases for both atoms. Inserting (3.10) into (3.9) we obtain:

$$\begin{cases} -m_1 \omega^2 \zeta_1 = \kappa_2 (\zeta_2 - \zeta_1) - \kappa_1 (\zeta_1 - \zeta_2 e^{-iqa}) \\ -m_2 \omega^2 \zeta_2 = \kappa_1 (\zeta_1 e^{iqa} - \zeta_2) - \kappa_2 (\zeta_2 - \zeta_1) \end{cases} \quad (3.3)$$

After simple calculations we obtain:

$$\begin{cases} \zeta_1 [m_1 \omega^2 - (\kappa_1 + \kappa_2)] + \zeta_2 [\kappa_2 + \kappa_1 e^{-iqa}] = 0 \\ \zeta_1 [\kappa_1 e^{-iqa} + \kappa_2] + \zeta_2 [m_2 \omega^2 - (\kappa_1 + \kappa_2)] = 0 \end{cases} \quad (3.4)$$

A nontrivial solution for ζ_1 and ζ_2 is obtained only when the determinant of above matrix equals:

$$\left[m_1 \omega^2 - (\kappa_1 + \kappa_2) \right] \left[m_2 \omega^2 - (\kappa_1 + \kappa_2) \right] - \kappa^2 = 0, \quad (3.5)$$

where

$$\kappa^2 = \kappa_1^2 + \kappa_2^2 + 2\kappa_1\kappa_2 \cos qa \quad (3.6)$$

and

$$|\kappa_2 - \kappa_1| \leq \kappa \leq \kappa_1 + \kappa_2. \quad (3.7)$$

If we put:

$$m_1 = m_2 = m \quad (3.8)$$

and simplifying the solution to the analytical one:

$$\left[m\omega^2 - \kappa_1 + \kappa_2 \right]^2 - \kappa^2 = 0 \quad (3.9)$$

we still have two solutions (two different vibrations) due to the difference of the string constants κ_1 and κ_2 :

$$\omega_{1,2} = \sqrt{\frac{\kappa_1 + \kappa_2 \pm \kappa}{m}}. \quad (3.10)$$

When $q = 0$ we have:

$$\omega_1 = 0 \quad \omega_2 = \sqrt{\frac{2 \kappa_1 + \kappa_2}{m}} \quad (3.11)$$

and when $q = \pm \frac{\pi}{a}$ we have:

$$\omega_1 = \sqrt{\frac{2\kappa_1}{m}} \quad \omega_2 = \sqrt{\frac{2\kappa_2}{m}}. \quad (3.12)$$

We obtain a discontinuity gap that is phonon energy gap:

$$E_g = \omega \hbar \sqrt{\frac{2}{m}} \left(\sqrt{\kappa_2} - \sqrt{\kappa_1} \right). \quad (3.13)$$

The dependence of both vibration frequencies in the whole wave vector zone are presented in the Fig. 3.1

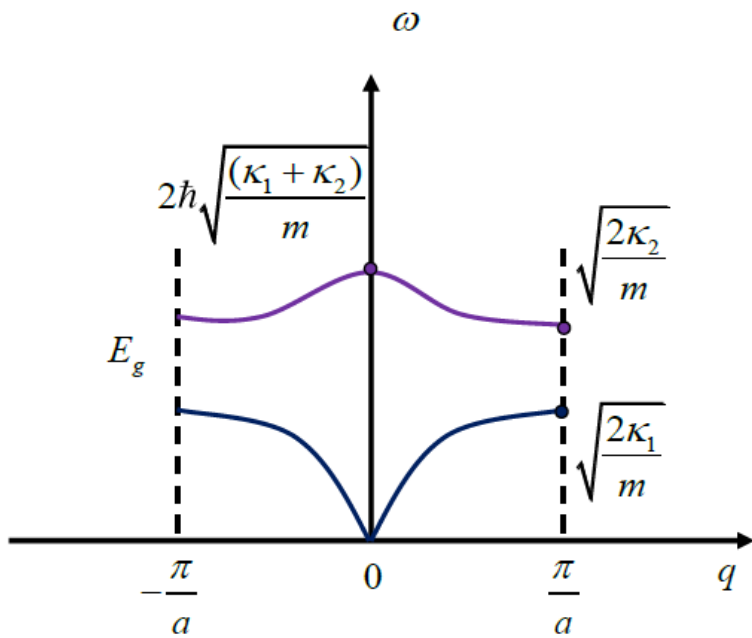


Fig 3.1. The energy dispersion of acoustic and optical phonons – lower and upper branch respectively.

4. Debye theory of the specific heat

Albert Einstein assumed in his specific heat calculations that both transversal and longitudinal vibrations frequency are independent on the vibrations wave vectors:

$$\begin{aligned}\omega_T &= \text{const} \\ \omega_L &= \text{const}.\end{aligned}\tag{4.1}$$

He extended Dulong-Pettite law which states that specific heat capacity of a crystal is constant and equals:

$$c_v = 3RT ,\tag{4.2}$$

but his calculations were not satisfied in very low temperatures.

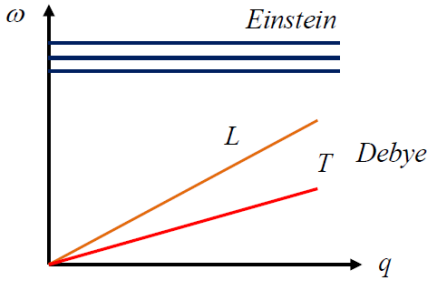


Fig. 4.1. The comparison between the Debye's dispersion of the vibration frequency and the Einstein's assumption.

Peter Debye assumed in his calculations linear dispersion on the vibration frequency:

$$\begin{aligned}\omega_T &= u_T q \\ \omega_L &= u_L q\end{aligned}\tag{4.3}$$

The density of states of vibrations in 3 dimensional wave vector space for each of three vibration branches equals to:

$$\rho \bar{q} = \frac{1}{8\pi^3} cm^{-3}.\tag{4.4}$$

The number of states in a sphere a of radius q and a width dq for one branch equals to:

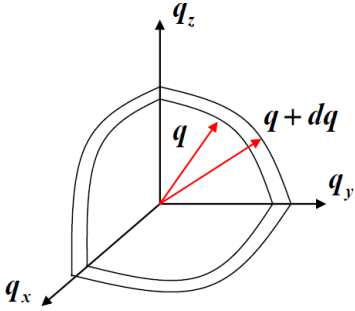


Fig.4.2 The sphere of wave vectors length from q to $q + dq$.

$$dN = \frac{1}{8\pi^3} 4\pi q^2 dq = \frac{q^2 dq}{2\pi^2}. \quad (4.5)$$

On the other hand taking density of state in one dimensional frequency state $Z(\omega)$ we obtain:

$$dN = Z_1 \omega d\omega, \quad (4.6)$$

also for one vibration branch. From equations 4.5 and 4.6 we have:

$$Z_1 \omega = \frac{3\omega^2}{2\pi^2 u^3}. \quad (4.7)$$

If we assume for simplicity that all three velocities of sound are the same we finally obtain the total density of states in a frequency space:

$$Z \omega = \frac{3\omega^2}{2\pi^2 u^3}. \quad (4.8)$$

Since the linear dependence of a vibration frequency is not proper we have to determine the maximum value of a vibration frequency following simple calculations:

$$3N = \int_0^{\omega_m} Z \omega d\omega = \frac{3\omega^2}{2\pi^2 u^3} \int_0^{\omega_m} \omega^2 d\omega = \frac{\omega_m^3}{2\pi^2 u^3}. \quad (4.9)$$

So that

$$\omega_m = u^3 \sqrt[3]{6\pi^2 N}, \quad (4.10)$$

this gives the shortest wavelength of vibrations:

$$\lambda_{\min} = \frac{2\pi}{\sqrt[3]{6\pi^2 N}} \approx \frac{1,6}{\sqrt[3]{N}}. \quad (4.11)$$

Phonons are bosons described by a Bose-Einstein statistic:

$$f_B(\omega) = \frac{1}{e^{\frac{\hbar\omega}{kT}} - 1}. \quad (4.12)$$

The value of a physical quantity A in thermal equilibrium can be expressed as:

$$A = \int_0^{\omega_m} \omega f_B(\omega) A(\omega) d\omega = \frac{3}{2\pi^2 (u\hbar)^3} = \int_0^{\frac{\hbar\omega_m}{kT}} A(\hbar\omega) \frac{(\hbar\omega)^2}{e^{\frac{\hbar\omega}{kT}} - 1} d(\hbar\omega). \quad (4.13)$$

Introducing so called Debye temperature T_D :

$$T_D = \frac{\hbar\omega_m}{k}, \quad (4.14)$$

a thermal equilibrium of quantity A equals:

$$A = \frac{3}{2\pi^2} \left(\frac{kT}{u\hbar} \right)^3 \int_0^{T_D/T} A(x) \frac{x^2 dx}{e^x - 1}, \quad (4.15)$$

where

$$x = \frac{\hbar\omega_m}{kT}. \quad (4.16)$$

Since

$$\frac{1}{u\hbar^3} = \frac{6\pi^2 N}{kT_D^3} \quad (4.17)$$

we finally have:

$$A\left(\frac{T}{T_D}\right) = 9 \left(\frac{T}{T_D}\right)^3 N \int_0^{T_D/T} A(x) \frac{x^2 dx}{e^x - 1}. \quad (4.18)$$

In order to calculate the specific heat of a solid we have to substitute $A(\omega) = \hbar\omega$ and $N = N_A$ where N_A is the Avogadro constant. After simple calculations we obtain:

$$U\left(\frac{T}{T_D}\right) = 9R\theta \left(\frac{T}{T_D}\right)^4 \int_0^{T_D/T} \frac{x^3 dx}{e^x - 1}, \quad (4.19)$$

where $R = kN_A$ is a gas constant.

I. High temperature limit

In the high temperature limit we have:

$$T \gg T_D \text{ and } x \ll 1 \quad (4.20)$$

and we can make simple approximation:

$$\frac{x^3}{e^x - 1} \approx \frac{x^3}{1 + x - 1} = x^2. \quad (4.21)$$

Finally we have a total energy of crystal equals to:

$$U = 9RT_D \left(\frac{T}{T_D} \right)^4 \int_0^{T_D/T} x^2 dx = 3RT. \quad (4.22)$$

A specific heat of a crystal is given by:

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = 3R. \quad (4.23)$$

We can also calculate the number of phonons simply putting $A \omega = 1$:

$$\bar{n} = 9N \left(\frac{T}{T_D} \right)^3 \int_0^{T_D/T} x dx = \frac{9}{2} N \left(\frac{T}{T_D} \right). \quad (4.24)$$

From equations (3.22) and (3.24) we have the average energy of phonons:

$$\langle \hbar\omega \rangle = \frac{U}{\bar{n}} = \frac{2}{3} kT_D. \quad (4.25)$$

II. Low temperature limit

$$T_D \gg T \quad (4.26)$$

In low temperatures we can put $T_D/T \rightarrow \infty$:

$$U = 9RT_D \left(\frac{T}{T_D} \right)^4 \int_0^\infty \frac{x^3 dx}{e^x - 1}. \quad (4.27)$$

Since

$$\int_0^{\infty} \frac{x^3 dx}{e^x - 1} = \frac{\pi^4}{15} \quad (4.28)$$

we have that the total energy of crystal:

$$U = \frac{3\pi^4}{5} R\theta \left(\frac{T}{\theta}\right)^4. \quad (4.29)$$

A specific heat of a crystal:

$$C_V = \frac{12\pi^4}{5} R \left(\frac{T}{\theta}\right)^3. \quad (4.30)$$

The number of phonons is:

$$\bar{n} = 9 \left(\frac{T}{\theta}\right)^3 N \int_0^{\theta/T} \frac{x^2 dx}{e^x - 1} \xrightarrow{\theta \gg T} 9N \left(\frac{T}{\theta}\right)^3 \int_0^{\infty} \frac{x^2 dx}{e^x - 1}, \quad (4.31)$$

this gives:

$$\bar{n} \sim T^3. \quad (4.32)$$

From equations (3.29) and (3.32) we have the average energy of phonons:

$$\langle \hbar\omega \rangle = \frac{U}{\bar{n}} \sim T. \quad (4.33)$$

5. Quantum Mechanics

Why quantum mechanics is indispensable in solid state physics?

In order to describe so complicated system we have to use quantum mechanics formalism. Obviously we always have to use quantum mechanics when we consider physical problems in an atomic scale but even in particle physics we often apply classical methods to have a simplified, general view of a problem in question. So why do we really need to use quantum mechanics and what are the arguments that convince us that without quantum mechanics we cannot understand what really occurs in solid state.

The most direct argument comes from the theory of conductance. The classical mechanical description of conductance proposed by Paul Drude almost at the same time when Ernest Rutherford proposed his model of atom consisting of positive heavy nuclei and light electrons. Drude interpreted conductivity as a movement of free electron gas in crystal lattice of positively charged ions. In this model the conductance is given by a formula:

$$\sigma = \frac{e^2 \cdot n \cdot l}{m \cdot v}, \quad (5.1)$$

where n is an electron concentration, m – the mass of an electron, v – the electrons velocity and l – the mean free path of an electron. The eq. 5.1 can be converted into form for mean free path of an electron l :

$$l = \frac{\sigma \cdot m \cdot v}{e^2 \cdot n}. \quad (5.2)$$

All physical quantities on the right side of eq. 5.2 can be estimated with very good accuracy. The mass and charge of electron is known. The conductivity and concentration can be determined in experiment (measurement of resistance and Hall effect) and velocity can be evaluated from thermodynamical considerations. It turns out that the mean free path of an electron is of the range of $5 \times 10^{-6} \text{m}$ (50 nm) in a room temperature and increase up to 1cm in $T=1\text{K}$. The similar mean free path is evaluated in semiconductors.

The distance between atoms in lattice is of the range 0,3 nm so even in a room temperature the mean free path of electrons is of the range of a few hundred lattice constants. In classical picture it state that in spite of Coulomb interactions between an electron and ionized atom

cores electron can move a path of hundreds lattice constants without collision, it is scattering with them. When we go down with temperature the path between scatterings can exceed a million lattice constant. This means that solid state is actually transparent for an electron movement.

Above phenomena cannot be interpreted with the use of classical methods. Nevertheless the classical model is considered an electron due to Coulomb interaction should scatter almost with each atom on his path. Its movements should be zigzag type and its mean free path should be of the range of one lattice constant.

One has to put reproach that the formula 4.1 is not true. The mean free path can be however determined directly from experiment. When dimensions of the conductor are big enough their properties are govern by bulk properties. When in turn the size of conductor is lowered below the mean free path of electrons it should be observed as an abrupt decrease of its conductivity. And such effects are observed in experiments. Hence the accurate determination of conductance of metals in low temperatures requires samples big enough.

This simple example shows that we cannot obtain valuable results on properties of electrons in a solid state without a use of quantum mechanics methods.

The Hamiltonian for a crystal can be described in a form:

$$\hat{H} = \sum_i \frac{\hat{p}_i^2}{2m_i} + \sum_j \frac{\hat{p}_j^2}{2M_j} + \frac{1}{2} \sum_{\substack{j,j \\ j \neq i}} \frac{Z_j Z_j e^2}{4\pi\epsilon |\mathbf{R}_j - \mathbf{R}_j|} - \sum_{j,i} \frac{Z_j e^2}{4\pi\epsilon |\mathbf{r}_i - \mathbf{R}_j|} + \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \frac{e^2}{4\pi\epsilon |\mathbf{r}_i - \mathbf{r}_j|}, \quad (5.3)$$

where \mathbf{r}_i denotes the positions of valence electrons and \mathbf{R}_j denotes the positions of ion cores, it is nucleus with core electrons strongly bound with nuclei.

Since the problem is too complicated due to a huge number of particles involved ($N \sim 10^{23}$) we have to make a number of simplifications except the already made with dividing electrons for valence and core ones.

Hamiltonian in the adiabatic approximation can be expressed in a form:

$$H = H_{ions}(\mathbf{R}_j) + H_e(\mathbf{r}_i, \mathbf{R}_{j0}) + H_{e-ion}(\mathbf{r}_i, \delta\mathbf{R}_j). \quad (5.4)$$

The electronic Hamiltonian is expressed in a form:

$$H_e = \sum_i \frac{p_i^2}{2m_i} + \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \frac{e^2}{4\pi\epsilon |\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,j} \frac{Z_j e^2}{4\pi\epsilon |\mathbf{r}_i - \mathbf{R}_{j0}|}. \quad (5.5)$$

The mean field approximation also called one electron approximation:

$$H_{1e} \Phi_n(\mathbf{r}) = \left(\frac{p^2}{2m} + V(\mathbf{R}) \right) \Phi_n(\mathbf{r}) = E_n \Phi_n(v), \quad (5.6)$$

where $V(\mathbf{R})$ reflects crystal lattice potential. In this approximation we of course do not know the exact form of crystal potential but only its symmetry. Fortunately the unknown data can be determined in experiment in some extent.

6. Bloch function and the $\hat{k}\hat{p}$ method

In crystals in the mean field approximation we assume that the potential encountered by electron has lattice translation symmetry:

$$V(\bar{r}) = V(\hat{T}\bar{r}) = V(\bar{r} + \bar{R}_n) , \quad (6.1)$$

where \bar{R}_n is an arbitrary lattice vector.

We have to solve the Schrödinger equation:

$$\hat{H}\Psi(\bar{r}, t) = E\Psi(\bar{r}, t) \quad (6.2)$$

With a time independent Hamiltonian:

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\bar{r}) = -\frac{\hbar^2}{2m}\Delta + V(\bar{r}) \quad (6.3)$$

and energy operator:

$$E = i\hbar \frac{\partial}{\partial t} . \quad (6.4)$$

So we have to solve following equation:

$$\left(-\frac{\hbar^2}{2m}\Delta + V(\bar{r}) \right) \Psi(\bar{r}, t) = i\hbar \frac{\partial}{\partial t} \Psi(\bar{r}, t) . \quad (6.5)$$

Since the Hamiltonian is time independent we can look for the solution in the form:

$$\Psi(\bar{r}, t) = \psi(\bar{r}) \varphi(t) \quad (6.6)$$

and after simple calculations we obtain a wave function in a form:

$$\Psi(\bar{r}, t) = \psi(\bar{r}) e^{-i\frac{E}{\hbar}t} , \quad (6.7)$$

where $\psi(\bar{r})$ is a solution of time independent equation, so called stationary Schrödinger equation:

$$\hat{H}\psi(\bar{r}) = E\psi(\bar{r}) . \quad (6.8)$$

Bloch function

If we know the wave function of electron in each point of primitive crystal cell $\varphi_{\bar{\rho}}$ we also know it at any point in crystal:

$$\psi_{\bar{R} + \bar{\rho}} = \varphi_{\bar{\rho}} A, \quad (6.9)$$

where according to quantum mechanics:

$$|A|^2 = 1. \quad (6.10)$$

Since $A=A(\mathbf{R})$ we can write:

$$\psi_{\bar{R} + \bar{\rho}} = \varphi_{\bar{\rho}} e^{if(\bar{R})}. \quad (6.11)$$

Since the translations form a group two translations by vectors \mathbf{R}_1 and \mathbf{R}_2 have to satisfy three equations:

$$\hat{T}_{\bar{R}_1} \psi_{\bar{r}} = \psi_{\bar{R}_1 + \bar{\rho}} = \varphi_{\bar{\rho}} e^{if(\bar{R}_1)}, \quad (6.12)$$

$$\hat{T}_{\bar{R}_2} \psi_{\bar{r}} = \psi_{\bar{R}_2 + \bar{\rho}} = \varphi_{\bar{\rho}} e^{if(\bar{R}_2)}, \quad (6.13)$$

$$\hat{T}_{\bar{R}_1 + \bar{R}_2} \psi_{\bar{r}} = \psi_{\bar{R}_1 + \bar{R}_2 + \bar{\rho}} = \varphi_{\bar{\rho}} e^{if(\bar{R}_1 + \bar{R}_2)}, \quad (6.14)$$

hence

$$\hat{T}_{\bar{R}_1 + \bar{R}_2} = \hat{T}_{\bar{R}_1} \circ \hat{T}_{\bar{R}_2} \quad (6.15)$$

and we have:

$$\begin{cases} f(\bar{R}_1 + \bar{R}_2) = f(\bar{R}_1) + f(\bar{R}_2) \\ f(\hat{0}) = 0 \end{cases}. \quad (6.16)$$

The only function satisfying these conditions is linear function:

$$f(\bar{R}) = \bar{k} \cdot \bar{R}. \quad (6.17)$$

Inserting (6.17) to (6.11) we have

$$\psi \bar{R} + \bar{\rho} = \varphi \bar{\rho} e^{i\bar{k} \cdot \bar{R}}. \quad (6.18)$$

Since $\bar{r} = \bar{R} + \bar{\rho}$ we have:

$$\psi \bar{r} = \psi \bar{R} + \bar{\rho} = \left[\varphi \bar{\rho} e^{-i\bar{k} \cdot \bar{\rho}} \right] e^{i\bar{k} \cdot \bar{r}} = u_{\bar{k}} \bar{r} e^{i\bar{k} \cdot \bar{r}}. \quad (6.19)$$

This is so called Bloch function:

$$\psi \bar{r} = u_{\bar{k}} \bar{r} e^{i\bar{k} \cdot \bar{r}}, \quad (6.20)$$

where $u_{\bar{k}} \bar{r}$ has the periodicity of the lattice:

$$u_{\bar{k}} \bar{r} = u_{\bar{k}} \bar{r} + \bar{R}. \quad (6.21)$$

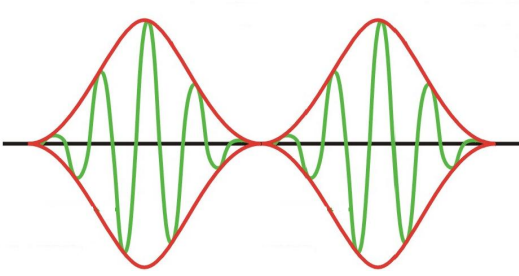


Fig. 6.1 Bloch function

The full wave function has a form:

$$\Psi \bar{r}, t = u_{\bar{k}} \bar{r} e^{-i\left(\bar{k} \cdot \bar{r} - \frac{E}{\hbar} t\right)}. \quad (6.22)$$

$\bar{k} \hat{p}$ equation

When we insert the Bloch wave function:

$$\psi \bar{r} = u_{\bar{k}} \bar{r} e^{i\bar{k} \cdot \bar{r}} \quad (6.23)$$

to the Schrödinger equation:

$$\hat{H} \psi \bar{r} = E \psi \bar{r}, \quad (6.24)$$

we have:

$$\left(-\frac{\hbar^2}{2m} \Delta + V \bar{r} \right) u_{\bar{k}} \bar{r} e^{i\bar{k}\bar{r}} = E u_{\bar{k}} \bar{r} e^{i\bar{k}\bar{r}} . \quad (6.25)$$

After simple calculations we can eliminate $e^{i\bar{k}\bar{r}}$ and obtain an equation for $u_{\bar{k}} \bar{r}$ only:

$$\left[-\frac{\hbar^2}{2m} \Delta - \frac{\hbar^2}{m} i\bar{k}\nabla + \frac{\hbar^2 k^2}{2m} + V \bar{r} \right] u_{\bar{k}} \bar{r} = E u_{\bar{k}} \bar{r} . \quad (6.26)$$

We can rewrite this equation in a form:

$$\left\{ \left[-\frac{\hbar^2}{2m} \Delta + V \bar{r} \right] + \frac{\hbar}{m} \bar{k}\hat{p} \right\} u_{\bar{k}} \bar{r} = \left(E - \frac{\hbar^2 k^2}{2m} \right) u_{\bar{k}} \bar{r} . \quad (6.27)$$

This so called $\bar{k}\hat{p}$ equation. To solve it we can use the perturbation theory:

$$\hat{H}_0 + \hat{H}' u_{\bar{k}} \bar{r} = E' u_{\bar{k}} \bar{r} , \quad (6.28)$$

where

$$\hat{H}_0 = -\frac{\hbar^2}{2m} \Delta + V \bar{r} \quad (6.29)$$

and

$$\hat{H}_0 u_0 \bar{r} = E_0 u_0 \bar{r} \quad E_0 = E(k=0) \quad (6.30)$$

is the solution for $k=0$. The term

$$\hat{H}' = \frac{\hbar}{m} \bar{k}\hat{p} \quad (6.31)$$

is the perturbation and

$$E' = E - \frac{\hbar^2 k^2}{2m} \quad (6.32)$$

is renormalized energy.

Using non-degenerate perturbation theory and limit the extension to the term of the second order we have:

$$E_n' \bar{k} = E_n' 0 + H_m' + \sum_{l \neq n} \frac{H_{nl}'^2}{E_n' - E_l'} + \dots, \quad (6.33)$$

where

$$H_{nl}' = \int u_{n0}^* \bar{r} \hat{H}' u_{l0} \bar{r} d^3r = -\frac{i\hbar^2}{m} \bar{k} \int u_{n0}^* \bar{r} \nabla u_{l0} \bar{r} d^3r. \quad (6.34)$$

We can express energy in a form:

$$E_n \bar{k} = E_n' 0 + \sum_{i=1}^3 a_i k_i + \sum_{i=1}^3 \sum_{j=1}^3 \left(\frac{\hbar^2}{2m} \delta_{ij} + b_{ij} \right) k_i k_j + \dots \quad (6.35)$$

When there is an energy extreme at $\bar{k} = 0$ than linear term equals to zero and we can express the energy of electron in the crystal in a form:

$$E_n \bar{k} = E_n' 0 + \sum_{i=1}^3 \sum_{j=1}^3 \frac{\hbar^2 k_i k_j}{2m_{ij}^*}. \quad (6.36)$$

We limited solution to second order terms. Here, the term m_{ij}^* is defined as an effective mass.

If we choose axis of the frame of reference along to the main crystal directions we can simplify above equation to:

$$E_n \bar{k} = E_n' 0 + \frac{\hbar^2}{2} \left(\frac{k_1^2}{m_1^*} + \frac{k_2^2}{m_2^*} + \frac{k_3^2}{m_3^*} \right). \quad (6.37)$$

When a crystal has only one distinguished axis the electron energy can be expressed in a form:

$$E_n \bar{k} = E_n' 0 + \frac{\hbar^2}{2} \left(\frac{k_1^2 + k_2^2}{m_{\perp}^*} + \frac{k_3^2}{m_{\parallel}^*} \right), \quad (6.38)$$

where m_{\perp}^* and m_{\parallel}^* are the effective mass perpendicular and parallel to distinguished axis.

For cubic crystals in which all three axes are equivalent, it is physical quantities are identical in all directions we have only one effective mass and the electron energy has a form:

$$E_n \bar{k} = E_n' 0 + \frac{\hbar^2 k^2}{2m^*}. \quad (6.39)$$

This is the case of more well known and commonly used semiconductors as Silicon and Gallium Arsenide.

7. Effective mass tensor

Group velocity

Since each linear combination of wave function

$$\Psi_{\bar{k}} \bar{r} = u_{\bar{k}} \bar{r} e^{i \bar{k}\bar{r} - \omega t} \quad (7.1)$$

is a solution of Schrödinger equation we can take the solution in the form:

$$\Psi \bar{r}, t = A \int u_{\bar{k}} \bar{r} e^{i \bar{k}\bar{r} - \omega t} d^3k \dots\dots\dots(7.1.a)$$

in a certain vicinity of a given point in wave vector space \bar{k} :

$$\bar{k} = \bar{k}_0 + \bar{\kappa}, \quad (7.2)$$

$$\omega \bar{k} = \omega_0 \bar{k}_0 + \nabla_k \omega \bar{\kappa}. \quad (7.3)$$

After long but not complicated calculations we obtain solution as a function:

$$\Psi \bar{r}, t = A u_{\bar{k}_0} \bar{r} e^{i \bar{k}_0 \bar{r} - \omega_0 t} J_1 J_2 J_3, \quad (7.4)$$

this also has a form of the Bloch function.

Integrals J_j equal:

$$J_j = \int_{-\Delta k}^{\Delta k} e^{i k_j (x_j - \frac{d\omega}{dk_j} t)} dk_j = J_j = \frac{2 \sin \left[\Delta k \left(x_j - \frac{d\omega}{dk_j} t \right) \right]}{\Delta k \left(x_j - \frac{d\omega}{dk_j} t \right)} \quad (7.5)$$

Integrals have maximum when

$$\bar{r} - \nabla_k \omega t = 0. \quad (7.6)$$

So the wave packet velocity

$$\bar{v} = \frac{1}{\hbar} \nabla_k E \bar{k} \quad (7.7)$$

equals to group velocity.

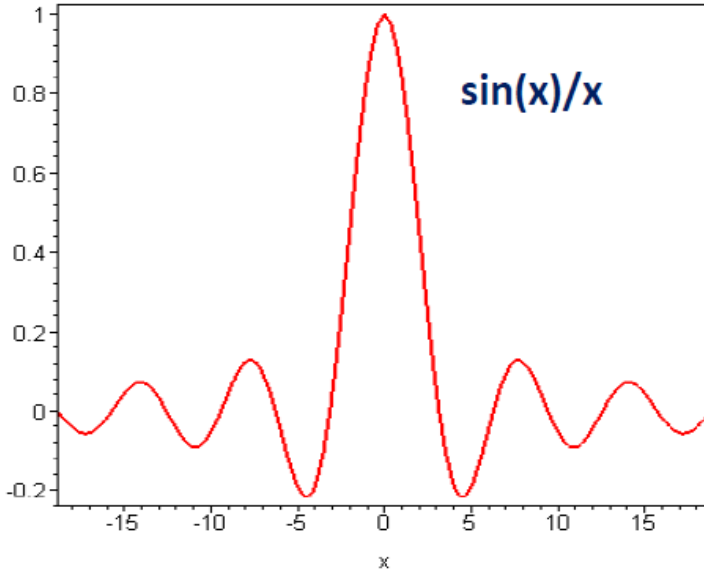


Fig. 7.1. The schematic draw of $\frac{\sin x}{x}$ function.

For parabolic bands:

$$E(\bar{k}) = \frac{\hbar}{2} \left(\frac{k_1^2}{m_1^*} + \frac{k_2^2}{m_2^*} + \frac{k_3^2}{m_3^*} \right), \quad (7.8)$$

an electron velocity is:

$$\bar{v} = \hbar \left(\frac{\bar{k}_1}{m_1^*} + \frac{\bar{k}_2}{m_2^*} + \frac{\bar{k}_3}{m_3^*} \right). \quad (7.9)$$

Generally we have an expression:

$$\bar{m}^* \bar{v} = \hbar \bar{k}. \quad (7.10)$$

We can introduce momentum mass

$$m_i v_i = \hbar k_i. \quad (7.11)$$

Combining equations (6.7) and (6.11) we finally have:

$$\left(\frac{1}{m_i} \right)_{\text{momentum}} = \frac{1}{\hbar^2 k_i} \left(\frac{\partial E}{\partial k_i} \right). \quad (7.12)$$

Influence of external fields on an electron motion.

Let us introduce some useful formulas. When an external field is applied to the crystal we can write:

$$\bar{F} \cdot \bar{v} = \frac{dE}{dt} = \nabla_k E \cdot \bar{k} \frac{d\bar{k}}{dt} = \hbar \dot{\bar{k}} \cdot \bar{v}. \quad (7.13)$$

The field changes the pseudo momentum of an electron

$$\bar{F} = \hbar \dot{\bar{k}}. \quad (7.14)$$

This could be e.g. Lorentz force:

$$\bar{F} = q \bar{E} + \bar{v} \times \bar{B}. \quad (7.15)$$

Effective mass tensor

Further we can calculate an acceleration of an electron:

$$\dot{\bar{v}} = \frac{1}{\hbar} \frac{d}{dt} \nabla_k E(\bar{k}) = \frac{1}{\hbar} \nabla_k \nabla_k E(\bar{k}) \cdot \dot{\bar{k}} = \frac{1}{\hbar^2} \nabla_k \nabla_k E(\bar{k}) \cdot \bar{F}. \quad (7.16)$$

Since

$$\dot{\bar{v}} = m^{-1} \bar{F} \quad (7.17)$$

we have a formula for effective mass tensor:

$$\bar{m}^{-1} = \frac{1}{\hbar^2} \nabla_k \nabla_k E = \frac{1}{\hbar^2} \begin{pmatrix} \frac{\partial^2 E}{\partial k_1^2} & \frac{\partial^2 E}{\partial k_1 \partial k_2} & \frac{\partial^2 E}{\partial k_1 \partial k_3} \\ \frac{\partial^2 E}{\partial k_2 \partial k_1} & \frac{\partial^2 E}{\partial k_2^2} & \frac{\partial^2 E}{\partial k_2 \partial k_3} \\ \frac{\partial^2 E}{\partial k_3 \partial k_1} & \frac{\partial^2 E}{\partial k_3 \partial k_2} & \frac{\partial^2 E}{\partial k_3^2} \end{pmatrix}. \quad (7.18)$$

When we direct axis of a frame along the main axis of the crystal, the effective mass tensor is limited to diagonal terms only:

$$\bar{m}^{-1} = \begin{pmatrix} \frac{1}{m_1^*} & 0 & 0 \\ 0 & \frac{1}{m_2^*} & 0 \\ 0 & 0 & \frac{1}{m_3^*} \end{pmatrix}. \quad (7.19)$$

8. Brillouine zone

General properties of energy gaps

We will prove that the energy of electron in crystal obeys two general equalities. The conjugation of Schrodinger equation:

$$\hat{H}\psi(\bar{r}) = E\psi(\bar{r}), \quad (8.1)$$

$$\hat{H}\psi^*(\bar{r}) = E\psi^*(\bar{r}) \quad (8.2)$$

is

$$\hat{H}\psi^*(\bar{r}) = E\psi^*(\bar{r}). \quad (8.3)$$

Since conjugation of a product is product of conjugations and both energy and all constants in Hamiltonian are real.

When we take a wave function in the form of Bloch function:

$$\Psi_k(x) = e^{ikx} u_k(x) \quad (8.4)$$

we immediately obtain

$$\Psi_k^*(\bar{r}) = u_k^*(\bar{r}) e^{-ikr}. \quad (8.5)$$

Both functions are the solution of the same Hamiltonian \hat{H} so we have first equality:

$$E_n(\bar{k}) = E_n(-\bar{k}). \quad (8.6)$$

The second equality is a consequence of the symmetry of the Bloch function (8.4). We will proof it for simplicity only for one dimensional crystal but the equality holds also in three dimensions. We can transform the Bloch function (8.4):

$$\Psi_k(x) = e^{i\left(k + \frac{2\pi}{a}n\right)x} \left[e^{-\frac{2\pi}{a}inx} u_k(x) \right], \quad (8.7)$$

where $n = \pm 1, \pm 2, \dots$

It is easy to show that the function in brackets has the same lattice periodicity as $u_k(x)$.

To prove this statement we make a substitution:

$$x \rightarrow x + ma, \quad (8.8)$$

where $m = \pm 1, \pm 2, \dots$

We have:

$$e^{-\frac{2\pi}{a}in(x+ma)} u_k(x+ma) = e^{-\frac{2\pi}{a}inx} u_k(x) e^{-2\pi imn} = e^{-\frac{2\pi}{a}inx} u_k(x) = u_{k+\frac{2\pi}{a}n}(x), \quad (8.9)$$

this states that in a crystal both functions are equivalent:

$$\Psi_k(x) = e^{ikx} u_k(x) = e^{i\left(k+\frac{2\pi}{a}n\right)x} u_{k+\frac{2\pi}{a}n}(x) \quad (8.10)$$

and have the same energy:

$$E_{\bar{k}} = E\left(\bar{k} + \frac{2\pi}{a}n\right). \quad (8.11)$$

In three dimensions it states:

$$E_{\bar{k}} = E_{\bar{k}} + 2\pi\bar{R}^* \quad (8.12)$$

Brillouine zone in one dimensional model

Those two periodicity conditions allow to reduce the wave vector space in one dimension to $2\pi/a$. It is useful to choose the centre of this space in $\mathbf{k}=\mathbf{0}$. This gives the so called reduced k vector zone:

$$-\frac{\pi}{a} < k < \frac{\pi}{a}. \quad (8.9)$$

This zone is named a Brillouine zone.

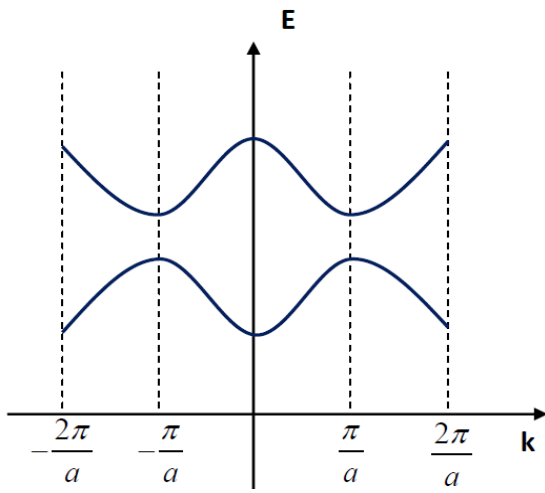


Fig.8.1 Brillouine zone in 1dimensional model.

9. Nearly empty lattice. Energy gap

The free electron is described by a function

$$\Psi = e^{ikx}, \quad (9.1)$$

where we put normalization constant $A=1$. Its energy is described by a simple square dependence on wave vector k :

$$E(k) = \frac{\hbar^2 k^2}{2m}. \quad (9.2)$$

The electron moves in constant potential with arbitrary period a . Let us assume that the lattice constant is equal a and potential energy $V=0$. We can formally reduce dependence (9.2) to first Brillouine zone:

$$-\frac{\pi}{a} < k < \frac{\pi}{a} \quad (9.3)$$

and write down its energy as:

$$E(k) = \frac{\hbar^2}{2m} \left(k + \frac{2\pi}{a} n \right)^2, \quad (9.4)$$

where

$$n = \pm 0, \pm 1, \pm 2, \dots \quad (9.5)$$

denotes for different energy bands. The electron energies and functions for given bands can be written in a form:

$$E_1 = \frac{\hbar^2 k^2}{2m} \quad \Psi_1 = e^{ikx}, \quad (9.6a)$$

$$E_2 = \frac{\hbar^2 \left(|k| - \frac{2\pi}{a} \right)^2}{2m} \quad \Psi_2 = e^{i \left(|k| - \frac{2\pi}{a} \right) x}, \quad (9.6b)$$

$$E_3 = \frac{\hbar^2 \left(|k| + \frac{2\pi}{a} \right)^2}{2m} \quad \Psi_3 = e^{i \left(|k| + \frac{2\pi}{a} \right) x}, \quad (9.6c)$$

$$E_4 = \frac{\hbar^2 \left(\left| k - \frac{4\pi}{a} \right| \right)^2}{2m} \quad \Psi_4 = e^{i \left(\left| k - \frac{4\pi}{a} \right| \right) x}, \quad (9.6d)$$

$$E_5 = \frac{\hbar^2 \left(\left| k + \frac{4\pi}{a} \right| \right)^2}{2m} \quad \Psi_5 = e^{i \left(\left| k + \frac{4\pi}{a} \right| \right) x}. \quad (9.6e)$$

If we do not want to use absolute value of the wave vector we can write down the wave function for positive and negative value separately:

$$\Psi_2 = e^{ikx} u_2(x) \quad u_2(x) = \begin{cases} e^{-i\frac{\pi}{a}x} & 0 \leq k < \frac{\pi}{a} \\ e^{+i\frac{\pi}{a}x} & -\frac{\pi}{a} \leq k < 0 \end{cases}. \quad (9.7)$$

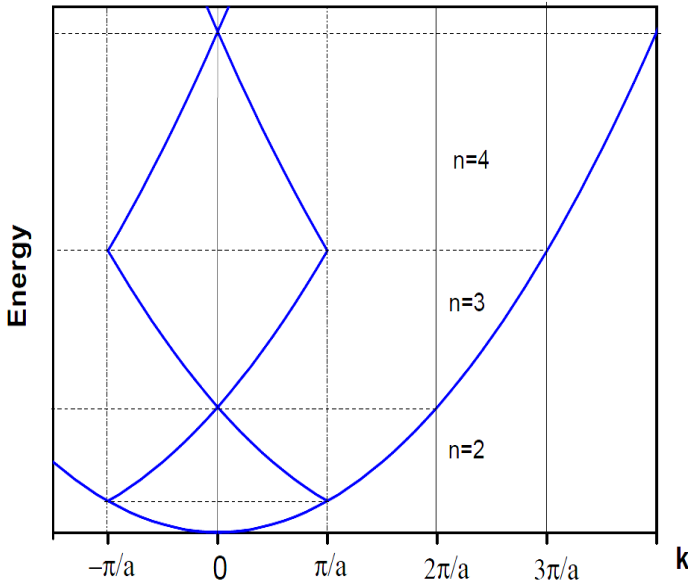


Fig. 9.1 Band structure of free electrons in the empty lattice.

Nearly empty lattice. Energy gap. Energy gap at the border of energy zone

Let us introduce to the empty one dimensional lattice with lattice constant a the potential energy of the same periodicity in simple harmonic function form:

$$V(x) = V_0 \cos\left(\frac{2\pi}{a}x\right) = \frac{V_0}{2} \left(e^{i\frac{2\pi}{a}x} + e^{-i\frac{2\pi}{a}x} \right). \quad (9.8)$$

We have to solve Schrodinger equation:

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] \psi(x) = E \psi(x). \quad (9.9)$$

We will solve it treating $V(x)$ as a perturbation. We could expect the stronger influence on electron energy of perturbation $V(x)$ near points where bands intersect, it is in a case of degeneration at $k=0$ or $k=\pi/a$. Let us solve eq. (9.9) near $k=\pi/a$ for wave vectors:

$$k = \frac{\pi}{a} - \kappa, \quad (9.10)$$

where κ is a small displacement. When we write down the energy and the wave function for first two bands at above points in (9.7) notation we have:

$$E_1 = \frac{\hbar^2}{2m} \left(\frac{\pi}{a} - \kappa \right)^2 \quad \psi_1 = e^{i\left(\frac{\pi}{a} - \kappa\right)x}, \quad (9.11a)$$

$$E_2 = \frac{\hbar^2}{2m} \left(\frac{\pi}{a} + \kappa \right)^2 \quad \psi_2 = e^{-i\left(\frac{\pi}{a} + \kappa\right)x}. \quad (9.11b)$$

When we put in those functions to equation (9.9) we have

$$\begin{cases} \left[\frac{\hbar^2}{2m} \left(\frac{\pi}{a} - \kappa \right)^2 - E \right] e^{i\left(\frac{\pi}{a} - \kappa\right)x} + \frac{V_0}{2} e^{-i\left(\frac{\pi}{a} - \kappa\right)x} = -\frac{V_0}{2} e^{i\left(\frac{3\pi}{a} - \kappa\right)x} \\ \frac{V_0}{2} e^{i\left(\frac{\pi}{a} - \kappa\right)x} + \left[\frac{\hbar^2}{2m} \left(\frac{\pi}{a} + \kappa \right)^2 - E \right] e^{-i\left(\frac{\pi}{a} + \kappa\right)x} = -\frac{V_0}{2} e^{-i\left(\frac{3\pi}{a} + \kappa\right)x} \end{cases}. \quad (9.12)$$

If we remove from above equations all terms $3\pi/a$ which describe higher bands (here third) we obtain linear set of equations for two functions $\psi_1 = e^{i\left(\frac{\pi}{a} - \kappa\right)x}$ and $\psi_2 = e^{-i\left(\frac{\pi}{a} + \kappa\right)x}$:

$$\begin{bmatrix} \left[\frac{\hbar^2}{2m} \left(\frac{\pi}{a} - \kappa \right)^2 - E \right] & \frac{V_0}{2} \\ \frac{V_0}{2} & \left[\frac{\hbar^2}{2m} \left(\frac{\pi}{a} + \kappa \right)^2 - E \right] \end{bmatrix} \begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}, \quad (9.13)$$

which has nontrivial solution only when the matrix determinant is equal to zero:

$$\left[\frac{\hbar^2}{2m} \left(\frac{\pi}{a} - \kappa \right)^2 - E \right] \cdot \left[\frac{\hbar^2}{2m} \left(\frac{\pi}{a} + \kappa \right)^2 - E \right] - \frac{V_0}{4} = 0. \quad (9.14a)$$

So we have solved simple quadratic equation:

$$E^2 - \frac{\hbar^2}{m} \left(\frac{\pi^2}{a^2} + \kappa^2 \right) E + \frac{\hbar^4}{4m^2} \left(\frac{\pi^2}{a^2} + \kappa^2 \right)^2 - \frac{1}{4} V_0^4 = 0, \quad (9.14b)$$

$$\Delta = \frac{\hbar^4}{m^2} \left(\frac{\pi^2}{a^2} + \kappa^2 \right)^2 - \frac{\hbar^4}{m^2} \left(\frac{\pi^2}{a^2} - \kappa^2 \right)^2 + V_0^2 = \frac{4\hbar^4}{m^2} \frac{\pi^2}{a^2} \kappa^2 + V_0^2, \quad (9.14c)$$

which solutions are:

$$E_{\pm} \kappa = \frac{\hbar^2}{2m} \left(\frac{\pi^2}{a^2} + \kappa^2 \right) \pm \sqrt{4 \left(\frac{\hbar^2}{2m} \right)^2 \frac{\pi^2}{a^2} \kappa^2 + \frac{V_0^2}{4}}. \quad (9.15)$$

At Brillouine border at $\mathbf{k}=\pi/a$ we immediately obtain the energy gap:

$$E_{\pm} \left(\frac{\pi}{a} \right) = \frac{\hbar^2}{2m} \frac{\pi^2}{a^2} \pm \frac{V_0}{2} = E_a \pm \frac{E_g}{2}, \quad (9.16)$$

where

$$E_a = \frac{\hbar^2}{2m} \frac{\pi^2}{a^2} \quad \text{and} \quad E_g = V_0. \quad (9.17)$$

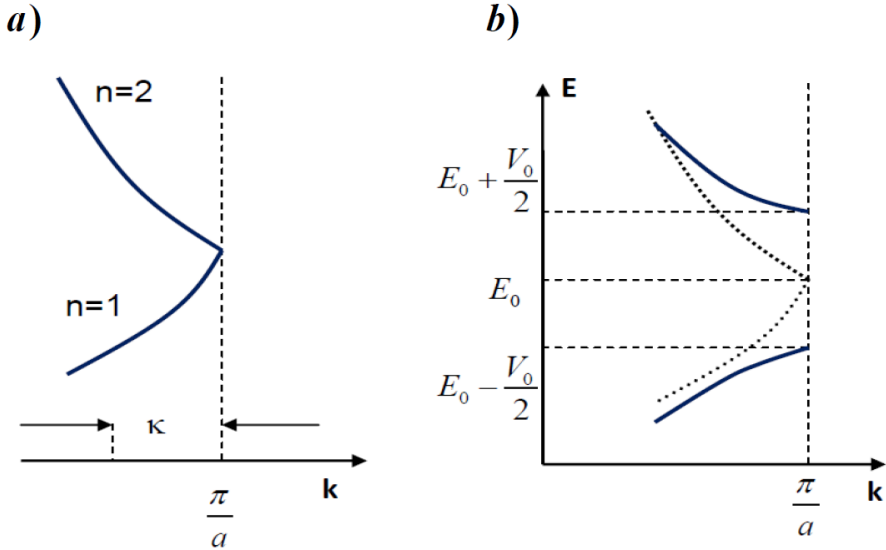


Fig. 9.1 a) Band structure of free electrons in the empty lattice b) Band structure of electrons in nearly empty lattice.

Effective mass at the border of energy zone

When we approximate dependence (9.15) by polynomials up to second order (Taylor's theorem) we obtain:

$$E_{\pm \kappa} = \frac{\hbar^2 \pi^2}{2m a^2} \pm \frac{V_0}{2} + \frac{\hbar^2 \kappa^2}{2m} \pm \frac{4}{V_0} \frac{\hbar^2 \kappa^2}{2m} \frac{\hbar^2 \pi^2}{2m a^2}, \quad (9.18)$$

what we can write in a short form:

$$E_{\pm \kappa} = E_0 \pm \frac{E_g}{2} + \frac{\hbar^2 \kappa^2}{2m_{\pm}^*}, \quad (9.19)$$

where

$$m_{\pm}^* = \frac{m}{1 \pm \frac{4E_0}{E_g}} \quad (9.20)$$

is an effective mass.

We obtained two different effective masses. Since for most of semiconductors E_0 is usually at least one order of magnitude greater than E_g we can make an approximation:

$$m_{\pm}^* = \pm \frac{mE_g}{4E_0}. \quad (9.20)$$

We obtained two very important information: 1^o the effective mass has opposite sign for two nearest bands, 2^o the effective mass is proportional to energy gap.

$\overline{k\hat{p}}$ methods

We can obtain similar results in $\overline{k\hat{p}}$ methods (see lecture):

$$\hat{H} + H' u = E' u, \quad (9.21a)$$

where

$$\hat{H}' = \frac{\hbar}{m} \overline{k\hat{p}} \quad (9.21b)$$

and

$$E' = E - \frac{\hbar^2 k^2}{2m}. \quad (9.21c)$$

In the perturbation theory in approximation up to the second order we have:

$$E_n = E_{n0} + \frac{\hbar^2 k^2}{2m} + \frac{\hbar^2 k^2}{m} \left(\sum_{l \neq n} \frac{|P_{ln}|^2}{E_n - E_l} \right) + \dots \quad (9.22)$$

When we take into account only two energy levels at $k = 0$, the last occupied by electrons E_{10} and the first unoccupied E_{20} , it is assumed that the rest of the levels are separated from them and the energy gap equals to:

$$E_{20} - E_{10} = E_g, \quad (9.23)$$

and we have an expression for the electron energy in a form:

$$E_{\pm}(k) = E_{\pm 0} \pm \frac{\hbar^2 k^2}{2m_{\pm}^*}, \quad (9.24)$$

where an effective mass is expressed by a simple formula:

$$m_{\pm}^* = \frac{m}{1 \pm \frac{2|P_{12}|^2}{mE_g}}, \quad (9.25)$$

It is convenient to define a term:

$$E_p = \frac{2|P_{12}|^2}{m}, \quad (9.26)$$

which has an energy dimension.

Then the effective mass is expressed in a form:

$$m_{\pm}^* = \frac{m}{1 \pm \frac{E_p}{E_g}}. \quad (9.27)$$

The E_p is proportional to the energy width of the energy band which is about 10meV for semiconductors and the energy gap E_g for semiconductors is in the order of 1-2 meV and we can make a simple approximation to evaluate the effective mass:

$$m_{\pm}^* \approx \pm \frac{mE_g}{E_p} \quad (9.28)$$

We see that the effective mass is proportional to energy gap and has opposite sign for upper and lower bands, called the conduction band and the valence band respectively.

Brillouine zone in 3 dimensions

In three dimensions both general energy dependences holds, it is:

$$E(\vec{k}) = E(-\vec{k}) \quad (9.29)$$

and

$$E_{\bar{k}} = E_{\bar{k}} + 2\pi\bar{R}^* , \quad (9.30)$$

where

$$\bar{R}^* = m_1\bar{a}_1^* + m_2\bar{a}_2^* + m_3\bar{a}_3^* \quad (9.31)$$

are vectors in reciprocal lattice.

To prove dependence (9.24) we have to show that wave function for \mathbf{k} :

$$\psi_{\bar{k}}(\bar{r}) = e^{i\bar{k}\bar{r}} u_{\bar{k}}(\bar{r}) \quad (9.32)$$

are identical with those for $\mathbf{k}+2\pi\mathbf{R}^*$. We can write:

$$\psi_{\bar{k}}(\bar{r}) = e^{i(\bar{k} + 2\pi\bar{R}^*)\bar{r}} e^{-i2\pi\bar{R}^*\bar{r}} u_{\bar{k}}(\bar{r}) . \quad (9.33)$$

The function $e^{-i2\pi\bar{R}^*\bar{r}}$ is an periodical function since:

$$\begin{aligned} e^{-i2\pi\bar{R}^*(\bar{r} + \bar{R})} &= e^{-i2\pi\bar{R}^*\bar{r}} e^{-i2\pi\bar{R}^*\bar{R}} = \\ e^{-i2\pi\bar{R}^*\bar{r}} e^{-i2\pi(m_1\bar{a}_1^* + m_2\bar{a}_2^* + m_3\bar{a}_3^*)(m_1\bar{a}_1 + m_2\bar{a}_2 + m_3\bar{a}_3)} &= \\ e^{-i2\pi\bar{R}^*\bar{r}} e^{-i2\pi(m_1n_1 + m_2n_2 + m_3n_3)} &= e^{-i2\pi\bar{R}^*\bar{r}} \cdot 1 \end{aligned} \quad (9.34)$$

We can include this function term to periodic Bloch function:

$$u_{\bar{k} + 2\pi R^*}(\bar{r}) = e^{-2\pi i \bar{R}^* \bar{r}} u_{\bar{k}}(\bar{r}) \quad (9.35)$$

and then we obtain the Bloch function in a form:

$$\psi_{\bar{k} + 2\pi R^*}(\bar{r}) = e^{i(\bar{k} + 2\pi\bar{R}^*)\bar{r}} u_{\bar{k} + 2\pi R^*}(\bar{r}) . \quad (9.36)$$

Construction of the first Brillouine zone:

With the use of dependence of (9.23) and (9.24) we can construct first Brillouine zone. The centre of Brillouine zone is at $k = 0$. All vectors belonging to first Brillouine zone has to obey the rule:

$$\frac{\bar{k}\bar{R}^*}{|\bar{R}^*|} = 2\pi \frac{|\bar{R}^*|}{2}. \quad (9.37)$$

Which is a projection of \bar{k} on any vector in reciprocal space. The \bar{R}^* must be not greater than halve of \bar{R}^* times 2π .

It can be also written in a form:

$$\bar{k}\bar{R}^* = \pi |\bar{R}^*|^2. \quad (9.38)$$

In the Fig. 9.1 the Brillouine for the cubic face centered lattice (FCC) is presented. Also the names most important points and directions are introduced.

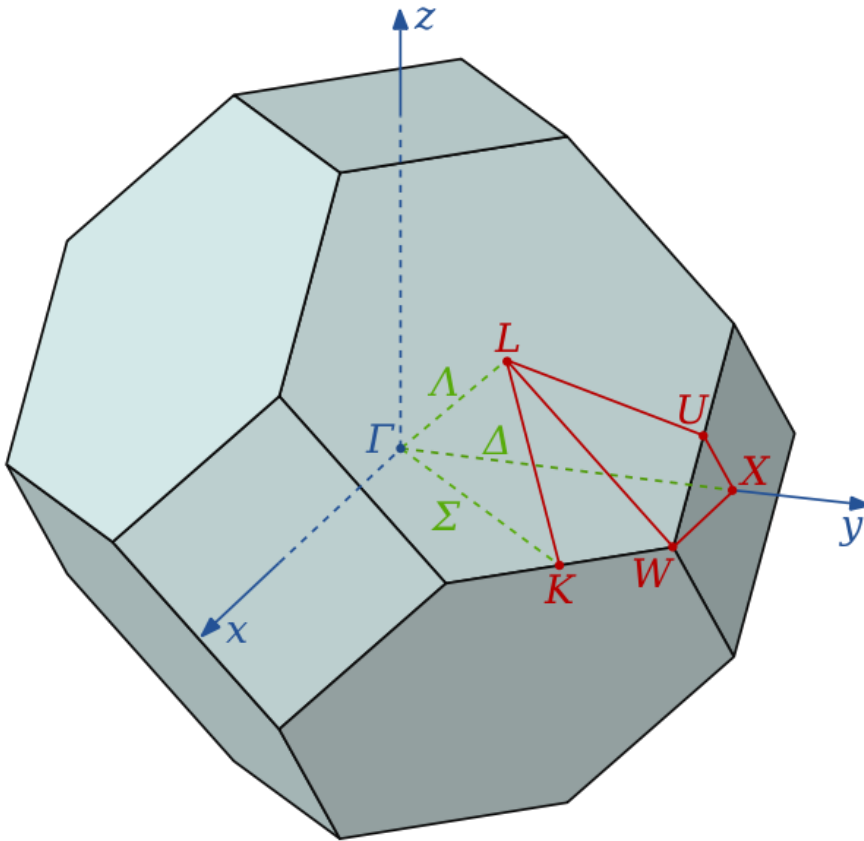


Fig. 9.2 The I Brillouine zone with the names of characteristic points and directions.

10. Tight binding model. Born-Karman periodicity lemma

Crystal as a set of interacting atoms

When we bring closer two identical atoms due to symmetry we obtain two symmetrical and anti-symmetrical combinations of degenerated functions $\Psi(1)$ and $\Psi(2)$ describing an electron on atoms 1 and 2:

$$\begin{aligned}\Psi_s &= \Psi(1) + \Psi(2) \\ \Psi_a &= \Psi(1) - \Psi(2)\end{aligned}\quad (10.1)$$

Above wave function are presented schematically in the Fig. 10.1.

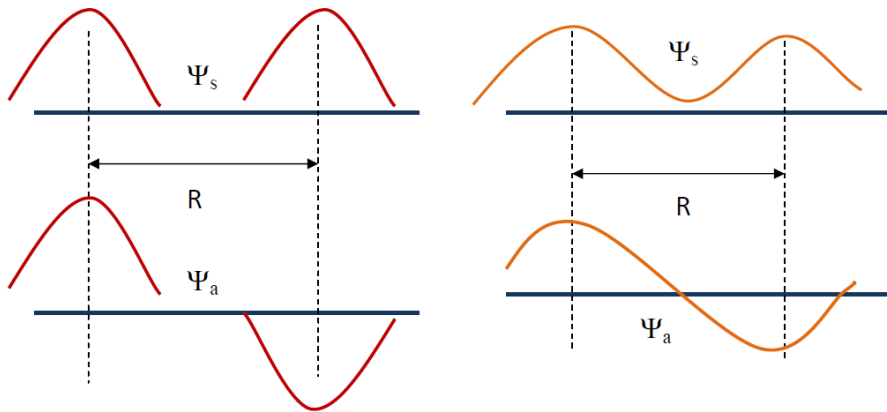


Fig. 10.1. The schematic picture of the symmetric and anti-symmetric functions of a two identical electrons.

When we increase the distance between atoms, an initial energy state equal for both electrons, splits into two energy levels (see Fig. 10.2).

Fig. 10.2. The splitting of energy of an electron state into two symmetric and anti-symmetric states.

When we bring together N atoms we obtain a band consist of N th very close electron energy level. Since the valence and conduction bands have usually the width in the range of about 10eV , so for a crystal consisting with $N \sim 10^{23}$ the energy in a band is a quasi continuous function with distance between energy levels equal to $\Delta E \sim 10^{-22}\text{eV}$.

Tight binding model in one dimension

Consider one dimensional crystal with N atoms and a lattice constant a . When atoms do not interact, they are far away from each other, the Hamiltonian can be written in a form:

$$\hat{H}_0 = -\frac{\hbar^2}{2m} \Delta + \sum_{i=1}^N \hat{V}_i, \quad (10.2)$$

where \hat{V}_i is the potential energy operator for i -th atom. When we assume that the eigenfunction for the valence electron is not degenerated we have:

$$\hat{H}_i \psi_i = E_0 \psi_i. \quad (10.3)$$

When atoms form a crystal the additional perturbation periodic potential appears:

$$\hat{V}_p = \hat{V}_{cr} - \hat{V}_i \quad (10.4)$$

which is the difference between crystal and atomic potential. So now we have the Hamiltonian in a form:

$$\hat{H} = \hat{H}_0 + \hat{V}_p. \quad (10.5)$$

Let us assume that this potential mixes only functions of nearest atoms:

$$-V = \int \psi_{i-1}^* \hat{V}_p \psi_i d^3 r = \int \psi_i^* \hat{V}_p \psi_{i+1} d^3 r, \quad (10.6)$$

where $V > 0$ which denotes that the total energy of the crystal is smaller than separate atoms. According to a general rule of quantum mechanics we are looking for the solution as a linear combinations of atomic functions ψ_i :

$$\Psi = \sum_{i=1}^N b_i \psi_i. \quad (10.7)$$

The Schrodinger equation can be written in a form:

$$\widehat{H} - E \Psi = \left[\widehat{H} - E + \widehat{V}_p \right] \Psi = \sum_{i=1}^N b_i \left[E_0 - E + \widehat{V}_p \right] = 0. \quad (10.8)$$

When we multiply both sides by function ψ_m^* and then integrate them we obtain:

$$b_m (E_0 - E) = b_{m-1} + b_{m+1} W. \quad (10.9)$$

We are looking for the solution in a form:

$$b_m = e^{ik_n m a} \quad (10.10)$$

and after simple calculations we obtain:

$$E = E_0 - 2W \cos k_s a. \quad (10.11)$$

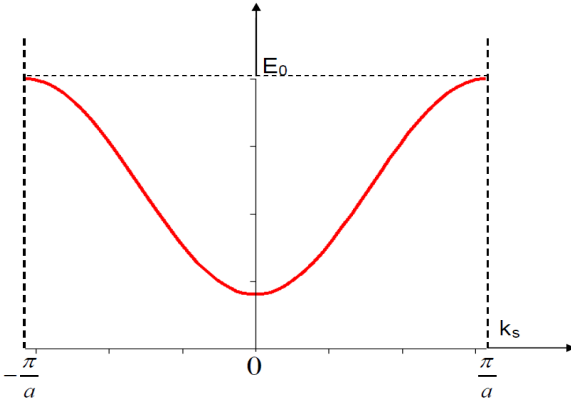


Fig. 10.1

Born – Karman periodicity conditions

Since all crystals are finite the translation symmetry does not hold. To omit this difficulties Born and Karman proposed a formula:

$$\Psi(\vec{r} + N_j \vec{a}_j) = \Psi(\vec{r}) \quad (10.12)$$

this means that

$$u_{\vec{k}}(\vec{r} + N_j \vec{a}_j) e^{i\vec{k}(\vec{r} + N_j \vec{a}_j)} = u_{\vec{k}}(\vec{r}) e^{i\vec{k}\vec{r}} e^{i\vec{k}N_j \vec{a}_j} = u_{\vec{k}}(\vec{r}) e^{i\vec{k}\vec{r}} e^{i\vec{k}N_j \vec{a}_j}. \quad (10.13)$$

since the Bloch term $u_{\vec{k}}(\vec{r})$ is periodic. From the definition it means that:

$$e^{i\vec{k}N_j \vec{a}_j} = 1 \quad (10.14)$$

it is

$$k\bar{a}_j = \frac{2\pi n_j}{N_j} \quad (10.15)$$

and further that the wave vector is quantized:

$$\bar{k}_{n_j} = \frac{2\pi n_j}{N_j} \bar{a}_j^* \quad (10.16)$$

where n_j may have N_j distinct values:

$$n_j = 1, 2, \dots, N_j$$

Density of states in 3 dimension wave vector space

In order to calculate the density of state in wave vector space we have to calculate the volume of the elementary cell in reciprocal space and divide the total number of state $N_1 N_2 N_3$ by its value:

$$V' = 2\pi^3 V^* = 8\pi^3 \bar{a}_1^* \bar{a}_2^* \times \bar{a}_3^* \quad (10.17)$$

where \bar{a}_i^* are the vectors of the reciprocal space:

$$\bar{a}_1^* = \frac{\bar{a}_2^* \times \bar{a}_3^*}{V_{el}} \quad \bar{a}_2^* = \frac{\bar{a}_3^* \times \bar{a}_1^*}{V_{el}} \quad \bar{a}_3^* = \frac{\bar{a}_1^* \times \bar{a}_2^*}{V_{el}} \quad (10.18)$$

and V_{el} is the volume of the elementary cell in the direct space.

After long calculations we obtain:

$$V' = \frac{8\pi^3}{V_{el}} \quad (10.19)$$

and the density of state:

$$\rho \bar{k} = \frac{N_1 N_2 N_3}{V'} = \frac{N_1 N_2 N_3 V_{el}}{8\pi^3} = \frac{V_{kr}}{8\pi^3} \quad (10.20)$$

Often in trial calculations we put $V_{kr} = 1 \text{ cm}^3$ and we have:

$$\rho \bar{k} = \frac{1}{8\pi^3} \text{ cm}^{-3} \quad (10.21)$$

As it can be easily calculated the density of state of electrons in the conduction band with the isotropic effective mass equals:

$$\rho E = \frac{1}{2\pi^2} \left(\frac{2m^*}{\hbar^2} \right) \sqrt{E} \quad (10.22)$$

11. Metals, semiconductors and dielectrics classification. The idea of a hole

Properties of fully occupied bands

Let us consider the fully occupied bands. In calculation of mean statistical values of physical quantities of electrons in conduction or valence bands it is more convenient to replace the sum by an integral:

$$\sum_k f \bar{k} \rightarrow \int_{SB} f \bar{k} \rho \bar{k} d^3k = \frac{1}{4\pi^3} \int_{SB} f \bar{k} d^3k. \quad (11.1)$$

In the case of fully occupied band all mean statistical physical values are equal to zero due to the symmetry of Brillouine zone.

Mean value of the electron pseudo-momentum

$$\sum_k \hbar \bar{k} = 0. \quad (11.2)$$

Mean value of the electron velocity

$$\langle \bar{v} \rangle = \sum \bar{v} \bar{k} = \frac{1}{4\pi^3 \hbar} \int_{SB} \nabla_k E \bar{k} d^3k = \frac{1}{4\pi^3 \hbar} \oint_{SB} E \bar{k} d\bar{\sigma} = 0. \quad (11.3)$$

Mean value of the electron effective mass

$$\begin{aligned} \langle \bar{M}^{-1} \rangle &= \sum_k \bar{m}^{-1} \bar{k} = \frac{1}{4\pi^3 \hbar^2} \int_{SB} \nabla_k \nabla_k E \bar{k} d^3k = \\ &= \frac{1}{4\pi^3 \hbar^2} \oint_{SB} \nabla_k E \bar{k} d\bar{\sigma} = \frac{1}{4\pi^3 \hbar} \oint_{SB} \bar{v} \bar{k} d\bar{\sigma} = 0 \end{aligned} \quad (11.4)$$

Mean value of the electron spin

$$S = \sum_{i=1}^{2N} \frac{\hbar}{2} \bar{G}_i = 0. \quad (11.5)$$

Current passing through a full band

$$\langle j \rangle = -e \sum_{i=1}^{2N} \bar{v}_i = -e \langle \bar{v} \rangle = 0. \quad (11.6)$$

Mean value of the electron acceleration

$$\langle \dot{\bar{v}} \rangle = \sum_{i=1}^{2N} \bar{m}^{-1} \bar{p} \langle \bar{M}^{-1} \rangle \bar{p} = 0. \quad (11.7)$$

Concept of a hole and its properties

Let us remove one electron from fully occupied band. The lack of one electron can be described as a hole in the electron sea

$$f_h(k_e) = \sum_{i=1}^{2N-1} f_e(k_i) = \sum_{i=1}^{2N} f_e(k_i) - f_e(k_e). \quad (11.8)$$

Such an object can be treated as quasi-particle; it is a particle possessing all physical quantities of normal particle but only within the crystal.

The main properties of a hole are:

The wave vector of a hole is opposite to the wave vector of an electron:

$$\bar{k}_h = -\bar{k}_e. \quad (11.9)$$

The velocity of a hole is opposite to the velocity of an electron for the same wave vector of an electron \bar{k}_e :

$$\bar{v}_h \bar{k}_e = -\bar{v}_e \bar{k}_e \quad (11.10)$$

and is the same for opposite wave vectors (see equation 11.9):

$$\bar{v}_h \bar{k}_d = \bar{v}_e \bar{k}_e. \quad (11.11)$$

The effective mass of a hole is opposite to the effective mass of an electron:

$$m_h \bar{k} = -m_e \bar{k}. \quad (11.12)$$

The charge of a hole is positive:

$$\hbar \dot{\bar{k}}_h = -\hbar \dot{\bar{k}}_e = +e\bar{\mathcal{E}}. \quad (11.13)$$

When the energy of all electrons in a full band is:

$$E_0 = \sum_k E_e \bar{k}, \quad (11.14)$$

than the energy of a hole is:

$$E_h \bar{k} = E_0 - E_e \bar{k}. \quad (11.15)$$

When we consider an electron in a valence band than since the energy is lowered by E_g in respect to conduction band and effective mass of electron in a valence band is negative we have:

$$E_e = -E_g - \frac{\hbar^2 k^2}{2|m_e^*|}. \quad (11.16)$$

So the energy of the hole in a valence band is:

$$E_h = E_g + \frac{\hbar^2 k^2}{2m_h^*}. \quad (11.17)$$

The hole translation velocity can be calculated from energy dependence on wave vector in the same way as for the electron:

$$\bar{v}_h = \frac{1}{\hbar} \nabla_{k_d} E_{k_h}. \quad (11.18)$$

The influence of external field is expressed in a form:

$$\hbar \dot{\bar{k}}_h = e\bar{\mathcal{E}}. \quad (11.19)$$

When one has started to count the energy from the bottom of the valence band the energy of a hole is expressed by simple formula:

$$E = \frac{\hbar^2 k^2}{2m_h^*}. \quad (11.20)$$

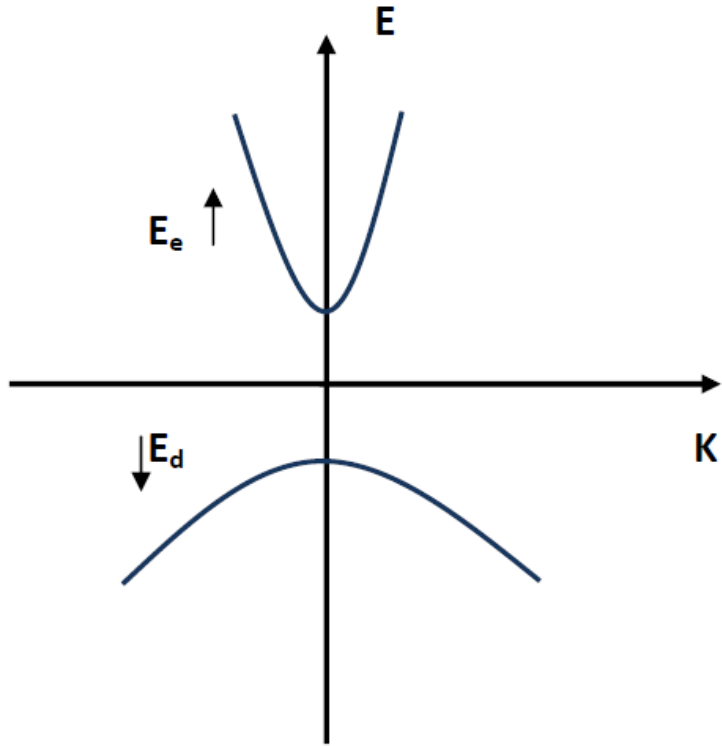


Fig. 11.2. The notation of calculation of the energy for electrons in the conduction band and holes in the valence band.

12. Effective mass approximation. Excitons

Effective mass approximation

The Schrödinger equation can be expressed in a form:

$$-\frac{\hbar^2}{2} \nabla m^{-1} \nabla \Psi = E \Psi. \quad (12.1)$$

In pure crystal, without imperfections and external fields, an electron can be described by the Bloch function:

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\vec{r}} u_{\vec{k}}(\vec{r}) \quad (12.2)$$

and energy expressed in a form:

$$E(\vec{k}) = E_0 + \sum_{i,j=1}^3 \frac{\hbar^2 k_i k_j}{2m_{ij}^*} = E_0 + \frac{\hbar^2}{2} \vec{k} \cdot \bar{m}^{-1} \cdot \vec{k}, \quad (12.3)$$

where $\bar{m}^{-1} = \frac{1}{2m_{ij}^*}$ is an effective mass tensor.

In the presence of additional potentials (except crystal potentials) and excitations of electrons the Bloch function is not longer a good solution of the Schrodinger equations. When those fields are weak and slowly varying in space one can use the wave function in a form $\Psi(\vec{r}) = \phi_{\vec{k}}(\vec{r}) u_{\vec{k}}(\vec{r})$, where $\phi_{\vec{k}}(\vec{r})$ is so called envelope function. Without additional fields it can be shown (but unfortunately after long and complicated calculations) that the envelope function is the solution of similar equation as (12.1) but with effective mass tensor:

$$-\frac{\hbar^2}{2} \nabla \bar{m}^{-1} \nabla \phi_{\vec{k}_0} = E \phi_{\vec{k}_0}. \quad (12.4)$$

In case of cubic crystals with one effective mass m^* (scalar) this equation can be written in the simplified form:

$$-\frac{\hbar^2}{2m^*} \Delta \phi_{\vec{k}_0} = E \phi_{\vec{k}_0}. \quad (12.5)$$

It can be proved that in the presence of slowly varying fields equation (12.5) transforming into:

$$\left[-\frac{\hbar^2}{2m_*} \Delta + \hat{V}_{slow}(\bar{r}) \right] \phi_{\bar{k}} = E \phi_{\bar{k}}. \quad (12.6)$$

This equation is named an effective mass equation, or an effective mass approximation.

Spin-orbit interaction

Spin, fourth degree of freedom of an electron appears as a natural solution of Dirac equation. Since this equation is complicated, dependences of electron energy due to spin are introduced to Schrodinger equation in a simplified form:

$$\hat{H} + \hat{H}_{so} \Psi(\bar{r}, \bar{\sigma}) = E \Psi(\bar{r}, \bar{\sigma}), \quad (12.7)$$

where

$$\Psi(\bar{r}, \bar{\sigma}) = \psi(\bar{r}) \chi(\bar{\sigma}). \quad (12.8)$$

$\psi(\bar{r})$ and $\chi(\bar{\sigma})$ describe the wave function of electron in real 3 dimensional space and spin respectively.

The interaction of the spin magnetic moment $\bar{\mu}_s$ with magnetic field B produce by orbital motion of an electron can be easily estimated. Crystal field can be expressed by crystal potential:

$$\bar{\mathcal{E}}_{cr} = -\frac{1}{e} \nabla V_{cr}. \quad (12.9)$$

The movement of electron in varying electric field produces magnetic field:

$$\bar{B} = -\frac{\bar{v}}{c} \times \bar{\mathcal{E}}_{cr} = -\frac{1}{mec} \nabla V_{cr} \times \bar{p}. \quad (12.9)$$

The energy of magnetic moment in magnetic field is:

$$E = -\bar{\mu}_s \bar{B} = -\frac{e\hbar}{2mc} \bar{\sigma} \bar{B}, \quad (12.10)$$

where

$$\vec{\sigma} = \sigma_x, \sigma_y, \sigma_z \quad \sigma_x = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (12.11)$$

are so called Pauli matrices describing the spin.

Hence spin-orbit interaction energy can be expressed in e form:

$$E = \frac{\hbar}{2m^2c^2} \vec{\sigma} \cdot \nabla V_{cr} \times \vec{p} \quad (12.12)$$

or included into Hamiltonian as additional term:

$$\hat{H}_{so} = \frac{\hbar^2}{2mc^2} \vec{\sigma} \cdot [\nabla V_{cr} \times \vec{p}] \quad \vec{p} = i\hbar \nabla. \quad (12.13)$$

It can be also shown that the whole dependence on a spin in Hamiltonian is expressed in a form:

$$\hat{H}_{so} e^{i\vec{k}\vec{r}} u_k(\vec{r}) \chi \vec{\sigma} = e^{i\vec{k}\vec{r}} \left[\hat{H}_{so} + \frac{\hbar^2}{2mc^2} \vec{k} \cdot [\vec{G} \times \nabla V_{cr}] \right] u_k(\vec{r}) \chi \vec{\sigma}. \quad (12.14)$$

Introducing the spin change one of general rule of energy dependence on wave vector into:

$$E_{\vec{k}, \uparrow} = E_{-\vec{k}, \downarrow}. \quad (12.15)$$

13. Electron and hole concentrations in semiconductors and dielectrics

The electrons in metals are not longer described by the Maxwell-Boltzmann statistics

$$f(E) = Ne^{-\frac{E}{k_B T}} \quad (13.1)$$

but by the quantum Fermi-Dirac distribution function:

$$f_e(E_e) = \frac{1}{e^{\frac{(E_e - E_F)}{k_B T}} + 1} \quad 0 \leq f(E_e) \leq 1, \quad (13.2)$$

where E_F is so called the Fermi Energy.

Since the hole in the valence band means that there is a lack of an electron, we have:

$$f_d(E_d) = 1 - f_e(E) = \frac{1}{e^{\frac{(E_d + E_F)}{k_B T}} + 1} \quad (13.3)$$

where we use the equality $E_d = -E_e$.

In intrinsic semiconductors it is convenient to count the energy of electrons and holes from the middle of the forbidden energy gap E_g :

$$E'_e = -\frac{E_g}{2} + E_e, \quad (13.4)$$

$$E'_d = \frac{E_g}{2} + E_d. \quad (13.5)$$

From the symmetry reason, it is if we notice that probability of finding an electron in the conduction band is almost the same as finding a hole in the valence band we can assume that the Fermi energy is located close to the middle of the energy gap E_g . Also we have:

$$E_g \gg kT. \quad (13.6)$$

So we can approximate the distribution function for electrons and holes by formulas:

$$f_e = \frac{1}{e^{\frac{E_g}{2kT}} e^{\frac{E_F - E_e}{kT}} + 1} \approx e^{-\frac{E_g}{2kT}} e^{\frac{E_F - E_e}{kT}} \quad (13.7)$$

and

$$f_d = \frac{1}{e^{\frac{E_g}{2kT}} e^{\frac{E_d + E_F}{kT}} + 1} \approx e^{-\frac{E_g}{2kT}} e^{-\frac{E_F}{kT}} e^{-\frac{E_d}{kT}} \quad (13.8)$$

In order to obtain the concentrations of electrons in the conduction band and holes in the valence band we have to calculate two integrals:

$$n = \int f_e(E) \rho(E) dE, \quad (13.9)$$

$$p = \int f_d(E) \rho(E) dE. \quad (13.10)$$

Taking into account approximation (13.7) the concentration of electrons is:

$$n = \int_0^{\infty} \frac{1}{2\pi^2} \left(\frac{2m_e^*}{\hbar^2} \right)^{3/2} e^{-\frac{E_g}{2kT}} e^{\frac{E_F}{kT}} \sqrt{E} e^{-\frac{E}{kT}} dE = \quad (13.11)$$

$$\frac{1}{2\pi^2} \left(\frac{2m_e^* kT}{\hbar^2} \right)^{3/2} e^{-\frac{E_g}{2kT}} e^{\frac{E_F}{kT}} \int_0^{\infty} \sqrt{x} e^{-x} dx.$$

The integral in equation (13.11) is:

$$\int_0^{\infty} \sqrt{x} e^{-x} dx = \Gamma\left(\frac{3}{2}\right) = \frac{\sqrt{\pi}}{2} \quad (13.12)$$

so the electron concentration in the conduction band is:

$$n = 2 \left(\frac{m_e^* kT}{2\pi \hbar^2} \right)^{3/2} e^{-\frac{E_g}{2kT}} e^{\frac{E_F}{kT}} \quad (13.13)$$

In similar way we can calculate the concentrations of holes in the valence band equals to:

$$p = 2 \left(\frac{m_d^* kT}{2\pi \hbar^2} \right)^{3/2} e^{-\frac{E_g}{2kT}} e^{-\frac{E_F}{kT}} \quad (13.14)$$

In the case of the intrinsic semiconductor without any impurities the concentrations of electrons in the conduction band and holes in the valence band are equal and we can name them n_s :

$$n_s = n = p \quad (13.15)$$

It is easy to show that the intrinsic Fermi level is:

$$E_{Fs} = \frac{3}{4}kT \ln \left(\frac{m_d^*}{m_e^*} \right) \quad (13.16)$$

so it is exactly in the middle of the energy gap and at $T = 0$ and very slowly increases towards higher energy with the increase of the temperature.

The intrinsic concentration is:

$$n_s = 2 \left(\frac{m^* kT}{2\pi\hbar^2} \right)^{3/2} e^{-\frac{E_g}{2kT}} \quad (13.17)$$

where we introduce the term:

$$m^* = \sqrt{m_e^* m_d^*} \quad (13.18)$$

In the case of moderately doped of semiconductors by shallow impurities we can also show that the concentrations for electrons and holes are equal to:

$$n = n_s e^{\left(\frac{E_F - E_{Fs}}{kT} \right)}, \quad (13.19)$$

$$p = n_s e^{-\left(\frac{E_F - E_{Fs}}{kT} \right)} \quad (13.20)$$

and we obtain an equality:

$$np = n_s^2 \quad (13.21)$$

This is a very important law. It shows that we cannot have higher concentrations of both electrons and holes and their product is constant.

14. Shallow donors and acceptors in semiconductors

When we substitute the host crystal atom by an atom with one more electron, and an ion radius of both atoms are not very different, for example Si from the IV group by As from the V group we can treat an additional electron as bound with the positive centre. Then we can calculate the energy of such an electron as the energy of electron in a Hydrogen atom taking into account the effective mass m_e^* different from the mass of the electron mass m_e and the relevant permittivity ϵ_0 . We obtain the Hydrogen like energy levels:

$$E_n = -\frac{e^4 m}{2\hbar^2 n^2 \epsilon_0^2} \left(\frac{m_e^*}{m_e}\right) = -\frac{13.6 \text{ eV}}{n^2} \frac{1}{\epsilon_0^2} \left(\frac{m_e^*}{m_e}\right) \quad (14.1)$$

$$r_B = \frac{\hbar^2}{e^2 m_0} \epsilon_0 \left(\frac{m_e^*}{m_0}\right) = 0.5 A \epsilon_0 \left(\frac{m_e^*}{m_0}\right) \quad (14.2)$$

The binding energy of such an electron, called donor is equal to:

$$E_D = 13.6 \text{ eV} \frac{1}{\epsilon_0^2} \left(\frac{m_e^*}{m_0}\right). \quad (14.3)$$

The effective mass of the order of $m_e^* \sim 0.1m_e$ and permittivity $\epsilon_0 \sim 10$ so the binding energy is in the range of meV and the electron can be easy ionized to the conduction band at room temperature This explains the name donor given to electron since it is a source of electrons to the conduction band energy. The scheme of the energy levels of a donor is presented in the Fig. 14. 1.

In the opposite case when we introduce into a host lattice an atom with one less electron having weakly bound hole called an acceptor.

$$E_A = 13.6 \text{ eV} \frac{1}{\epsilon_0^2} \left(\frac{m_d^*}{m_0}\right) \quad (14.4)$$

The electron from the valence band can be bound on such a state giving holes in the valence band which can conduct a current. The mechanism of transfer of electrons (acceptation) gives name of this state.

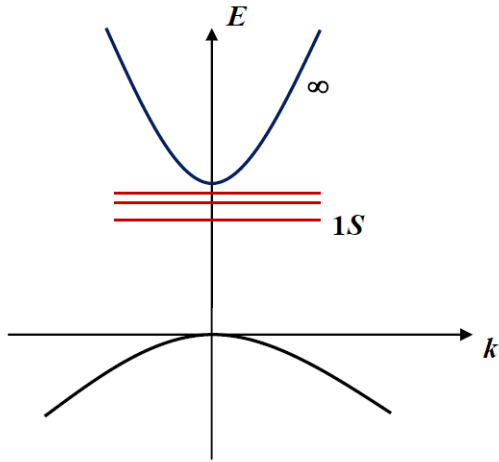


Fig 14.1 Diagram of the three bound states of a shallow donor electron near conduction band.

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