# PHYS 342/555 Condensed Matter in a Nutshell

Instructor: Dr. Pengcheng Dai **Professor of Physics** The University of Tennessee (Room 407A, Nielsen, 974-1509) (Office hours: TR 1:10PM-2:00 PM) Lecture room 314 Nielsen Chapter 8: More Band structure and Semiconductors Lecture in pdf format will be available at: http://www.phys.utk.edu

# **Energy Bands**



# The periodic potential



$$H\psi = \left(-\frac{\hbar^2}{2m}\nabla^2 + U(\vec{r})\right)\psi = \varepsilon\psi$$

# **Bloch's theorem**

The eigenstates  $\psi$  of the one-electron Hamiltonian

$$H = \left(-\frac{\hbar^2}{2m}\nabla^2 + U(\vec{r})\right), \text{ where } U(\vec{r} + \vec{R}) = U(\vec{r}) \text{ for all } \vec{R} \text{ in }$$

a Bravias lattice, can be chosen to have the form of a plane wave times a function with the periodicity of the Bravias lattice:

$$\psi_{n\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{n\vec{k}}(\vec{r}), \text{ where } u_{n\vec{k}}(\vec{r}+\vec{R}) = u_{n\vec{k}}(\vec{r})$$

for all  $\vec{R}$  in the Bravias lattice. or

$$\psi(\vec{r}+\vec{R})=e^{i\vec{k}\cdot\vec{R}}\psi(\vec{r})$$

## The effect of a periodic potential

The periodic potential has form:  $U = U_0 + U_1 \cos \frac{2\pi x}{a}$ , where *a* is lattice parameter and  $U_1 \ll U_0$ . If  $U_1 = 0$  then we have the free electron gas case where  $\varepsilon = \frac{\hbar^2 k^2}{2m}$ Second allowed band Forbidden band  $\mathbf{1} E_{\nu}$ First allowed band  $\frac{\pi}{a}$  $-\frac{\pi}{a}$ (a) (b) Dai/PHYS 342/555 Spring 2012 Chapter 8-5 Also, for small  $\vec{k}$ ,  $U_1$  effectively averages to zero so it still looks like the free electron case where

$$\psi(\vec{r}) = Ae^{i\vec{k}\cdot\vec{r}}$$
 and  $\varepsilon = \hbar^2 k^2 / 2m$   
As  $\vec{k}$  approaches  $\pi/a$  ( $k = 2\pi / \lambda = \pi / a$ ), we expect a Bragg  
reflection or a standing wave. We can form two different standing  
waves from the two traveling waves  $\exp(\pm i\pi x/a)$ , or  
 $\psi(+) = \exp(+i\pi x/a) + \exp(-i\pi x/a) = 2\cos(\pi x/a)$ ;  
 $\psi(-) = \exp(+i\pi x/a) - \exp(-i\pi x/a) = 2i\sin(\pi x/a)$   
Both standing waves are composed of equal parts of right- and left-  
directed traveling waves.

# Origin of the energy gap

The two standing waves  $\psi(+)$  and  $\psi(-)$  pile up electrons at different regions, and therefore the two waves have different values of the potential energy. This is the origin of the energy gap. The probability density  $\rho$  of a particle is  $\psi^* \psi = |\psi|^2$ . For a standing wave  $\psi(+)$ ,  $\rho(+) = |\psi(+)|^2 \propto \cos^2 \pi x / a$ . This function piles up electrons (negative charge) on the positive ions centered at x = 0, a, 2a, ... where the potential energy is lowest.

For the other standing wave  $\psi(-)$  the probability density is  $\rho(-) = |\psi(-)|^2 \propto \sin^2 \pi x / a.$ 



The potential energy of  $\rho(+)$  is lower than that of the traveling wave, and that of  $\rho(-)$  is higher than the traveling wave. The difference is the energy gap.

## Magnitude of the energy gap

The wavefunction at the Brillouin zone boundary  $k = \pi/a$  are  $\sqrt{2} \cos \pi x/a$  and  $\sqrt{2} \sin \pi x/a$ , normalized over unit length of line. If the potential energy of an electron in the crystal at point x is  $U(x) = U \cos 2\pi x/a$ 

The first-order energy difference between the two standing wave states is

$$E_g = \int_0^1 dx U(x) [|\psi(+)|^2 - |\psi(-)|^2]$$
  
=  $2 \int dx U \cos(2\pi x/a) (\cos^2 \pi x/a - \sin^2 \pi x/a) = U$ 

## **Crystal momentum of an electron**

Under a crystal lattice translation we have  $\psi_k(\vec{r} + \vec{T}) = e^{i\vec{k}\cdot\vec{T}}e^{i\vec{k}\cdot\vec{r}}u_k(\vec{r} + \vec{T}) = e^{i\vec{k}\cdot\vec{T}}\psi_k(\vec{r}).$ 

If the lattice potential vanishes, the result recovers to that of free electron gas.

 $\hbar \vec{k}$  is called the crystal momentum of an electron. If an electron  $\vec{k}$  absorbs in a collision a phonon of wavevector  $\vec{q}$ , the selection rule is  $\vec{k} + \vec{q} = \vec{k} + \vec{G}$ .



### **Empty lattice approximation**

The free electron energy can be written as

$$\varepsilon(k_x, k_y, k_z) = (\hbar^2 / 2m)(\vec{k} + \vec{G})^2$$
  
=  $(\hbar^2 / 2m) \Big[ (k_x + G_x)^2 + (k_y + G_y)^2 + (k_z + G_z)^2 \Big]$ 

## Approximate solution near a zone boundary

At the zone boundary the kinetic energy of the waves  

$$k = \pm \frac{1}{2}G \text{ are equal. } (\lambda - \varepsilon)C(k) + \sum_{G}U_{G}C(k - G) = 0.$$

$$(\lambda - \varepsilon)C(G/2) + UC(-G/2) = 0$$

$$(\lambda - \varepsilon)C(-G/2) + UC(G/2) = 0$$

$$(\lambda - \varepsilon)^{2} = U^{2}; \quad \varepsilon = \lambda \pm U = \frac{\hbar^{2}}{2m}(\frac{1}{2}G)^{2} \pm U.$$

Thus the potential energy has created an energy gap 2U at the zone boundary.

Consider the free electron energy bands of an fcc crystal lattice in the approximation of an empty lattice, but in the reduced zone scheme in which all *k*'s are transformed to lie in the first Brillouin zone. Plot roughly in the [111] direction the energies of all bands up to six times the lowest band at the zone boundary at

 $k = (2\pi/a)(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}).$ 



Figure 14 Primitive basis vectors of the face-centered cubic lattice.

#### **Reciprocal Lattice to fcc Lattice**

The primitive translation vectors of the fcc lattice of Fig. 14 are

$$\mathbf{a}_1 = \frac{1}{2}a(\hat{\mathbf{y}} + \hat{\mathbf{z}}) \ ; \quad \mathbf{a}_2 = \frac{1}{2}a(\hat{\mathbf{x}} + \hat{\mathbf{z}}) \ ; \quad \mathbf{a}_3 = \frac{1}{2}a(\hat{\mathbf{x}} + \hat{\mathbf{y}}) \ .$$

The volume of the primitive cell is

$$V = |\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3| = \frac{1}{4}a^3$$

The primitive translation vectors of the lattice reciprocal to the fcc lattice are

$$\mathbf{b}_1 = (2\pi/a)(-\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}) ; \qquad \mathbf{b}_2 = (2\pi/a)(\hat{\mathbf{x}} - \hat{\mathbf{y}} + \hat{\mathbf{z}}) ; \mathbf{b}_3 = (2\pi/a)(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}}) .$$
(36)

These are primitive translation vectors of a bcc lattice, so that the bcc lattice is reciprocal to the fcc lattice. The volume of the primitive cell of the reciprocal lattice is  $4(2\pi/a)^3$ .



#### Intrinsic Electrical Conductivity

In a very pure sample the conductivity of a semiconductor is due to the excitation of electrons from the valence to the conduction band by thermal fluctuations. For a semiconductor at room temperature the resistivity is between  $10^{-2}\Omega$ -cm and  $10^{9}\Omega$ -cm depending on the band gap of the material. In contrast, a typical metal has a resistivity of  $10^{-6}\Omega$ -cm and a typical insulator satisfies  $10^{14}\Omega$ -cm  $\leq \rho \leq 10^{22}\Omega$ -cm. A plot of carrier concentration versus temperature and a plot of conductivity versus temperature is shown in Figure 7.1(a) and (b).



Fig. 7.1. Temperature dependence of carrier concentration (a) and electrical conductivity (b) of a typical semiconductor

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# **Semiconductor crystals**

A solid with an energy gap will be nonconducting at T = 0unless electric breakdown occurs or unless the AC field is of such high frequency that  $\hbar\omega$  exceeds the energy gap. However, when  $T \neq 0$  some electrons will be thermally excited to unoccupied bands (conduction bands). If the enegy gap  $E_g \approx 0.25$  eV, the fraction of electrons across the gap is of order  $e^{-E_g/2k_BT} \approx 10^{-2}$ , and observable conductivity will occur. These materials are semiconductors.

Table 7.1. Comparison of energy gaps of Si, Ge, and various III-V compound semiconductors

Crystal	Type of Energy Gap	$E_{\rm G}[{\rm eV}]$ at 0K
Si	indirect	1.2
Ge	indirect	0.8
InSb	direct	0.2
InAs	direct	0.4
InP	direct	1.3
GaP	indirect	2.3
GaAs	direct	1.5
GaSb	direct	1.8
GaN	direct	3.5
ZnO	direct	3.4





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The energy gap can be measured by optical absorption. If the conduction band minimum occurs at the same point in k-space as the valence band maximum, the energy gap can be directly determined from the optical threshold. If the minima and maxima occur at different points in k-space, then for phonon must also participate in the process.

The energy can may also be deduced from the temperature dependence of the intrinsic conductivity, varying as  $e^{-E_g/2k_BT}$ .

# **Equations of motion**

The group velocity  $v_g = d\omega/dk$ ,  $\omega = \varepsilon/\hbar$ , so  $v_g = \hbar^{-1}d\varepsilon/dk$ . The work  $\delta\varepsilon$  in interval  $\delta t$  is  $\delta\varepsilon = -eEv_g\delta t$ . Note  $\delta\varepsilon = (d\varepsilon/dk)\delta k = \hbar v_g\delta k$ .  $\hbar\delta k = -eE\delta t$ , Hence  $\hbar \frac{d\vec{k}}{dt} = -e\vec{E} = \vec{F}$ . The electron in the crystal is subject to forces from the crystal lattice as well as from external sources.

$$\vec{F} = -eE - \frac{e}{c}v \times \vec{B}.$$

### Holes



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1. The total wavevector of the electrons in a filled band is zero:  $\sum \vec{k} = 0$  or  $\vec{k}_h = -\vec{k}_e$ .

2. The energy of the hole is opposite in sign to the energy of the missing electron, because it takes more work to remove an electron from a low orbital than from a high orbital.

$$\varepsilon_h(\vec{k}_h) = -\varepsilon_e(\vec{k}_e).$$
  
3.  $\vec{v}_h = \vec{v}_e.$  The velocity of the hole is equal to the velocity of the missing electron.

4. 
$$m_h = -m_e$$
.  
5.  $\hbar \frac{d\vec{k}_h}{dt} = (e\vec{E} + \frac{1}{c}\vec{v}_h \times \vec{B})$ 



## **Effective Mass**

For U positive, an electron near the lower edge of the second band has an energy:  $\varepsilon(k) = \varepsilon_c + (\hbar k)^2 / (2m_e)$ Here k is the wavevector measured from the zone boundary, and  $m_e$  denotes the effective mass of the electron near the second band.

The group velocity  $v_g = d\omega/dk, \omega = \varepsilon/\hbar$ , so  $v_g = \hbar^{-1}d\varepsilon/dk$ .  $\frac{dv_g}{dt} = \frac{1}{\hbar} \frac{d^2\varepsilon}{dkdt} = \frac{1}{\hbar} \left( \frac{d^2\varepsilon}{dk^2} \frac{dk}{dt} \right) = \frac{1}{\hbar} \left( \frac{d^2\varepsilon}{dk^2} \right) \left( \frac{dk}{dt} \right) = \frac{1}{\hbar} \left( \frac{d^2\varepsilon}{dk^2} \right) \left( \frac{F}{\hbar} \right)$ F = ma, then we have  $\frac{1}{m^*} = \frac{1}{\hbar^2} \left( \frac{d^2\varepsilon}{dk^2} \right)$ .

### **Physical interpretation of Effective Mass**



Near the bottom of the lower band,  $\psi = e^{ikx}$  with momentum  $\hbar k$ ;  $m^* \approx m$ . Positive  $m^*$  means that the band has upward curvature  $(d^2\varepsilon / dk^2 > 0)$ . A negative effective mass means that on going from state k to state  $k + \Delta k$ , the momentum transfer to the lattice from the electron is larger than the momentum transfer from the applied force to the electron.

## **Effective Mass in Semiconductors**

The angular rotation frequency  $\omega_c$  of the current carriers is:  $\omega_c = \frac{eB}{m^*c}$ , where  $m^*$  is the effective mass.

Crystal	Electron $m_e/m$	Heavy hole $m_{hh}/m$	Light hole m <sub>lh</sub> /m	Split-off hole $m_{soh}/m$	Spin-orbit $\Delta$ , eV
InSb	0.015	0.39	0.021	(0.11)	0.82
InAs	0.026	0.41	0.025	0.08	0.43
InP	0.073	0.4	(0.078)	(0.15)	0.11
GaSb	0.047	0.3	0.06	(0.14)	0.80
GaAs	0.066	0.5	0.082	0.17	0.34
Cu <sub>2</sub> O	0.99	-	0.58	0.69	0.13

Table 2	Effective	masses o	of electrons	and l	holes in	n direct	gap	semiconductors
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### Intrinsic carrier concentration

In semiconductor physics  $\mu$  is called Fermi level. If  $\varepsilon - \mu \gg k_B T$ , the Fermi-Dirac distribution function reduces to  $f_e \simeq \exp[(\mu - \varepsilon)/k_B T]$ . The energy of an electron in the conduction band is  $\varepsilon_k = E_c + \hbar^2 k^2 / 2m_e$ . Note the total number of electrons N:

$$N = \frac{V}{3\pi^2} \left(\frac{2m\varepsilon}{\hbar^2}\right)^{3/2}, D(\varepsilon) \equiv \frac{dN}{d\varepsilon} = \frac{1}{2\pi^2} \left(\frac{2m_e}{\hbar^2}\right)^{3/2} \left(\varepsilon - E_c\right)^{1/2}.$$

The concentration of electrons in the conduction band is

$$n = \int_{E_c}^{\infty} D_e(\varepsilon) f_e(\varepsilon) d\varepsilon = 2 \left(\frac{m_e k_B T}{2\pi\hbar^2}\right)^{3/2} \exp[(\mu - E_c)/k_B T].$$

The distribution function  $f_h$  for holes is  $f_h = 1 - f_e$ .

We have 
$$f_h = 1 - \frac{1}{\exp[(\varepsilon - \mu)/k_B T] + 1} \cong \exp[(\varepsilon - \mu)/k_B T].$$

If the holes near the top of the valence band behave as particles with effective mass  $m_h$ , the density of hole states is given

$$D_{h}(\varepsilon) \equiv \frac{dN}{d\varepsilon} = \frac{1}{2\pi^{2}} \left(\frac{2m_{h}}{\hbar^{2}}\right)^{3/2} \left(E_{v} - \varepsilon\right)^{1/2}$$

The concentration of holes in the valence band is

$$p = \int_{-\infty}^{E_v} D_h(\varepsilon) f_h(\varepsilon) d\varepsilon = 2 \left(\frac{m_h k_B T}{2\pi\hbar^2}\right)^{3/2} \exp[(E_v - \mu)/k_B T].$$

The energy gap  $E_g = E_c - E_v$ ,

$$np = 4 \left(\frac{k_B T}{2\pi\hbar^2}\right)^3 \left(m_e m_h\right)^{3/2} \exp(-E_g / k_B T).$$

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In an intrinsic semiconductor,  $n = p, E_g = E_c - E_v$ ,

$$n = 2 \left(\frac{k_B T}{2\pi \hbar^2}\right)^{3/2} \left(m_e m_h\right)^{3/4} \exp[(E_g / 2k_B T]].$$

### **Intrinsic carrier mobility**

The mobility is the magnitude of the drift velocity per unit electric field:  $\mu = |v|/E$ The electric conductivity is the sum of the electron and hole contributions.  $\sigma = (ne\mu_e + pe\mu_h)$ 

Crystal	Electrons	Holes	Crystal	Electrons	Holes
Diamond	1800	1200	GaAs	8000	300
Si	1350	480	GaSb	5000	1000
Ge	3600	1800	PbS	550	600
InSb	800	450	PbSe	1020	930
InAs	30000	450	PbTe	2500	1000
InP	4500	100	AgCl	50	_
AlAs	280		KBr (100 K)	100	-
AlSb	900	400	SiC	100	10 - 20

Table 3	Carrier	mobilities	at	room	temperature,	in	cm <sup>2</sup> /V-	S
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## Impurity conductivity

Impurities that contribute to the carrier density of a semiconductor are called *donors* if they supply additional electrons to the conduction band, and *acceptors* if they supply additional holes to (*i.e.*, capture electrons from) the valence band.

The impurities are at  $N_D$  fixed attractive centers of charge +e, per unit volume, along with the same # of additional electrons. If the impurity were not embedded in the semiconductor, but in empty space, the binding energy of the electron would just be the first ionization potential of the impurity ion, 9.81 eV for arsenic. However, since the impurity is embedded in the medium of the pure semiconductor, this binding energy is enormously reduced (to 0.013 eV for arsenic in Ge). 1. The field of the charge representing the impurity must be reduced by the static dielectric constant  $\varepsilon$  (16 for Ge) of the semiconductor. 2. A electron moving in the medium of the semiconductor should be described by the semiclassical relation, where  $\hbar k$  is the electron crystal momentum. The additional electron introduced by impurity should be thought of as being in a superposition of conduction band levels of the pure host material. The electron can minimize its energy by using only levels near the bottom of the conduction band. We have a particle of charge -e and mass  $m^*$ , moving in free space in the presence of an attractive center of charge  $e/\varepsilon$ .

The radius of the first Bohr orbit,  $a_0 = \hbar^2 / me^2$ , becomes

 $r_0 = \frac{m}{m^*} \varepsilon a_0$ , and the ground-state binding energy,  $me^4 / \hbar^2 = 13.6 \text{ eV}$ 

becomes 
$$\varepsilon = \frac{m^2}{m} \frac{1}{\varepsilon^2} \times 13.6 \text{ eV}. r_0 = 100 \text{ angstrom}.$$



### Consider the energy surface

 $\varepsilon(k) = \hbar^2 \left( \frac{k_x^2 + k_y^2}{2m_t} + \frac{k_z^2}{2m_l} \right)$ , where  $m_t$  and  $m_l$  are transvers and longitudinal mass parameter. Use equation of motion to show that

 $\omega_c = eB/(m_l m_t)^{1/2} c$  when the static magnetic field *B* lies in the *x*, *y* plane.

Pentavalent impurities Impurity atom with 5 <u>valence electrons</u> produce n-type semiconductors by contributing extra electrons.

#### **Trivalent impurities**

Impurity atoms with 3 valence electrons produce p-type semiconductors by producing a "<u>hole</u>" or electron deficiency.



The addition of pentavalent <u>impurities</u> such as antimony, arsenic or phosphorous contributes free electrons, greatly increasing the conductivity of the <u>intrinsic semiconductor</u>. Phosphorous may be added by diffusion of phosphine gas (PH3).



The addition of trivalent <u>impurities</u> such as boron, aluminum or gallium to an <u>intrinsic semiconductor</u> creates deficiencies of valence electrons, called "holes". It is typical to use  $B_2H_6$  diborane gas to diffuse boron into the silicon material.





Fig. 7.4. Impurity levels and chemical potential across the p-n junction

#### **Semiconductor Current**

Both <u>electrons and holes</u> contribute to current flow in an <u>intrinsic</u> <u>semiconductor</u>.



#### **Depletion Region**

When a <u>p-n junction</u> is formed, some of the free electrons in the n-region diffuse across the junction and combine with <u>holes</u> to form negative ions. In so doing they leave behind positive ions at the donor <u>impurity</u> sites.



#### **P-N Energy Bands**

For a <u>p-n junction</u> at equilibrium, the <u>fermi levels</u> match on the two sides of the junctions. <u>Electrons and holes</u> reach an equilibrium at the junction and form a <u>depletion</u> region. The upward direction in the diagram represents increasing electron energy. That implies that you would have to supply enery to get an electron to go up on the diagram, and supply energy to get a hole to go down.



#### **P-N Energy Bands**

To reverse-bias the <u>p-n junction</u>, the p side is made more negative, making it "uphill" for electrons moving across the junction. The conduction direction for electrons in the diagram is right to left, and the upward direction represents increasing electron energy.



#### -N Energy Bands

To forward bias the <u>p-n junction</u>, the p side is made more positive, so that it is "downhill" for electron motion across the junction. An electron can move across the junction and fill a vacancy or "hole" near the junction. It can then move from vacancy to vacancy leftward toward the positive terminal, which could be described as the hole moving right. The conduction direction for electrons in the diagram is right to left, and the upward direction represents increasing electron energy.



When the <u>p-n junction</u> is <u>forward biased</u>, the electrons in the <u>n-type</u> material which have been elevated to the conduction band and which have diffused across the junction find themselves at a higher energy than the holes in the <u>p-type</u> material. They readily combine with those holes, making possible a continuous forward current through the junction.



### **Forward Biased Conduction**

The forward current in a <u>p-n junction</u> when it is <u>forward-biased</u> (illustrated below) involves electrons from the <u>n-type</u> material moving leftward across the junction and combining with holes in the <u>p-type</u> material. Electrons can then proceed further leftward by jumping from hole to hole, so the holes can be said to be moving to the right in this process.



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