

Why?

- When chemical elements crystallize to become solids, some are good *conductors*, some are *insulators*, and yet others are *semiconductors* with electrical properties that vary greatly with temperature.
- □ These differences are not minor, but rather remarkable.
- □ The resistivity may vary from $\rho \sim 10^{-8}$ ohm-m for a good conductor to $\rho \sim 10^{22}$ ohm-m for a good insulator.

QMFE

- □ In the *quantum mechanical free electron* (QMFE) model, we assumed that the potential energy inside the solid was *uniform*.
- □ It would be more realistic to assume that it is a *periodic* (alternating uniformly) function of *x*, *y*, *z*.
- □ This is reasonable because of the periodic distribution of the lattice ions in a *crystalline solid*.

Models

- When the interaction between the electrons and the lattice ions is considered, we will find some unusual properties possessed by the electrons in the crystal.
- □ There are several methods (or models) to show the existence of bands and to find the shape of the band.
- The existence of bands and the general characteristics can be achieved with *idealized models* and by using qualitative arguments.

Bloch's Theorem

- Before we proceed to study the motion of an electron in a *periodic potential*, we should mention a general property of the wave functions in such a periodic potential.
- □ For a free electron with U = constant, the space part of the wave function $\Psi(x, t)$, called the eigenfunction $\psi(x)$, is written as,

$$\psi(x) = e^{\pm ikx}$$

Bloch's Theorem

- □ If the spacing of the ions in the *x* direction in a solid is *d*, then the potential energy of an electron at a point *x* distance from the origin is equal to the potential energy at a point x + d from the origin.
- This *potential energy* is equal in turn to that at point x + 2d from the origin, and so on. Therefore, we can generalize and take any point x in the lattice and state that the potential energy at that point is equal to the potential energy at point x + d.

Bloch's Theorem

□ Mathematically,

U(x) = U(x+d)

□ This is known as a *periodic potential*. There is a theorem by Bloch which states that for a particle moving in a periodic potential, the eigenfunctions $\psi(x)$ are of the form,

$$\psi(x) = u_k(x)e^{\pm ikx}$$

 $u_k(x) = u_k(x+d)$

□ where,

Bloch's Theorem

- □ These eigenfunctions are plane waves modulated by a function $u_k(x)$, where $u_k(x)$ has the same periodicity as the potential energy.
- Because the potential energy U(x) = U(x + d), one expects that the probability of finding a particle at a given x is the same as that of finding it at x + d.

Bloch's Theorem

□ This is seen by the periodicity of u_k and can be seen in the following expression for the probability density

$$\psi^*(x)\psi(x) = u_k^*(x)e^{-ikx}u_k(x)e^{+ikx} = u_k^*(x)u_k(x)$$

□ Therefore, when

$$u_k(x) = u_k(x+d)$$

□ Then

$$\psi^*(x)\psi(x) = \psi^*(x+d)\psi(x+d)$$

□ The specific form of the function $u_k(x)$ will depend on the form of the function U(x).

- Let us try to understand what the potential energy of an electron in a crystalline solid may look like.
- □ Consider a positively charged ion q and an electron e at a distance x from q as shown in Figure 1.
- The electric potential energy from the coulomb attraction experienced by the electron is

$$U(x) = -\frac{1}{4\pi\varepsilon_0} \frac{q|e|}{x}$$



- Suppose we now place another charge q at a point d away from the first.
- The potential energy *U* at any point on the *x* axis will be equal to the algebraic sum of the potential energies due to each individual charge, as illustrated in Figure 2.
- □ The dashed lines represent the potential energy due to the individual *q*'s and the solid lines represent the sum of the dashed lines.



- If we now place a long array of q's separated by a distance d from each other to form a periodic array, the potential energy U looks like that shown in Figure 3.
- □ The main features of the potential energy in Figure 3 are:
 - it is periodic with a period *d*,
 - the maxima are halfway between the ions, and
 - the potential energy tends to ∞ as the position of the ions is approached



- We can replace the potential energy of Figure 3 with one that is mathematically simpler to handle while retaining the essential features of the actual one.
- We replace the potential energy of Figure 3 by one consisting of periodically spaced rectangular wells as shown in Figure 4.
- □ The potential energy is a series of rectangular wells of width c, spaced a distance b apart so that the periodicity d = b + c.



- The energy of the wells is $-U_0$. However, it is convenient to shift the zero of potential energy so that the bottoms of the wells are at potential energy U = 0 and tops are at $U = U_0$.
- The potential energy of Figure 4 has the same periodicity as the lattice; the potential energy is lower in the vicinity of the ions and highest between the ions.
- This potential energy model is known as the Kronig-Penney model.

- □ Because U is either 0 or U_0 , we solve for ψ separately in both regions I and II.
- □ We then impose the conditions of continuity for ψ and $d\psi/dx$, while meeting the periodicity requirements.
- We will consider the case where $U < U_0$.

Kronig-Penney Model

□ In region I; U = 0, and the Schrodinger equation is written as

$$\frac{d^2\psi_I}{dx^2} + \frac{2m}{\hbar^2}E\psi_I = 0$$

• where ψ_I is the eigenfunction in region I. Rearranging terms, we get $d^2 \psi$

$$\frac{d^2\psi_I}{dx^2} + \gamma^2\psi_I = 0$$

□ where

- From Bloch's theorem, $\psi_I(x) = u_I(x)e^{ikx}$
- □ If we substitute this ψ_I in last equation, we get a differential equation for u_I , d^2u , du, d

$$\frac{d^{2}u_{I}}{dx^{2}} + 2ik\frac{du_{I}}{dx} + (\gamma^{2} - k^{2})u_{I} = 0$$

- □ The solution of this equation can be found by the standard methods $u_I(x) = Ae^{i(\gamma-k)x} + Be^{-i(\gamma+k)x}$
- \square where *A* and *B* are constants.

Kronig-Penney Model

□ In region II; $U = U_0$, and the Schrodinger equation is written as

$$\frac{d^2\psi_{II}}{dx^2} + \frac{2m}{\hbar^2} (E - U_0)\psi_{II} = 0$$

• where ψ_{II} is the eigenfunction in region II. Rearranging terms, we get d^2w

$$\frac{d^2\psi_{II}}{dx^2} - \chi^2\psi_{II} = 0$$

□ where

$$\chi = \sqrt{\frac{2m(U_0 - E)}{\hbar^2}}$$

- From Bloch's theorem, $\psi_{II}(x) = u_{II}(x)e^{ikx}$
- □ If we substitute this ψ_{II} in last equation, we get a differential equation for u_{II} , d^2u , du = (u + v)

$$\frac{d^2 u_{II}}{dx^2} + 2ik\frac{du_{II}}{dx} - (\chi^2 + k^2)u_{II} = 0$$

- □ The solution of this equation can be found by the standard methods $u_{II}(x) = Ce^{(\chi ik)x} + De^{-(\chi + ik)x}$
- \square where *C* and *D* are constants.

Kronig-Penney Model

□ It is seen in Figure 4 that regions I and II join at x = c/2, therefore, both the eigenfunctions and their first derivatives must be continuous across a boundary. It means

$$\psi_{I}\left(\frac{c}{2}\right) = \psi_{II}\left(\frac{c}{2}\right)$$
$$\frac{d\psi_{I}}{dx}\left(\frac{c}{2}\right) = \frac{d\psi_{II}}{dx}\left(\frac{c}{2}\right)$$

□ In addition, the periodicity requirements must be satisfied.

- □ This can be done by choosing points separated by the period of the lattice d, such as x = -c/2 and x = b + c/2.
- When we substitute Bloch functions for the ψ functions, that is, $\psi(x) = u(x)e^{ikx}$

$$u_{I}\left(-\frac{c}{2}\right) = u_{II}\left(b + \frac{c}{2}\right)$$
$$\frac{du_{I}}{dx}\left(-\frac{c}{2}\right) = \frac{du_{II}}{dx}\left(b + \frac{c}{2}\right)$$

- □ These four conditions on the eigenfunctions lead to four linear algebraic equations for the constant *A*, *B*, *C*, and *D*.
- □ In solving these equations, it is found that a solution exists only if $-\sin \frac{\gamma d}{2}$

• where
$$P = \frac{mU_0bd}{\hbar^2}$$
 $\gamma = \sqrt{\frac{2mE}{\hbar^2}}$

- □ If this condition is not satisfied, the boundary conditions on ψ cannot be satisfied, and the corresponding ψ 's are not acceptable solutions.
- □ In arriving at this equation, we used one of the forms of Bloch functions, namely, $\psi(x) = u(x)e^{ikx}$
- □ The same result will be obtained if we use the other form, that is, $\psi(x) = u(x)e^{-ikx}$

Allowed and Forbidden Energy Bands

□ Finding a direct analytical expression is not possible but we can get the result by qualitatively plotting the left side of this equation, calling it $f(\gamma d)$.

$$f(\gamma d) = P \frac{\sin \gamma d}{\gamma d} + \cos \gamma d$$

- □ For example, let $P = 5/2 \pi$.
- The sine function is periodic, as in Figure 5, and $P/\gamma d$ behaves as in Figure 6.









- Between 0 and π we have to be careful, particularly close to γd = 0, because when $\gamma d = 0$, $P \sin \gamma d / \gamma d = P 0 / 0$, which is undetermined.
- □ We can, however, use the L'Hospital rule on limits that

$$\lim_{x \to 0} \frac{\sin x}{x} = \lim_{x \to 0} \frac{\frac{d}{dx} \sin x}{\frac{d}{dx} x} = \lim_{x \to 0} \frac{\cos x}{1} = 1$$



- □ Thus, in the limit as $\gamma d \rightarrow 0$, $\sin \gamma d / \gamma d \rightarrow 1$.
- □ To get the entire function $f(\gamma d)$, we must add to Figure 7 the term $\cos \gamma d$, Figure 8.
- □ Between 0 and π both functions decrease; therefore, $f(\gamma d)$ decreases and becomes -1 when $\gamma d = \pi$.
- After π , the first term continues decreasing, while the second begins to increase. Because $\cos\gamma d$ changes slowly near the maximum and minimum, $f(\gamma d)$ continues to decrease below 1.

Allowed and Forbidden Energy Bands

- Somewhere between π and $3/2 \pi$ the trend reverses itself and $f(\gamma d)$ begins to increase, reaching the value of + 1 at 2π . After 2π the first term of $f(\gamma d)$ continues increasing while the second decreases.
- Again, just as before, the first term increases at a faster rate than the rate of decrease of the second term, and as a result $f(\gamma d)$ continues (for a while) to increase past + 1.
- □ Somewhere between 2π and $5/2\pi$ the trend will reverse.







- Because $\cos kd$ takes values ranging from +1 to -1, this means that this condition can be satisfied only by those values of γ for which $f(\gamma d)$ lies within those limits.
- □ The values of γ for which $f(\gamma d)$ is outside these limits correspond to γ 's for which the boundary conditions cannot be satisfied and, therefore, these γ 's (and the corresponding E's) are not physically acceptable.

- We conclude that, the electron may possess energies within certain bands of energy but not outside of them: There are allowed and forbidden bands of energy available to electrons moving in a periodic lattice.
- □ The width of the allowed energy bands increases with increasing γ (increasing energy E).

Dispersion Relation

□ For a free particle the relation between the energy *E* and the momentum *p* is p^2

| | $E = \frac{1}{2m}$ |
|----------------------------|----------------------|
| From de Broglie's relation | on, $p=h/\lambda$ |
| \square and because, | $\lambda = 2\pi / k$ |
| □ it follows that, | $p = \hbar k$ |
| | $dp = \hbar dk$ |

Dispersion Relation Substitution of this relation for *p* into the energy relation

□ Substitution of this relation for p into the energy relation shows that the energy of the particle can be expressed in terms of the wave vector k as,

$$E = \frac{\hbar^2 k^2}{2m}$$

- □ The relation between the energy of a particle and its wave vector is often referred to as the *dispersion relation*. $E \propto k^2$
- □ For a free particle, this relation is parabolic. This dependence is illustrated by the dashed lines of Figure 10.



Dispersion Relation

- When the particle is not free, the dispersion relation is usually more complicated.
- Thus, as we have seen, for an electron moving in one dimensional array of potential wells the dispersion relation is given by,

$$P\frac{\sin\gamma d}{\gamma d} + \cos\gamma d = \cos kd$$

 $\gamma = \sqrt{\frac{2mE}{\hbar^2}}$

□ where

Dispersion Relation

- □ If we solve the relation numerically for different values of E and the corresponding values of k, we find that there are energy intervals for which no real solution for k exists.
- □ These are the values of E for which the left side of relation is either greater than + 1 or less than -1.
- As indicated in the K-P Model, this is physically unacceptable and, therefore, these energy values are forbidden.
- □ Results are illustrated by the solid lines of Figure10.

Dispersion Relation

- □ These solid lines yield the values of E and the corresponding values of k for certain ranges of E.
- For other energy intervals the value of k is not defined by the solid lines, these are the forbidden energies.
- The curvature of the solid lines is not the same as that of the dashed line, which represents the dispersion relation for the free particle.
- This has important implications concerning the *effective mass* of the electrons

Effective Mass

- □ When an electric field ξ ; acts on a *free electron*, it exerts a force $e\xi$.
- That, from Newton's law, will produce an acceleration inversely proportional to its mass,

$$a = e\xi / m$$

What happens when the electron to be accelerated is not free but happens to be in a crystal under the influence of the potential of the lattice ions?

Effective Mass

- The answer is that it will still accelerate according to Newton's law; however, the electron responds as if it had some *effective mass*, which is different from its true mass.
- As we will show, this is because ξ; is not the only electric field acting on the electron inside the crystal.

Effective Mass

- We will introduce this concept by using a semi-classical picture: an argument that is half classical and half quantum mechanical.
- □ The quantum mechanical part lies in the fact that the motion of an electron is governed by a wave, and that the velocity of the electron is equal to the group velocity v_{group} of the wave, that is, the velocity of the envelope, of the wave packet.

Effective Mass In our treatment of matter waves and wave packets, we saw that the group velocity is given by \$\nu_{group} = \frac{dE}{dp}\$ where *E* is the energy of the particle and *p* is its momentum. In the case of a free particle, we can readily show that the group velocity is equal to the particle velocity.

Effective Mass

□ For a free particle, the energy

$$E = \frac{1}{2}mv_{particle}^2 = \frac{p^2}{2m}$$

□ Therefore,

$$v_g = v_{group} = \frac{dE}{dp} = \frac{d}{dp} \left(\frac{p^2}{2m}\right) = \frac{p}{m} = \frac{mv_{particle}}{m} = v_{particle} = v_p$$

□ Although we have shown that $v_g = v_p$ for the free particle case only, it can be shown that the relation holds even when the particle is not free, such as the case of an electron in a lattice.

Effective Mass

- □ Now we define the group velocity in terms of *E* and *k*. This can be done by using de Broglie's relation, $p = h/\lambda$
- and the fact that, $\lambda = 2\pi / k$
- $\Box \text{ We have, } p = \hbar k \qquad dp = \hbar dk$
- □ Substituting this, we obtain

$$v_g = \frac{1}{\hbar} \frac{dE}{dk}$$

Effective Mass

- The classical part of the argument uses the definition from mechanics that if a force does work dW on a particle, the energy of that particle increases by the same amount, that is, dE = dW.
- □ Applying this to the present case, we have

$$dE = dW = e\xi dx = e\xi \frac{dx}{dt} dt = e\xi v_g dt$$

Effective Mass

• The rate at which the energy of the particle is changing is therefore dF

$$\frac{dE}{dt} = e\xi v_g$$

- We also know from Newton's law that when a force acts on a particle, it will be accelerated.
- \square By definition, the acceleration *a* is,

$$a = \frac{dv_{particle}}{dt} = \frac{dv_g}{dt}$$

Effective Mass

■ Substituting for
$$v_g$$
 we obtain
 $a = \frac{1}{\hbar} \frac{d}{dt} \frac{dE}{dk}$
 $a = \frac{1}{\hbar} \frac{d}{dk} \frac{dE}{dt}$
 $a = \frac{e\xi}{\hbar} \frac{dv_g}{dk}$
 $a = \frac{1}{\hbar^2} \frac{d^2 E}{dk^2} e\xi$
 $v_g = \frac{1}{\hbar} \frac{dE}{dk}$

Effective Mass • Noting that $e\xi$ is the force of the externally applied electric field, we conclude has the form $F = m^*a$, where $m^* = \frac{\hbar^2}{\frac{d^2 E}{dk^2}}$ • The response of the electron in the solid to an externally applied electric field is as if it had an effective mass m^* given by the above expression.

Effective Mass

□ For the free electron,

$$E = \frac{\hbar^2 k^2}{2m}; \frac{dE}{dk} = \frac{\hbar^2 k}{m}; \frac{d^2 E}{dk^2} = \frac{\hbar^2}{m}$$

\Box Substitute this result into m^* and we obtain,

$$m^* = \frac{\hbar^2}{\frac{\hbar^2}{m}} = m$$

Effective Mass

- □ When the electron is free, the effective mass m^* is the true mass m, as it should be.
- □ However, when the electron is in a crystal, m^* is different from *m* because the energy is not proportional to k^2 , as we saw in the Kronig-Penney model.
- The reason is that the electron in the crystal moves under the influence of internal forces exerted by the electric fields of the ions of the lattice and the external force resulting from the externally applied electric field.





Effective Mass

- We may draw the following conclusions about the effective mass m* of an electron moving in a periodic lattice.
 - \square *m*^{*} is not always equal to *m*.
 - \square *m*^{*} can be greater than *m* and, in fact, infinite.
 - \square *m*^{*} can be less than *m* or even negative.

$$n^* = \frac{\hbar^2}{\frac{d^2 E}{dk^2}}$$

- Suppose we have a conducting metal strip of width d and thickness t connected in a circuit and placed in a uniform magnetic field B as in Figure 12.
- □ Let the direction of the magnetic field be into the paper, indicated by the symbol ⊗, which suggests the tail of an arrow.



Hall Effect

- □ The electric field ξ_x responsible for the current *i* will be directed to the right.
- □ If we assume for the moment that the current is caused by positive charges, their drift velocity v will be in the direction of ξ_x as shown in Figure 12.



- □ Let us consider two points D and C on the metal strip such that the line joining the two points is perpendicular to ξ_x .
- Without the magnetic field, the potential difference between these two points is zero because no work is done in moving a charge from one point to the other.



Hall Effect When the magnetic field is turned on, the drifting charges will experience a force. We label this force F_B to indicate that this is the force caused by the magnetic field B. F_B = qv × B F_B = qvB

- This force causes the (Figure 13) positive charges to move to the upper part of the conducting strip while they are moving to the right.
- Because the sample as a whole must remain neutral, the lower part of the strip will become negatively charged.



Hall Effect

■ The accumulation of positive charges along the upper part and of negative charges along the lower part creates an electric field ξ_y that opposes the further upward drift of positive charges.



■ There will be a potential difference V_H between D and C associated with this electric field.

$$V_H = V_D - V_C = \xi_y d$$

• where it is assumed that in equilibrium ξ_y is constant and *d* is the width of the strip (the distance between D and C).



Hall Effect

- This voltage difference is called the Hall voltage after the physicist who first measured it, and the phenomenon is called the Hall effect.
- It is clear that the equilibrium Hall voltage V_H will be established when the downward force of ξ_y equals the upward force resulting from the magnetic field.



- When a magnetic field is applied to a current carrying conductor in a direction perpendicular to that of the flow of current, a potential difference or transverse electric field is created across a conductor.
- This phenomenon is known as Hall Effect and was discovered by Edwin Hall in 1879.





Because the Hall voltage can be readily measured by connecting a voltmeter between D and C, the Hall effect permits the experimental determination of the drift velocity of the charge carriers. As we know,

i = qNAv $v = \frac{i}{qNA}$ $V_{H} = \frac{iBd}{qNA}$

□ So,

Hall Effect

- \square Note that A is the cross-sectional area of the foil. Hence
- \square A = thickness (t) x width (d). Therefore

$$V_{H} = \frac{1}{qN} \frac{iB}{t}$$
$$V_{H} = R_{H} \frac{iB}{t}$$

□ or,

• where $R_H = 1/qN$, is called the Hall coefficient.

■ Because *i*, *B*, and *t* are measurable, the magnitude of the Hall voltage will yield the value of *N*, the density of charge carriers. N = 1

$$N = \frac{1}{qR_H}$$

- The polarity of the Hall voltage will tell which type of carrier is responsible for conduction.
- The semiconductors can be made to have either positive or negative charge carriers.



Application of Hall Effect

Determine the Type of Semiconductor

- By knowing the direction of the Hall Voltage, one can determine that the given sample is whether *n-type semiconductor* or *p-type semiconductor*.
- □ This is because Hall coefficient is negative for n-type semiconductor while the same is positive in the case of p-type semiconductor.



Application of Hall Effect

Determine the Mobility (Hall Mobility)

□ Mobility expression for the electrons (μ_n) and the holes (μ_p) , expressed in terms of Hall coefficient is given by,

$$\mu_n = \sigma_n R_H \qquad \qquad \mu_p = \sigma_p R_H$$

• where, σ_n and σ_p represent the conductivity due to the electrons and the holes, respectively.

Application of Hall Effect

Measure Magnetic Flux Density

This equation can be readily deduced from the equation of Hall voltage and is given by

$$B = \frac{V_H t}{R_H i}$$

Further, there are many commercially available types of equipment based on the principle of Hall effect including Hall-effect sensors and Hall-effect probes.

| Band Theory of Solids |
|-----------------------|
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