

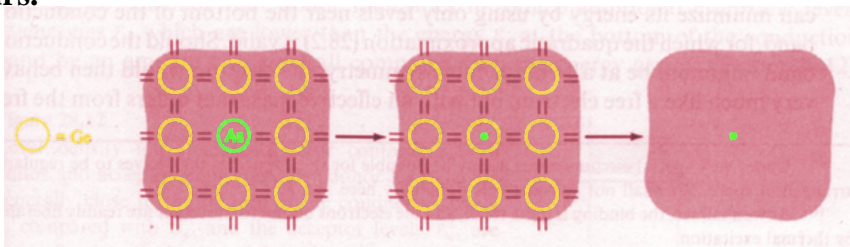
SEMICONDUCTORS - II

Lecture 23

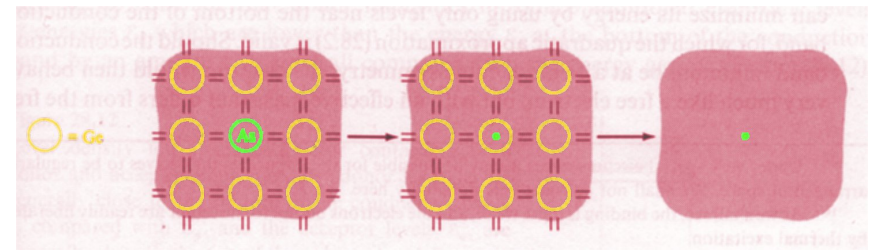
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9.6 Doping - donors and acceptors

Consider doping a 4-valent semiconductor (Si, Ge) with a 5-valent impurity (P, As, Sb). The impurity will *substitute* for a host atom – so that 4 of its 5 valence electrons are involved in bonds to its neighbours.



This leaves one electron unaccounted for – but the impurity nucleus has one extra positive charge to attract it.



Assume

- the extra electron is quite loosely bound to the impurity
- to a first approximation it is an electron in the conduction band with energy E_c
- so it ‘samples’ the crystalline potential – its mass is the electronic effective mass m_e^*
- also it sees the nucleus through the crystal – screened by the dielectric constant ϵ_r

9.6.1 Impurity states

The Hamiltonian for the extra electron of a 5-valent impurity is

$$\mathcal{H} = -\frac{\hbar^2}{2m_e^*} \nabla^2 - \frac{e^2}{4\pi\epsilon_r\epsilon_0 r}$$

which is just like the Hydrogen atom Hamiltonian

$$\mathcal{H} = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}$$

except with a scaled mass and with ϵ_0 replaced by $\epsilon_0\epsilon_r$.

If we take over the Hydrogen atom energies and wavefunctions,

$$E_n = -\frac{e^4 m_e}{32\pi^2 \epsilon_0^2 \hbar^2} \frac{1}{n^2} = -\frac{13.6}{n^2} \text{ eV}$$

and for the ground state

$$\psi(r) = N e^{-r/a_H}$$

where a_H is the Bohr radius,

$$a_H = \frac{4\pi\epsilon_0\hbar^2}{e^2 m_e} = 0.053 \text{ nm.}$$

Putting in the scaling factors, the impurity binding energy in its ground state is

$$E = -13.6 \frac{(m_e^*/m_e)}{\epsilon_r^2},$$

with a radius

$$a_0 = a_H \frac{\epsilon_r}{(m_e^*/m_e)}$$

If we take $m_e^* = 0.2m_e$ and $\epsilon_r = 11.7$ for Si we find

$$a_0 = 3 \text{ nm}$$

which is many interatomic spacings – consistent with our initial assumption that the electron samples a large region of the crystal. The binding energy in Si is then

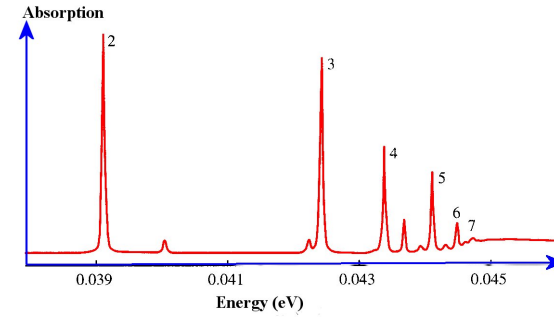
$$E = -0.02 \text{ eV,}$$

which, remember, is the lowering of energy relative to the bottom of the conduction band,

$$E_d = E_c + E.$$

As it is easy to excite electrons from these loosely-bound states into the conduction band, 5-valent impurities are called *donors*. Similarly, for 3-valent impurities we have a loosely-bound hole, in energy levels just above the valence band. These are called *acceptor* levels.

Far-infrared absorption of P in Si showing hydrogen-like transitions between $n=1$ ground state and higher levels.



We ignore this level structure from now on, and concentrate on the impurity ground state and the nearest band.

9.6.2 Typical binding energies

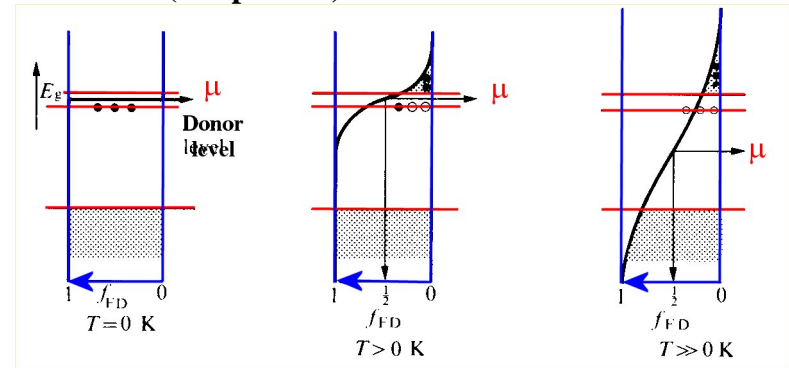
Donor ionization energies, meV			
	P	As	Sb
Si	45.0	49.0	39.0
Ge	12.0	12.7	9.6
Acceptor ionization energies, meV			
	B	Al	Ga
Si	45.0	57.0	65.0
Ge	10.4	10.2	10.8

Note that there is a small chemical effect. Donor and acceptor states are usually localised, but if the defects get close enough for their wavefunctions to overlap appreciably, we may get *impurity bands*.

9.6.3 Deep traps

Impurities with larger differences in valence from the host typically produce states which are much further from the band edges – called *deep levels*. These take more thermal energy to release carriers, so are less important in determining carrier concentrations. However, they can trap free carriers and allow them to interact with carriers of the opposite type, allowing *recombination*. The maintenance of the carrier density is a dynamic process, with a balance between thermal excitation and recombination. The recombination time τ is an important parameter of semiconductor devices, as we shall see later.

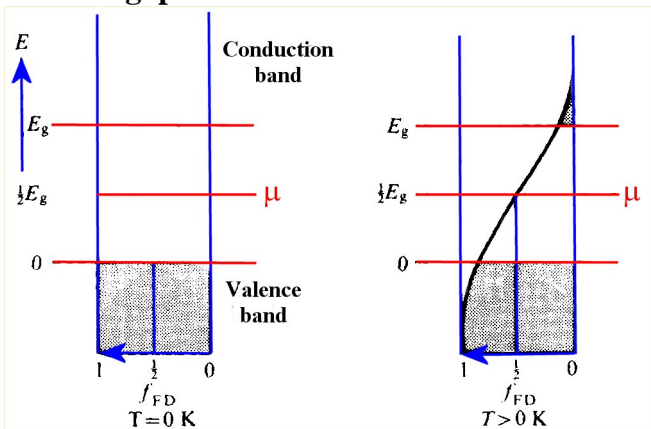
If we dope with donors only (*n-type doping*), then at absolute zero the highest occupied levels will be the donor levels, the lowest empty levels will be at the bottom of the conduction band, so the chemical potential will lie between the donor levels and the bottom of the conduction band (left picture).



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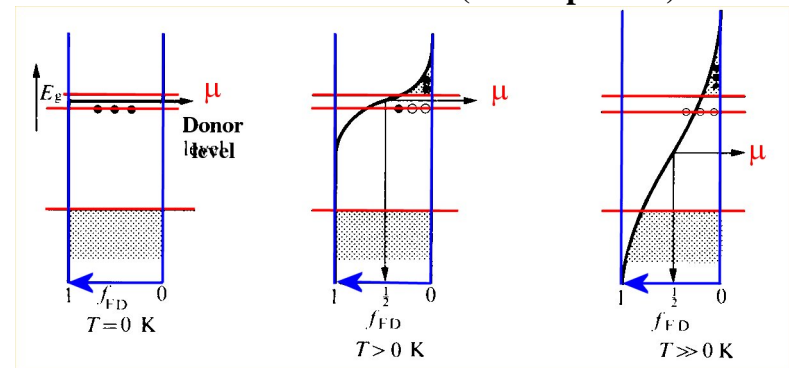
9.6.4 Locating the chemical potential

In an undoped material, we have seen that at absolute zero, where the Fermi function is a step function, the chemical potential is in the middle of the band gap.



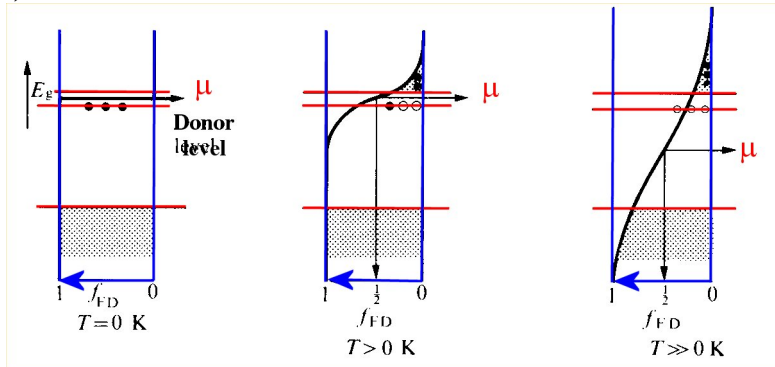
As we increase the temperature, it only moves slightly – at the same time the step in the Fermi function broadens out, and in the bands the function is well approximated by a Boltzmann form.

If we raise the temperature slightly, we excite electrons from the donor levels into the conduction band (centre picture).



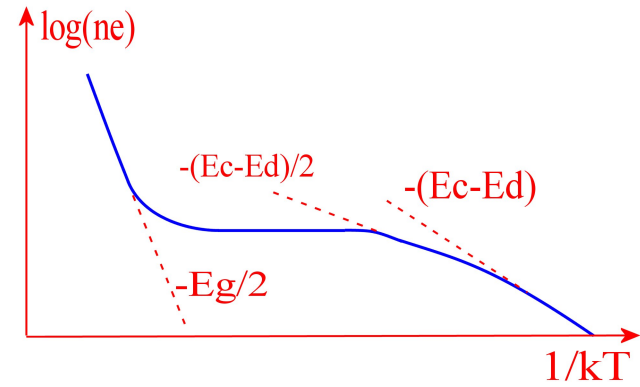
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As we raise the temperature more, we will exhaust the donor levels. Any further electrons must come from the valence band (right-hand picture)



We are then back in the *intrinsic* regime.

If we look at the electron density:



Note that no matter how hard we try, we can *never* have *only* donors in the system - there are bound to be some acceptors. The electronic energies for the acceptors are lower than those for the donors, so the few acceptors will ionize a few donors so the boundary between occupied and unoccupied levels lies somewhere amongst the donor levels. At very low T the chemical potential is 'pinned' at the donor levels in this case.