Lecture 5.
Gapless Semiconductors

Genesis of Energy Spectrum in Semiconductors

Let us begin with the energy spectrum of either an individual atom, or a whole unit cell. Let this system have spherical symmetry. [1] Therefore, its eigenstates can be classified by the value of the angular momentum $\mathbf{L}$. Typically, for semiconductors the upper valence level corresponds to p-states, while the s state with a higher principal number has only a slightly higher energy. (see Fig.1) An example is given by $GaAs$ with the empty $3s$-levels of Ga and totally occupied $3p$ levels of As.

If the spin-orbit interaction is taken into account, only the total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$ is a good quantum number. This leads to the splitting of a six-fold degenerate p-state into a four-fold $P_{3/2}$ and a two-fold $P_{1/2}$, as it is shown on Fig.1.

Now we are prepared to consider the fate of all levels in the crystal. According to Bloch's theorem, the wave functions of an electron in a crystalline lattice are the eigenfunctions of quasi-momentum $\mathbf{k}$ and have the canonic form:

$$\psi_s(\mathbf{r}, \mathbf{k}) = u_s(\mathbf{r}, \mathbf{k}) \cdot \exp[i\mathbf{r}\mathbf{k}], \tag{1}$$

where the sub-index s denotes internal degrees of freedom such as the spin projection α and the index of the band. In our

[1] As a matter of fact, we should consider a crystal field of a cubic symmetry, acting on the unit cell, but for s- and p-states the difference between the cubic symmetry group and complete group of rotation is negligible

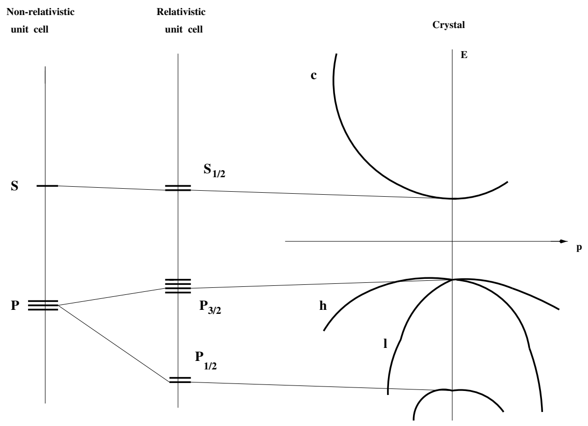

Figure 1: Genesis of Band spectra in cubic semiconductors

case, there are only two bands: a filled valence band v and an empty conduction band c. Therefore, either $s = (\alpha, v)$ or $s = (\alpha, c)$. The function $u_s(\mathbf{r}, \mathbf{k})$ in Eq (1) is periodic in both arguments with periods of the real lattice for $\mathbf{r}$ and those of the reciprocal lattice for $\mathbf{k}$. It is usually called the Bloch function. Let us assume now that at the centre of the Brillouin zone $\mathbf{\Gamma}$ the conduction band has an energy minimum E_c, the valence band has an energy maximum E_v and the width of the forbidden gap $E_g = E_c - E_v$ is small, compared with the band width. Then the band spectra at small $\mathbf{k}$ are determined by the mutual repulsion of these two bands. In order to describe it, we reduce the whole wave function to the form[2] :

$$\psi(\mathbf{r}, \mathbf{k}) = \exp[i\mathbf{r}\mathbf{k}] \cdot \left(\begin{array}{c} \phi_\alpha(\mathbf{r}) u_c(\mathbf{r}, 0) \\ \chi_i(\mathbf{r}) u_v(\mathbf{r}, 0) \end{array} \right) \tag{2}$$

[2]This reduction corresponds to the so called "effective mass approximation"

where ϕ and χ are slowly varying wave functions of electrons in the conduction and valence bands respectively [3] . These functions obey the equations

$$\left(\frac{k^2+\hat{p}^2}{2m}-E_c+\frac{\mathbf{k}\langle c|\hat{\mathbf{p}}|c\rangle}{m}\right)\phi+\frac{\mathbf{k}\langle c|\hat{\mathbf{p}}|v\rangle}{m}\chi=\hat{\epsilon}_c(k)\phi \qquad (3)$$

$$\left(\frac{k^2+\hat{p}^2}{2m}-E_v+\frac{\mathbf{k}\langle v|\hat{\mathbf{p}}|v\rangle}{m}\right)\chi+\frac{\mathbf{k}\langle v|\hat{\mathbf{p}}|c\rangle}{m}\phi=\hat{\epsilon}_v(k)\chi \qquad (4)$$

The effective single band Hamiltonians $\hat{\epsilon}_{c,v}$ are matrices in spins indices. However, we will see in two lines, that ϵ_c is proportional to the unit 2×2-matrix, while the effective Hamiltonian in the valence band has a non-trivial matrix form.

Since the vector $\mathbf{p}$ is momentum, i.e. an odd-parity operator, its diagonal matrix elements vanish and only off-diagonal band hybridization matrix elements $\langle c,\alpha|\hat{\mathbf{p}}|v,i\rangle$ remain. The effective hybridization is very strong because the forbidden gap E_g is small. Its dependence on the projections of the angular momentum i of the holes leads to the splitting of the valence band into two branches which correspond to heavy (h) and light (l) holes. As it is well seen from Eqs (3) and (4), a convenient direction of the spin quantization axis is that of quasi-momentum $\mathbf{k}$. Projecting onto it the vector of intrinsic angular momentum (σ for the c-band and $\mathbf{J}$ for the v-band), we see that the proper quantum numbers for the spectra are helicities $\mathcal{J}=\sigma\cdot\mathbf{k}/k=\pm 1/2$ and $\mathcal{J}=\mathbf{J}\cdot\mathbf{k}/k=\pm 3/2, \pm 1/2$ respectively. In this basis, the only non vanishing hybridization matrix elements (p_z-projection) are those diagonal in helicities. Therefore, only the holes with

[3] Remember that the spin index α in the conduction band can take two values, either $+1/2$ or $-1/2$, while the index i in the valence band can take four values: $+1/2,\ -1/2,\ +3/2$, and $-3/2$.

the helicities $\mathcal{J} = \pm 1/2$ ("light holes") are hybridized with electrons, obtaining a strong dispersion, while the "heavy holes" with $\mathcal{J} = \pm 3/2$ remain heavy.
If the unit cell has a centre of symmetry, then the odd powers of helicity cannot appear in the spectra and any branch is two-fold degenerate. Therefore, ϵ_c is a scalar

$$\epsilon_c = E_c + \frac{k^2}{2m_e}, \tag{5}$$

while ϵ_v remains a matrix:

$$\epsilon_v = E_v + Ak^2 + B(\mathbf{J} \cdot \mathbf{k})^2. \tag{6}$$

The matrix form (6) is called the Luttinger Hamiltonian. The valence band splits into two branches corresponding to heavy and light holes:

$$\epsilon_h = E_v + \left(A + \frac{9B}{4}\right) k^2 = E_v - \frac{k^2}{2m_h} \tag{7}$$

$$\epsilon_l = E_v + \left(A + \frac{B}{4}\right) k^2 = E_v - \frac{k^2}{2m_l} \tag{8}$$

At $k = 0$ these branches coincide, because a cubic crystal field does not split the 3/2-quartet.
Let us now count the number of electrons per unit cell. There are two atoms in the $GaAs$ unit cell: Ga with its 3 electrons and As with 5 electrons. Two electrons occupy the low lying s-level, two others the $p_{1/2}$ level. The remained four electrons fill the valence band. Therefore, $GaAs$ is a direct gap semiconductor. Many properties of semiconductors are determines by their energy spectrum (See problems to this lecture).

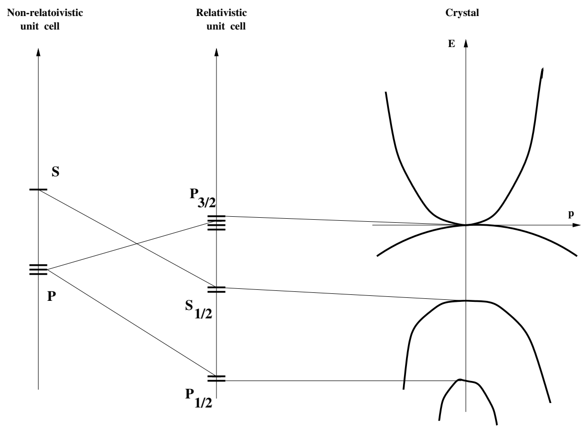

Figure 2: Genesis of Band spectra in cubic gapless semiconductors

Gapless Semiconductors

Consider now a special case of inversion ($HgTe$), when the s-level, which generates the conductance band in $GaAs$, lies below the $p_{3/2}$-level, but above the $p_{1/2}$-level. The origin of the bands near the $\mathbf{\Gamma}$ point will be essentially the same, except for m_e and m_l changing their sign to build the spectrum as it is shown in Fig2. Assuming the same number of electrons per unit cell, we find that now the last occupied branch will be that of heavy holes, while the empty branch will be that of light holes. The energy gap is zero, which gives the name to these compounds.

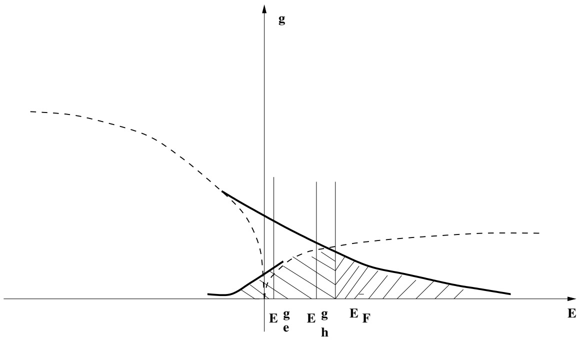

Figure 3: Overlapping the band tails of electrons and holes in gapless semiconductors

Self-doping in Gap-less Semiconductors

Experiment shows that naturally grown gapless semiconductors are always doped by negatively charged carriers. The explanation of this phenomenon comes from an assumption that the intrinsic disorder is always there. Disorder can arise, for instance, from the local violation of stechiometry of these compounds. The density of states in a disordered one-band conductor has a characteristic tail at classically forbidden energies, as it is shown in Fig 3. The heavier are the carriers, the longer is this tail for a given strength of the random potential. If the random potential due to disorder has a correlator

$$\langle U(\mathbf{r})U(\mathbf{r}')\rangle = \gamma\Phi\left(\frac{|\mathbf{r}-\mathbf{r}'|}{R_c}\right), \tag{9}$$

where R_c is of the order of inter-atomic distance a, then the probability P of having a fluctuation of the random potential $U(\mathbf{r})$ is

$$P\{U\} \sim \exp\left[-\frac{1}{\gamma a^3}\int d\mathbf{r}U^2(r)\right]. \tag{10}$$

If we want to have a bound state of energy E, we need to create a fluctuation potential well of depth $U \sim E$ and width $L_E \sim \hbar/\sqrt{2m^* E}$. The probability of such a fluctuation gives the tail of the density of states:

$$g(E) \sim \exp\left[-\frac{1}{\gamma a^3} E^2 L_E^3\right] \sim \exp\left[-\frac{E^{1/2}}{\gamma}\left(\frac{\hbar^2}{2m^* a^2}\right)^{3/2}\right] \qquad (11)$$

As a result, the energy width ΔE of the tail is

$$\Delta E \sim \gamma^2 \left(\frac{2m^* a^2}{\hbar^2}\right)^3 \qquad (12)$$

There are two tails in a gapless semiconductor: one for electrons and the other for holes. Since holes are much heavier, than electrons, the tails look as it is shown in Fig 3. Tail overlap leads to redistribution of the carriers, as it is shown in Fig 3, with equal numbers of electrons and holes. The difference occurs in the positions of the mobility edges $E_g^{(e,h)}$ (see lecture 14) because the mobility edge $E_g^{(h)}$ of heavy hole located at larger energy $E_g^(h)$, than that for electrons $E_g^{(h)} > E_g^{(e)}$. As a result, almost all the holes are localized, while almost all the electrons are mobile. This explains the puzzle of self-doping.