

NOTES 11: Common Types of Band Structures; Semiconductors

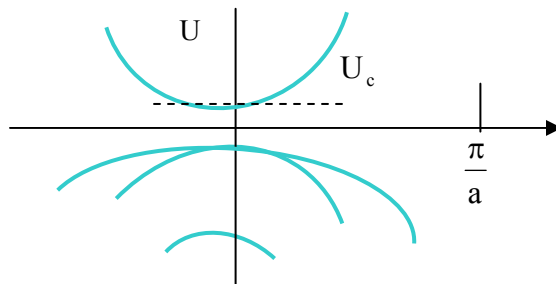
Conduction bands are the highest bands that occupy electrons under normal conditions.

1) Spherical (e.g., GaAs, InP, etc.)

$$U - U_c = \frac{\hbar^2 k^2}{2m_c^*}$$

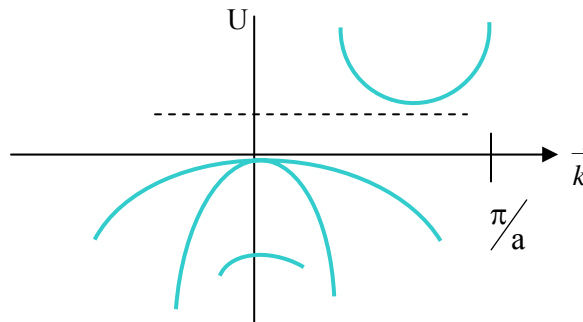
band edge at $k = 0 = k_{0x} = k_{0y} = k_{0z}$

$$k^2 = k_x^2 + k_y^2 + k_z^2$$



2) Spheroidal (e.g., Si, Ge)

Along some directions in \vec{k} space we have minima in U.



In general along any one of these directions,

$$U - U_c = \frac{\hbar^2}{2} \left(\frac{k_l^2}{m_l} + \frac{k_{t1}^2}{m_t} + \frac{k_{t2}^2}{m_t} \right)$$

e.g. Silicon is a special case of an ellipsoid of revolution in which all minima lie along six equivalent $\langle 100 \rangle$ axes of cubic Brillouin zone.

- along [100]

$$U - U_c = \frac{\hbar^2}{2} \left(\frac{(k_x - k_{ox})^2}{m_l} + \frac{k_y^2}{m_t} + \frac{k_z^2}{m_t} \right)$$

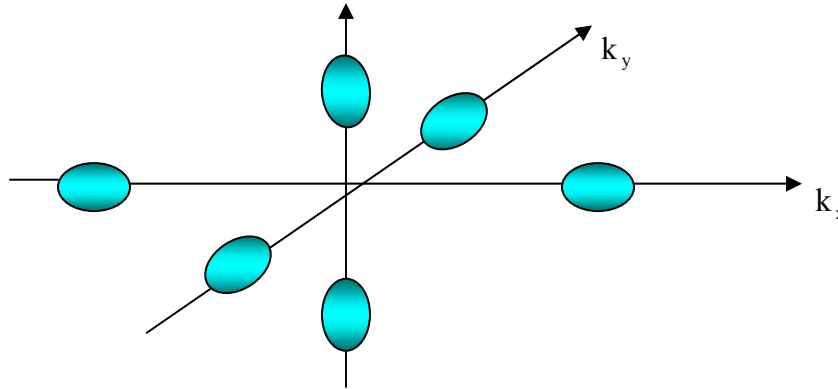
- along [010]

$$U - U_c = \frac{\hbar^2}{2} \left(\frac{k_x^2}{m_t} + \frac{(k_y - k_{oy})^2}{m_l} + \frac{k_z^2}{m_t} \right)$$

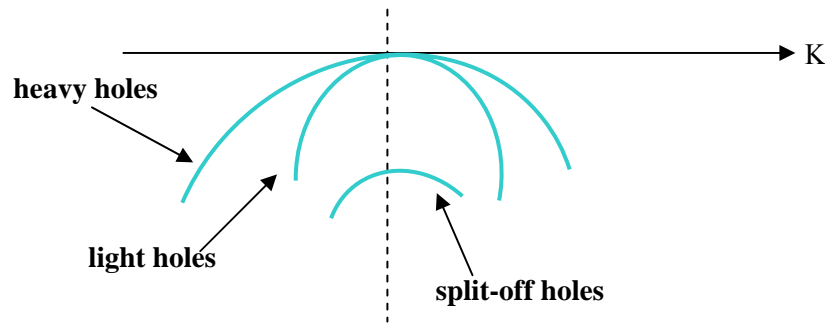
- along [001]

$$U - U_c = \frac{\hbar^2}{2} \left(\frac{k_x^2}{m_t} + \frac{k_y^2}{m_t} + \frac{(k_z - k_{oz})^2}{m_l} \right)$$

NOTE: Each of the above refers to two of six ellipsoids.



Valence bands are practically the same for all cubic semiconductors.



Holes are vacant orbitals in a band. The holes located closest to the band edge are characterized by two effective masses, light and heavy. These holes originate from P_{3/2} atomic orbital. Split-off band is another band formed at P_{1/2} atomic orbital.

Recall Convention:
 P → orbital angular momentum
 3/2 → orbital + spin momentum

Light and heavy hole

$$U_v - U = Ak^2 \pm [B^2 + k^2 + c^2(k_x^2 k_y^2 + k_y^2 k_z^2 + k_z^2 k_x^2)]^{1/2}$$

+ → light hole, - → heavy hole

Split-off Band

$$U_v - U = -\Delta + Ak^2$$

e.g., Silicon

$$A = -4.29 \quad |B| = 0.68$$

$$|C| = 4.87 \quad \Delta = 0.044$$

Effects of Band Structures on Density of States

- General definition can be derived for any band structure in any crystal.

$$g_n(U) = \int_{S_n(U)} \frac{2}{(2\pi)^3} \frac{ds}{|\nabla_{\mathbf{K}} U_n(\mathbf{K})|}$$

But this is difficult to evaluate in most cases. So we assume in semiconductors that all bands can be written in quadratic form.

- For spherical case

$$N(\mathbf{K}) = 2 \cdot \left(\frac{L}{2\pi}\right)^3 \cdot \frac{4}{3} \pi K^3 \quad \leftarrow \text{Volume of constant energy surface}$$

for
$$U = \frac{\hbar^2 K^2}{2m_c^*} \Rightarrow K^3 = \left(\frac{2m_c^* U}{\hbar^2}\right)^{3/2}$$

$$N(U) = \frac{V}{4\pi^3} \left(\frac{4}{3} \pi\right) \left(\frac{2m_c^* U}{\hbar^2}\right)^{3/2}$$

- To generalize this to ellipsoid of revolution, note theorem of geometry for volumes.

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} = 1$$

has a volume $V = \frac{4}{3}\pi(a.b.c)$

so ellipsoid volume is $= (\sqrt{2m_x} \cdot \sqrt{2m_y} \cdot \sqrt{2m_z})(U - U_c)^{3/2}/h^3$

and $g_n(U) = \frac{dN}{dU} = \frac{1}{2\pi^2} \left(\frac{2m_{d,c}^*}{\hbar^2} \right)^{3/2} (U - U_c)^{1/2}$

$m_{d,c}^* = (m_x m_y m_z)^{1/3}$ **density of states effective mass**

e.g., Si has six ellipsoids along [100] axes of conventional cubic unit cell.

- *Fundamental rule – can only have a density of states where allowed values of U exist in $U_n(\vec{K})$ vs \vec{K} relation yielding intuitive relation.*

$$g_n(U) = \int_{\text{cell}} \frac{2dK}{(2\pi)^3} \delta [U - U_n(\vec{K})]$$

integral over primitive cell

It can be shown this is equivalent to

$$g_n(U) = \int_{s_n} \frac{2ds}{(U - U_c)^3} \frac{1}{|\nabla U_n(\vec{K})|}$$

At extrema $U_n(\vec{K}) = U_{c,v} \pm \frac{\hbar^2}{2} \sum_{i,j} (K_i - K_{0i}) \left[\overline{\overline{M}}^{-1} \right]_{i,j} (K_j - K_{0j})$

This general “quadratic” form can always be diagonalized such that along some directions.

$$U = U_{c,v} \pm \frac{\hbar^2}{2} \left(\frac{(K_x - K_{0x})^2}{m_x} + \frac{(K_y - K_{0y})^2}{m_y} + \frac{(K_z - K_{0z})^2}{m_z} \right) \longleftarrow \text{spheroid}$$

The most common types of upper bands are:

- 1) Spherical (conducting band)
- 2) Ellipsoid of revolution (spheroidal)
- 3) Warped sphere (valence band)

For ellipsoid along K_x just before π/a

$$m_x = 0.98 \quad m_0 \equiv m_l$$

$$m_y = m_z = 0.19 \quad m_0 = m_t$$

$$m_{dc}^* = \sqrt[3]{m_x m_y m_z} = 0.33m_0$$

Since there are 6 equivalent ellipsoids

$$g_T = 6 \cdot g_n(U) = \frac{6}{2\pi^2} \left[\frac{2(0.33m_0)}{\hbar^2} \right]^{3/2} (U - U_c)^{1/2}$$

For valence band at band edge, we approximate the light hole band and heavy hole band as coincident and as having perfectly spherical bands.

so

$$g_v(U) = \frac{1}{2\pi^2} \left(\frac{2m_{d,v}^*}{\hbar^2} \right)^{3/2} (U_v - U)^{1/2}$$

where

$$m_{d,v}^* = \left[(m_{lh}^*)^{3/2} + (m_{hh}^*)^{3/2} \right]^{2/3}$$

e.g., Si $m_{lh}^* = 0.16m_0 \quad m_{hh}^* = 0.49m_0$

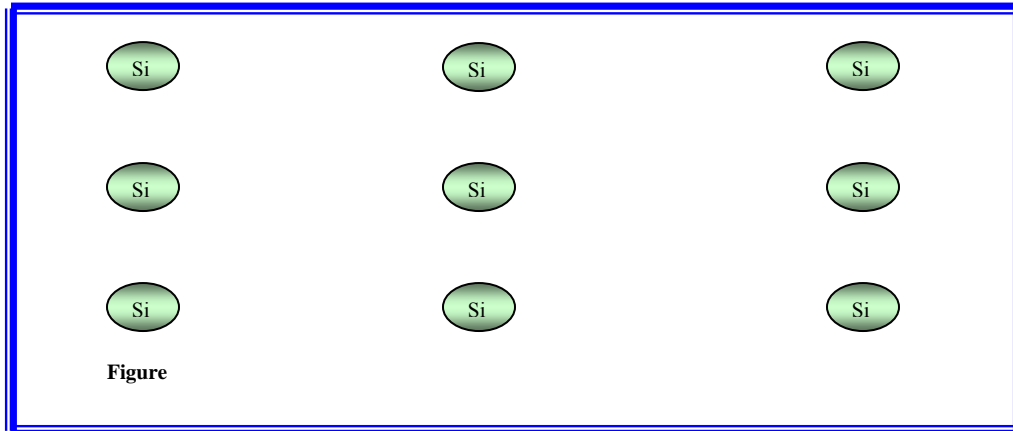
Note: DoS mass in valence band is higher than DoS mass in conduction band in general.

Key point

The density of states does not depend on whether the state is occupied (electron) or not occupied (hole). It is a fundamental parameter of the band structure.

Further effects of Band Structure and Effective Mass Theorem

- Substitutional impurity atoms have simple analysis if they are similar in size to intrinsic atom, e.g., phosphorous in Silicon.



Phosphorous P^{15} has one extra electron and proton over Si^{14} electrostatically it can be considered as $Si + 1$ proton $+ 1$ electron. But the H atom is embedded in the Si lattice. Since P is substitutional, it doesn't disrupt the translational symmetry \Rightarrow effect of lattice on electron $\rightarrow m^*$. Electrostatic field between extra proton and electron must be "dressed" by Si dielectric constant. In free space, hydrogen atom problem is soluble via *Schrodinger's equation* in spherical coordinates.

$$\frac{-\hbar^2}{2\mu} \nabla^2 \psi + V\psi = U_n \psi$$

where

$$V = \frac{-e^2}{4\pi\epsilon_0 r}$$

$$\mu = \frac{m_e m_p}{m_e + m_p} \text{ (reduced mass)}$$

yields energy *eigenvalues*

$$U_n = \frac{-\mu e^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2}$$

evaluation yields

$$U_n = \frac{-13.6\text{eV}}{n^2}$$

Each *eigenvalue* has an *eigenfunction* (at last one)

$$U_1 = \psi_1 = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0} \right)^{3/2} e^{-r/a_0}$$

$$U_2 = \psi_2 = \frac{1}{4\sqrt{2\pi}} \left(\frac{1}{a} \right)^{3/2} \left(2 - \frac{r}{a_0} \right) e^{-r/2a}$$

or

$$\frac{1}{4\sqrt{2\pi}} \left(\frac{1}{a_0} \right)^{3/2} \frac{r}{a_0} e^{-r/2a_0} \cos \theta$$

or

$$\frac{1}{8\sqrt{\pi}} \left(\frac{1}{a_0} \right)^{3/2} \frac{r}{a_0} e^{-r/2a_0} \sin \theta e^{+i\phi}$$

or

$$\frac{1}{8\sqrt{\pi}} \left(\frac{1}{a_0} \right)^{3/2} \frac{r}{a_0} e^{-r/2a_0} \sin \theta e^{-i\phi}$$

where

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2} \text{ (Bohr radius)} \approx 0.5 \text{ \AA}$$

If we go back and “re-dress” the atom

$$\mu \equiv \frac{m_e m_p}{m_e + m_p} \rightarrow \frac{m_e^* m_p}{m_e^* + m_p} \approx \frac{m_e^* m_p}{m_p} = m_e^*$$

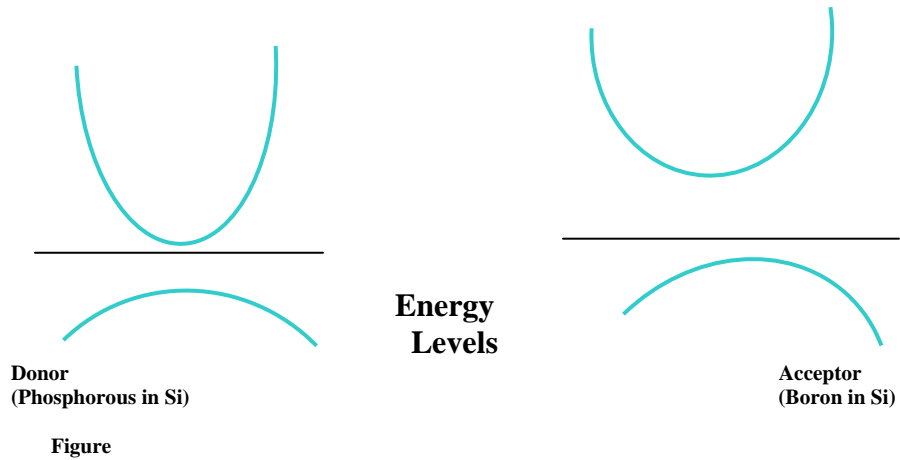
$$V = \frac{-e^2}{4\pi\epsilon_0 r} \rightarrow \frac{-e^2}{4\pi\epsilon_r \epsilon_0 r}$$

$$\Rightarrow U_n \rightarrow \frac{-m^* e^4}{(4\pi\epsilon_r \epsilon_0)^2 2\hbar^2 n^2} = \frac{-e^2}{8\pi\epsilon_r^2 \epsilon_0 a_0 n^2}$$

or

$$U_n \equiv \frac{\left(\frac{m_e^*}{\mu} \right)}{\epsilon_r^2} \left(\frac{-13.6}{n^2} \right)$$

Because in all common semiconductors, m^* is small and ϵ_r is rather large, there is a significant reduction in U_n and increase in a_0 .



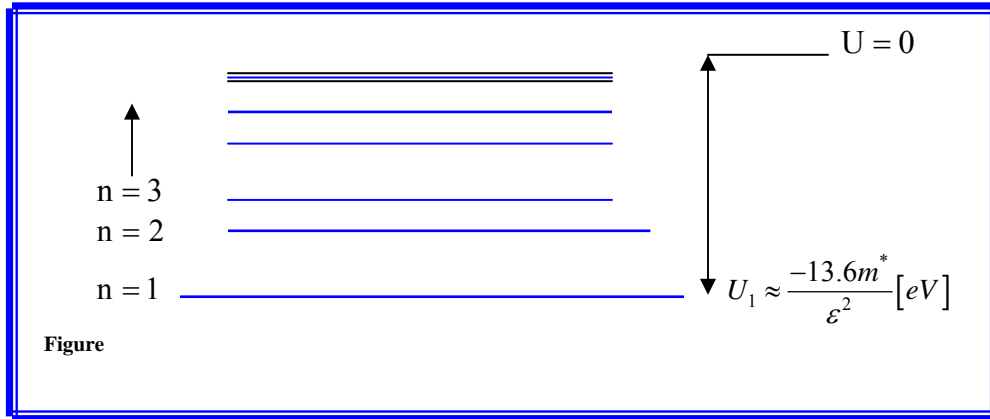
Example: Donor levels in Si:

$$m^* = 0.26m_0 \text{ (conduction-band electrons)}$$

$$\epsilon_r \approx 12.0$$

$$\Rightarrow U_n = \frac{-13.6 \left(\frac{m_c^*}{m_0} \right)}{n^2 \epsilon_r^2} = -0.025 eV \text{ for } n = 1 \text{ (good agreement with experiment)}$$

Note that the negative synergy is referenced to the conduction-band-edge, so that $n > 1$ decreases separation from conduction band. This separation is thus the “binding energy” or equivalently, the amount of energy required to “ionize” hydrogenic donor. Once ionized, the donor electron becomes a conduction-band electron and the donor atom appears like proton dressed by m^* and ϵ_r for that semiconductor.



Figure

Semiconductor Band Gaps

Perhaps the most important effect of band structure on solids besides the *Bloch Theorem* is the presence of band gaps that are small enough that (thermal effects e.g., phonons) can change the population of electrons in the highest bands (conduction = highest; valence = next highest) Band gap = separation in energy between the conduction band and valence band e.g., Si.

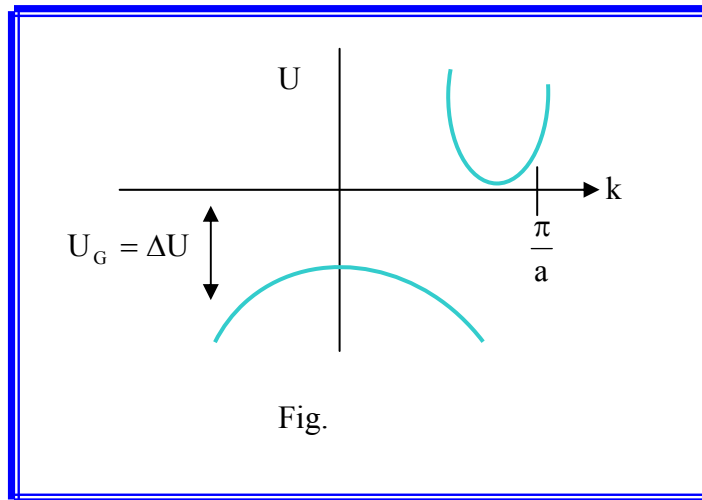


Fig.

As might be guessed intuitively, the band gap is strongly dependent on the atomic spacing and tends to get smaller as the spacing grows.

Classification of Band Gaps

Band gaps are the difference in energy between the lowest point of the conduction band (conduction band edge) and the highest point of the valence band (valence band edge). Band gaps are also classified by the size of band gap relative to $k_B T$ 300K ($\cong 25\text{meV}$). As temperature rises, electrons are thermally excited from the valence to the conduction band.

Electrons in the conduction band and holes left in the valence band contribute to the conductivity of electricity.

- $U_G \leq 10kT (= 0.25eV) \Rightarrow$ "narrow" gap
 - carrier concentrations can be significant from cross-gap effects at normal device operating between $\approx 300 - 450K$.
- $10kT \leq U_G \leq 100kT (\approx 2.5eV) \Rightarrow$ "normal gap"
 - carrier concentrations from cross-gap effects are not significant between $\approx 300 - 450K$. But carrier concentrations are very important from shallow donors or acceptors.
- $U_G \geq 100kT (\geq 2.5eV) \Rightarrow$ "wide" gap
 - carrier concentrations from cross-gap effects are never significant. Even carrier concentrations from donors and acceptors are difficult to make high.

Table

$\frac{a}{\text{\AA}}$	Semiconductor	$U_G (300k)$	Crystal Structure	Class of Band Gap
6.45	InSb	0.17	Zinc blende	Nanow
	InAs	0.36	Zinc blende	Nanow
5.43	Si	1.12	Diamond	Normal
	GaAs	1.42	Zinc blende	Normal
$\sim 4.35^*$	SiC	3.00	Wurtzite	Wide
	GaN	3.36	Wurtzite	Wide

*average along different axes

External Effects that Change Band Gaps

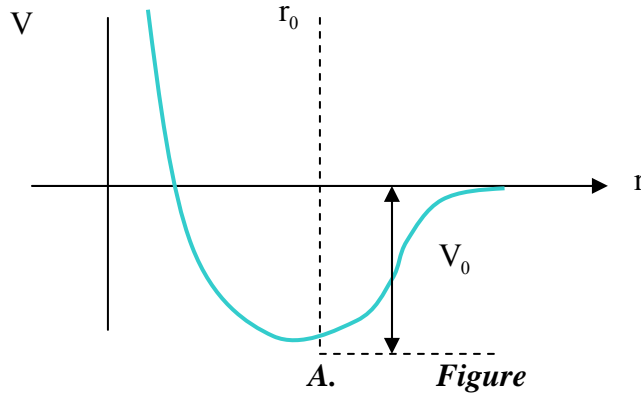
From a device Physics standpoint, the primary effects that change band gaps are temperature and pressure.

- *Temperature*

We found that the atoms sit in a potential energy well that is asymmetric about

$$V = V_0 c \delta r^2 + g \delta r^3 + f \delta r^4$$

$$\delta r = r - r_0, \quad c > 0, \quad g < 0$$



Using *Maxwell Boltzman Statistics*, we find

$$\langle \delta r \rangle \cong \int_{-\infty}^{\infty} \frac{\delta r e^{-V(r)/kT} d\delta r}{\int_{-\infty}^{\infty} e^{-V(r)/kT} d\delta r} \quad (\text{because atoms are distinguishable})$$

$$e^{-V(r)/kT} \approx e^{-c(\delta r)^2/kT} \left(1 - \frac{g\delta r^3}{kT} - \frac{f\delta r^4}{kT} \right)$$

If we set $V_0 = 0$, and if cubic quadratic terms are small. So,

$$\int_{-\infty}^{\infty} d\delta r (\delta r) e^{-V(r)/kT} \cong \int_{-\infty}^{\infty} e^{-c\delta r^2/kT} \left(\delta r - \frac{g\delta r^4}{kT} - \frac{f\delta r^5}{kT} \right) d\delta r$$

by symmetry δr and δr^5 term $\rightarrow 0$, so

$$\int_{-\infty}^{\infty} d\delta r e^{-U(r)/kT} \cong \int_{-\infty}^{\infty} e^{-c\delta r^2/kT} \left(-\frac{g\delta r^4}{kT} \right) = -\frac{3\sqrt{\pi}}{4} \frac{g}{c^{5/2}} \frac{1}{(kT)^{3/2}} \text{ by Gaussian integrals}$$

Similarly,

$$\int_{-\infty}^{\infty} d\delta r e^{-V(r)/kT} \cong \int_{-\infty}^{\infty} d\delta r e^{-c\delta r^2/kT} = \sqrt{\pi kT/c} \text{ by Gaussian integrals}$$

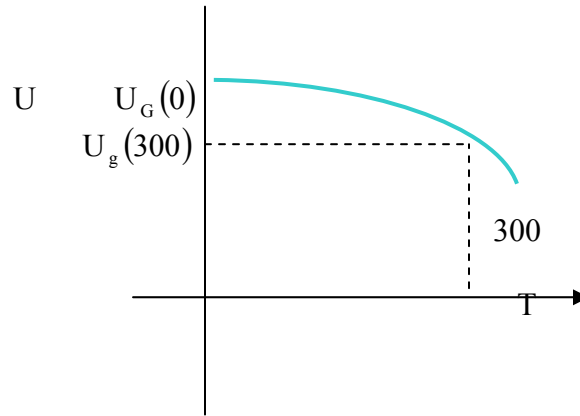
so that,

$$\langle \delta r \rangle = -\frac{3g}{4c^2} kT$$

Generally $g < 0 \Rightarrow \langle \delta r \rangle > 0$ for cubic materials. The lattice expands as temperature rises,

e.g., $g = -3.8 \times 10^{11}$ for NaCl.

As the lattice expands, we expect the band gap to shrink.



Figure

$\frac{dU_G}{dT}$ approximately linear around $T = 300\text{K}$ and roughly equal to 10^{-4} eV/K

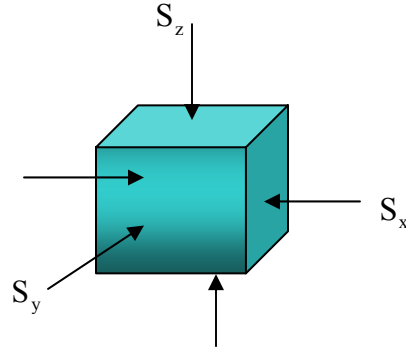
Common bandgaps with temperature

Semiconductor	U _g (300K)	U _g (0K)	Crystal Structure
Si (IV)	1.12	1.17	Diamond
GaAs (III – IV)	1.42	1.52	Zincblend
CdS (II – VI)	2.42	2.56	Zincblend
SiC (IV – IV)	3.00	3.03	Wurtzite
PbS (IV – VI)	0.41	0.29	Rocksalt

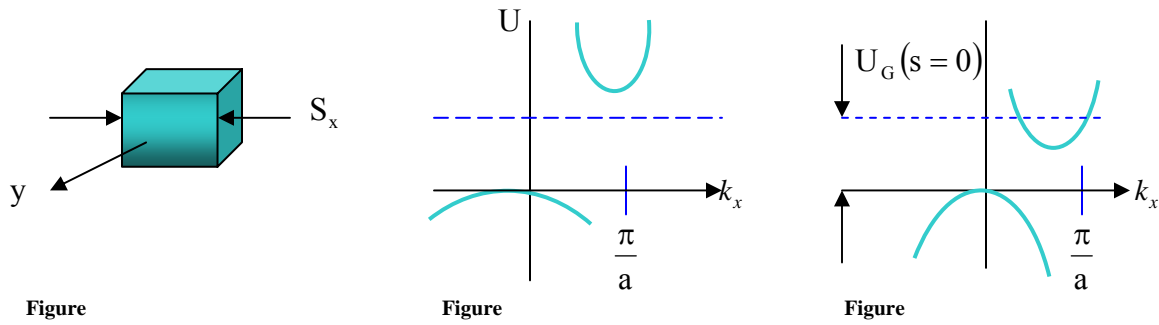
Note: rock salt structures break the trend.

- *Pressure*

Hydrostatic pressure – uniform compression (stress) from all directions will generally raise the gap uniformly along all directions in k space.



Uniaxial pressure will shrink band gap along some directions and raise it along others.



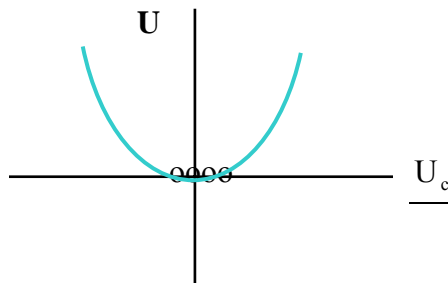
Because from *Poisson's ratio*, we know that the lateral spacing must increase to accommodate longitudinal spacing decrease. For uniaxial stress along the x axis, the two ellipsoids along k_x [100] and [T00] will have U_G increase the four ellipsoids along y

Carrier Concentrations in Equilibrium

- Conduction band

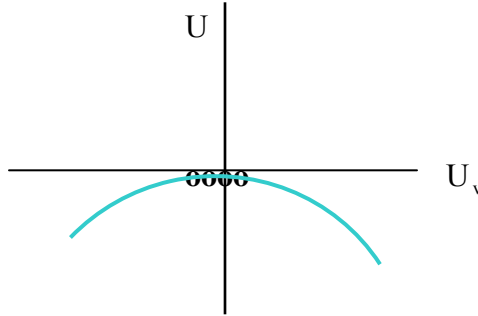
$$n_e \equiv n_c(T) = \int_{U_c}^{\infty} du g_c(u) f(u) \quad \leftarrow \text{Fermi-Dirac Factor}$$

↑
Total Density of States



- Valence band

$$n_h \equiv \rho_v(T) = \int_{-\infty}^{U_v} \text{d}u g_v(u) [1 - f(u)]$$



Recall,

$$1 - f(u) = 1 - \frac{1}{e^{\frac{u-\mu}{kT}} + 1} = \frac{e^{\frac{u-\mu}{kT}}}{e^{\frac{u-\mu}{kT}} + 1} = \frac{1}{1 + e^{\frac{\mu-u}{kT}}}$$

so,

$$p_v(T) = \int_{-\infty}^{U_v} \text{d}u g_v(u) \frac{1}{1 + e^{\frac{\mu-u}{kT}}}$$

These expressions are generally true, independent of impurities or excess carriers added by outside effects (e.g., light). These effects will change the chemical potential as required by *1st Law of Thermodynamics* $dU = TdS - \mu dN$. In general, the integrals are non-analytic and done numerically or via Fermi – Integral tables. But simplification results when μ is not near U_c or U_v , but in between, i.e., $U_c - \mu \gg k_B T$ or $\mu - U_v \gg k_B T$. In this case,

$$\frac{1}{e^{\frac{u-\mu}{kT}} + 1} \approx e^{-\frac{(u-\mu)}{kT}} \quad \text{for } U > U_c$$

$$\frac{1}{e^{\frac{\mu-u}{kT}} + 1} \approx e^{-\frac{(\mu-u)}{kT}} \quad \text{for } U < U_v < \mu$$

so that,

$$N_c(T) \approx \int_{U_c}^{\infty} \text{d}u g_c(u) e^{-\frac{(u-\mu)}{kT}} = e^{\frac{(\mu-U_c)}{kT}} \int_{U_c}^{\infty} \text{d}u g_c(u) e^{-\frac{(U-U_c)}{kT}}$$

$$\equiv e^{(\mu - U_c)/kT} N_c(T) \Rightarrow \mu = U_c + kT \ln \left[\frac{n_c(T)}{N_c(T)} \right]$$

$N_c \rightarrow$ effective density of states (conduction band)

$$p_v(T) = \int_{-\infty}^{U_v} dU g_v(U) e^{-(\mu - U)/kT} = e^{(U_v - \mu)/kT} \int_{-\infty}^{U_v} dU g_v(U) e^{-(U_v - U)/kT}$$

$$\equiv e^{(U_v - \mu)/kT} N_v(T) \Rightarrow \mu = U_v - kT \ln \left[\frac{p_v(T)}{N_v(T)} \right]$$

$N_v \rightarrow$ effective density of states (valence band)

For the three types of bands we have covered

$$g_c(U) = \frac{M(2m_d^*)^{3/2}}{2\hbar^3 \pi^2} \sqrt{|U - U_n|}$$

$m_d^* \rightarrow$ density of states – effective mass $M \rightarrow$ number of equivalent ellipsoids

so,

$$N_c(T) = \int_{U_c}^{\infty} \frac{M(2m_d^*)^{3/2}}{2\hbar^3 \pi^2} \sqrt{U - U_c} e^{-(U - U_c)/kT} dU$$

let

$$W = \left(\frac{U - U_c}{kT} \right) \quad dW = \frac{dU}{kT}$$

$$N_c(T) = \int_{U_c}^{\infty} \frac{M(2m_d^*)^{3/2} (kT)^{3/2}}{2\hbar^3 \pi^2} \sqrt{W} e^{-W} dW$$

Recall,

$$\int_0^{\infty} W^{1/2} e^{-W} dW = \Gamma\left(\frac{3}{2}\right) = \sqrt{\pi/2}$$

so that,

$$N_c(T) = \frac{M}{4} \left(\frac{2m_{d,c}^* kT}{\pi \hbar^2} \right)^{3/2}$$

Similar analysis shows that

$$N_v(T) = \frac{1}{4} \left(\frac{2m_{d,v}^* kT}{\pi \hbar^2} \right)^{3/2} \left. \vphantom{N_v(T)} \right\} \text{very useful in semiconductor devices}$$

Law of Mass Action

$$n_c \rho_v = e^{(\mu - U_c)/kT} N_c(T) \bullet e^{(U_v - \mu)/kT} N_v(T) = e^{(U_v - U_c)/kT} N_c N_v = e^{-U_G/kT} N_c(T) N_v(T)$$

This is true independent of doping.

Special case: Intrinsic Semiconductor

By definition $n_c(T) = p_v(T) \equiv n_i$ i.e., all electrons in the conduction band come from holes in valence band/one-to-one correspondence.

$$\Rightarrow n_i = (N_c P_v)^{1/2} e^{-U_G/2kT}$$

$$n_i = \frac{1}{4} \left(\frac{2kT}{\pi \hbar^2} \right)^{3/2} (m_{d,c}^* m_{d,v}^*)^{3/4} e^{-U_G/2kT}$$

Can also solve uniquely for μ as function of T.

$$n_i = e^{(\mu_i - U_c)/kT} N_c(T) = e^{(U_v - \mu_i)/kT} N_v(T)$$

\Rightarrow take log
$$\frac{(\mu_i - U_c)}{kT} + \ln N_c(T) = \frac{(U_v - \mu_i)}{kT} + \ln N_v(T)$$

or

$$2\mu_i - U_c - U_v = kT \ln \frac{N_v}{N_c}$$

$$\mu_i = \frac{U_c + U_v}{2} + \frac{kT}{2} \ln \frac{N_v}{N_c}$$

so as,

$$T \rightarrow 0 \quad \mu_i \rightarrow \frac{U_c + U_v}{2} \quad \text{“exact middle of the band gap”}$$

Example: Silicon @ T = 300K

$$m_{d,c}^* = 0.33 m_0, \quad m_{d,v}^* = 0.55 m_0, \quad U_G = 1.12 \text{ eV}$$

We find $n_i = 1.4 \times 10^{10} / \text{cm}^3$ far less than typical doping densities and even less than the purest forms of bulk Si.

Equilibrium Concentrations with Impurities

The addition of impurities affects the electrical properties of semiconductors.

Without impurities: $n_c(T) = p_v(T) = n_i(T)$

With impurities: $n_c(T) - p_v(T) = \Delta n \neq 0$

If we assume $U_c - \mu \gg kT$, *Boltzmann Statistics* still apply. so,

$$n_c(T)p_v(T) = n_i^2(T)$$

$$n_c(T) - \frac{n_i^2}{n_c(T)} = \Delta n$$

$$n_c^2 - n_i^2 = \Delta n n_c \text{ or } n_c^2 - n_c \Delta n - n_i^2 = 0$$

This is quadratic equation for n_c .

Solution: $n_c = \left[\Delta n \pm \sqrt{\Delta n^2 + 4n_i^2} \right] / 2$

Only + sign makes sense to preserve intrinsic limit.

$$n_c = \frac{1}{2} \left[\Delta n + \sqrt{\Delta n^2 + 4n_i^2} \right]$$

so that,

$$n_c \rightarrow n_i \text{ as } \Delta n \rightarrow 0$$

We could also write

$$\frac{n_i^2}{p_v} - p_v = \Delta n$$

$$n_i^2 - p_v^2 = \Delta n p_v \text{ or } p_v^2 + p_v \Delta n - n_i^2 = 0$$

$$p_v = \frac{-\Delta n \pm \sqrt{\Delta n^2 + 4n_i^2}}{2} = \frac{1}{2} \left[-\Delta n + \sqrt{\Delta n^2 + 4n_i^2} \right]$$

Again, only + sign makes sense.

We can write $\left\{ \begin{matrix} n_c \\ p_v \end{matrix} \right\} = \frac{1}{2} \left[\sqrt{\Delta n^2 + 4n_i^2} \pm \Delta n \right]$

To first order, effect of impurities can be accounted for by a change of chemical potential.

$$n_c(T) - \frac{n_i^2}{n_c} = \Delta n$$

$$n_i^2 = N_c p_v e^{U_g/kT} \quad n_c = N_c e^{(\mu - U_c)/kT}$$

$$\Rightarrow \Delta n = n_c(T) - p_v(T) = \frac{n_i^2}{p_v} - \frac{n_i^2}{n_c}$$

$$\frac{\Delta n}{n_i} = \frac{\sqrt{N_c p_v} e^{-(U_c - U_v)/2kT}}{p_v e^{(U_v - \mu)/kT}} - \frac{\sqrt{N_c p_v} e^{-(U_c - U_v)/2kT}}{N_c e^{\mu - U_c/kT}}$$

$$\frac{\Delta n}{n_i} = \sqrt{\frac{N_c}{p_v}} e^{-(U_c + U_v - 2\mu)/2kT} - \sqrt{\frac{p_v}{N_c}} e^{(U_c + U_v - 2\mu)/2kT}$$

define

$$\sqrt{\frac{N_c}{p_v}} e^{-(U_c + U_v)/2kT} \equiv e^{-\mu_i/kT}$$

so that,

$$\sqrt{\frac{p_v}{N_c}} e^{(U_c + U_v)/2kT} \equiv e^{\mu_i/kT}$$

and

$$\frac{\Delta n}{n_i} = e^{(\mu - \mu_i)/kT} - e^{-(\mu - \mu_i)/kT}$$

$$\frac{\Delta n}{n_i} = 2 \sinh \left(\frac{\mu - \mu_i}{kT} \right)$$

$$\mu_i \equiv -kT \left[\frac{-(U_c + U_v)}{2kT} + \ln \sqrt{\frac{N_c}{p_v}} \right]$$

$$\mu_i = \frac{U_c + U_v}{2} - \frac{1}{2} kT \ln \left(\frac{N_c}{p_v} \right)$$

To go further we must know the donor and acceptor ionization fraction as a function of temperature.

- Simplest and most common case is where each donor and acceptor has only one level and contributes only one electron or hole.

- Also we assume always that separation between adjacent donors or acceptors is great enough that they are distinguishable (wave functions do not overlap).

⇒ Apply *Maxwell Boltzmann Statistics* (grand canonical ensemble)

$$f_j = \frac{e^{-\frac{(U_j - \mu N_j)}{kT}}}{\sum_j e^{-\frac{(U_j - \mu N_j)}{kT}}} \quad f_j \rightarrow \text{probability of occupancy of state } j$$

Think of donor or acceptor atom as the “system” coupled to a bath at temperature T.

There are four possible “states” of this one possible level.

- 1) No electrons in level
- 2) One electron in level, spin up
- 3) One electron in level, spin down
- 4) Two electrons in level, one spin up and one spin down

$$U_1 = 0 \qquad N_1 = 0$$

$$U_2 = U_c - \phi_d \equiv U_d \qquad N_2 = 1$$

$$U_3 = U_c - \phi'_d > \phi_d \equiv U'_d \qquad N_4 = 2$$

So the mean occupancy $\langle N_j \rangle$ is given by

$$\langle N_j \rangle = \frac{\sum_j N_j e^{-\frac{(U_j - \mu N_j)}{kT}}}{\sum_j e^{-\frac{(U_j - \mu N_j)}{kT}}} = \frac{0 + e^{-\frac{(U_d - \mu)}{kT}} + e^{-\frac{(U_d - \mu)}{kT}} + 2e^{-\frac{(U'_d - 2\mu)}{kT}}}{1 + e^{-\frac{(U_d - \mu)}{kT}} + e^{-\frac{(U_d - \mu)}{kT}} + e^{-\frac{(U'_d - 2\mu)}{kT}}}$$

A good approximation is

$$e^{-\frac{(U_d - \mu)}{kT}} \ll e^{-\frac{(U_d - \mu)}{kT}}$$

so that,

$$\langle N_j \rangle \approx \frac{2e^{-\frac{(U_d - \mu)}{kT}}}{1 + 2e^{-\frac{(U_d - \mu)}{kT}}} \left\{ \text{looks like } \textit{Fermi-Dirac} \text{ distribution but not quite} \right.$$

For a concentration N_d of donors,

$$n_d = N_d \langle N_j \rangle = \frac{N_d}{1 + \frac{1}{2} \exp\left[\frac{(U_d - \mu)}{kT}\right]}$$

A similar derivation for acceptors (binding energy ϕ_a) yields

$$P_a = N_a \langle N_j \rangle = \frac{N_a}{1 + \frac{1}{2} \exp\left[\frac{(\mu - U_a)}{kT}\right]}$$

The balance between electrons and holes is determined by the requirement for space-charge neutrality.

- occupied donor is neutral $\rightarrow n_d$
- unoccupied (ionized) donor is positively charged $\rightarrow N_d - n_d$
- occupied acceptor is neutral $\rightarrow P_a$
- unoccupied (ionized) acceptor is negatively charged $\rightarrow N_a - P_a$

Total negative charges = $n_c + N_a - P_a \equiv \delta^-$

Total positive charges = $P_v + N_d - n_d \equiv \delta^+$

Space charge neutrality implies $\delta^- = \delta^+$ or $n_c + N_a - P_a = P_v + N_d - n_d$, so that

