3.23 Electrical, Optical, and Magnetic Properties of Materials
Fall 2007

THE LAW OF MASS ACTION

Last time

1. Band structure of oxides (perovskites), semiconductors (silicon, and compared with lead), late (fcc) transition metals (same period, or same group), graphene and nanotubes
2. Independent electron gas: states, energy, density, DOS
3. DOS of massive and massless bands in 1, 2 and 3 dimensions
4. Statistics of classical and quantum particles, Fermi-Dirac distribution, chemical potential

Study

- Chap 6 Singleton,

  or, much better,
- Chap 28 (Homogeneous semiconductors) Ashcroft-Mermin (to be posted)

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Sb-doped Germanium

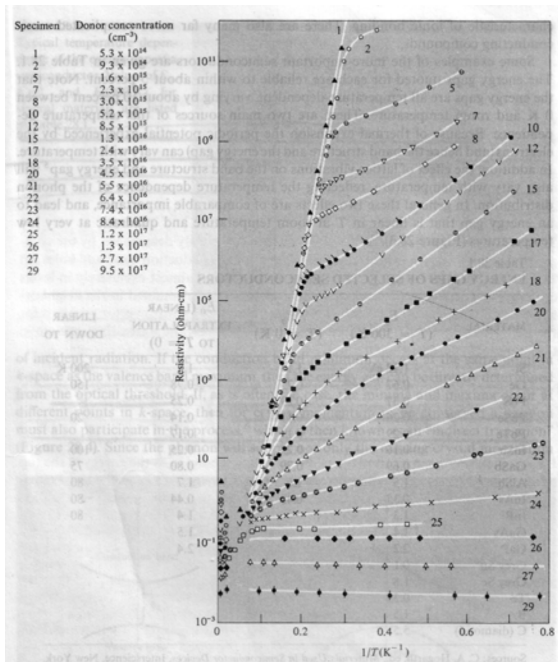

Figure 28.2
The resistivity of antimony-doped germanium as a function of $1/T$ for several impurity concentrations. (From H. J. Fritzsche, *J. Phys. Chem. Solids* **6**, 69 (1958).)

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Semiconductors

VEGARD'S LAW →

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Please see any graph of semiconductor band gaps vs. lattice constants, such as http://www.tf.uni-kiel.de/matwis/amat/semi_en/kap_5/illustr/bandgap_misfit.gif

Valence+conduction bands in Si

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Please see: Fig. 6.1 in Singleton, John. *Band Theory and Electronic Properties of Solids.* Oxford, England: Oxford University Press, 2001.

Band structure of Si, Ge, GaAs

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Please see any image of Si, Ge, and GaAs energy bands, such as http://ecee.colorado.edu/~bart/book/book/chapter2/gif/fig2_3_6.gif.

Conduction band minima (in 3d)

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Optical absorption in Ge

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Please see: Fig. 6.3 and 6.4 in Singleton, John. *Band Theory and Electronic Properties of Solids.* Oxford, England: Oxford University Press, 2001.

Impress your examiners (orals)

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Number of carriers at thermal equilibrum

$$n_c(T) = \int_{\varepsilon_c}^{\infty} d\varepsilon\, g_c(\varepsilon) \frac{1}{e^{(\varepsilon-\mu)/k_BT}+1}$$

$$p_v(T) = \int_{-\infty}^{\varepsilon_v} d\varepsilon\, g_v(\varepsilon) \left(1 - \frac{1}{e^{(\varepsilon-\mu)/k_BT}+1}\right)$$

$$= \int_{-\infty}^{\varepsilon_v} d\varepsilon\, g_v(\varepsilon) \left(\frac{1}{e^{(\mu-\varepsilon)/k_BT}+1}\right)$$

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Please see Fig. 2.16 in Pierret, Robert F. *Semiconductor Device Fundamentals.* Reading, MA: Addison-Wesley, 1996.

Conduction and valence DOS
(**non-degenerate sc**, isotropic effective mass)

$$\frac{1}{e^{(\varepsilon-\mu)/k_BT}+1} \approx e^{-(\varepsilon-\mu)/k_BT}, \ \varepsilon > \varepsilon_c$$

$$\frac{1}{e^{(\mu-\varepsilon)/k_BT}+1} \approx e^{-(\mu-\varepsilon)/k_BT}, \ \varepsilon < \varepsilon_v$$

$$n_c(T) = \underbrace{\int_{\varepsilon_c}^{\infty} d\varepsilon\, g_c(\varepsilon) e^{-(\varepsilon-\varepsilon_c)/k_BT}}_{N_c(T)} e^{-(\varepsilon_c-\mu)/k_BT}$$

$$p_v(T) = \underbrace{\int_{-\infty}^{\varepsilon_v} d\varepsilon\, g_v(\varepsilon) e^{-(\varepsilon_v-\varepsilon)/k_BT}}_{P_v(T)} e^{-(\mu-\varepsilon_v)/k_BT}$$

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Please see: Fig. 18 in Kittel, Charles. "Introduction to Solid State Physics." Chapter 8 in *Semiconductor Crystals.* New York, NY: John Wiley & Sons, 2004.

Density of available states

$$\underbrace{\int_{\varepsilon_c}^{\infty} d\varepsilon g_c(\varepsilon) e^{-(\varepsilon-\varepsilon_c)/k_BT}}_{N_c(T)}$$

$$g_c(\varepsilon) = \sqrt{2(\varepsilon-\varepsilon_c)}\frac{m_c^{3/2}}{\pi^2\hbar^3}$$

$$g_v(\varepsilon) = \sqrt{2(\varepsilon_v-\varepsilon)}\frac{m_v^{3/2}}{\pi^2\hbar^3}$$

$$N_c(T) = \frac{1}{4}\left(\frac{2m_ck_BT}{\pi\hbar^2}\right)^{3/2} \sim m_c^{3/2} T^{3/2}$$

$$P_v(T) = \frac{1}{4}\left(\frac{2m_vk_BT}{\pi\hbar^2}\right)^{3/2} \sim m_v^{3/2} T^{3/2}$$

Miracle ! Law of Mass Action

$$n_c(T) = \underbrace{\int_{\varepsilon_c}^{\infty} d\varepsilon g_c(\varepsilon) e^{-(\varepsilon-\varepsilon_c)/k_BT}}_{N_c(T)} e^{-(\varepsilon_c-\mu)/k_BT}$$

$$p_v(T) = \underbrace{\int_{-\infty}^{\varepsilon_v} d\varepsilon g_v(\varepsilon) e^{-(\varepsilon_v-\varepsilon)/k_BT}}_{P_v(T)} e^{-(\mu-\varepsilon_v)/k_BT}$$

$$N_c(T) = 2.5\left(\frac{m_c}{m}\right)^{3/2}\left(\frac{T}{300K}\right)^{3/2} 10^{19}/cm^3$$

$$P_v(T) = 2.5\left(\frac{m_v}{m}\right)^{3/2}\left(\frac{T}{300K}\right)^{3/2} 10^{19}/cm^3$$

$$n_c(T)p_v(T) = N_c(T)P_v(T)e^{-(\varepsilon_c-\varepsilon_v)/k_BT}$$

$$\stackrel{!}{=} N_c(T)P_v(T)e^{-E_{GAP}/k_BT}$$

Intrinsic case

$$n_c(T) = p_v(T) \equiv n_i(T)$$

$$n_i(T) = \sqrt{N_c P_v}\, e^{-E_g/2k_BT}$$

$$= 2.5 \left(\frac{m_c}{m}\right)^{3/4} \left(\frac{m_v}{m}\right)^{3/4} \left(\frac{T}{300K}\right)^{3/2} e^{-E_g/2k_BT}\; 10^{19}$$

Intrinsic case

$$n_c(T) = \underbrace{\int_{\varepsilon_c}^{\infty} d\varepsilon\, g_c(\varepsilon) e^{-(\varepsilon-\varepsilon_c)/k_BT}}_{N_c(T)} e^{-(\varepsilon_c-\mu)/k_BT}$$

$$p_v(T) = \underbrace{\int_{-\infty}^{\varepsilon_v} d\varepsilon\, g_v(\varepsilon) e^{-(\varepsilon_v-\varepsilon)/k_BT}}_{P_v(T)} e^{-(\mu-\varepsilon_v)/k_BT}$$

$$n_i = \sqrt{N_c P_v}\, e^{-E_g/2k_BT}$$

$$\mu_i = \varepsilon_v + \frac{1}{2} E_g + \frac{1}{2} k_BT \ln\left(\frac{P_v}{N_c}\right)$$

$$n_c(T) = N_c(T)\, e^{-\left[\varepsilon_c - \varepsilon_v - \frac{1}{2}E_g - \frac{1}{2}k_BT \ln(P_v/N_c)\right]/k_BT}$$

$$= N_c(T)\, e^{-\frac{1}{2}E_g/k_BT} \cdot e^{+\left[\frac{1}{2}\ln(P_v/N_c)\right]}$$

Extrinsic case

$$n_c(T) - p_v(T) = \Delta n$$

$$n_c p_v = n_i^2$$

$$\left.\begin{matrix} n_c = \\ p_v = \end{matrix}\right. \frac{1}{2}\left[(\Delta n)^2 + 4n_i^2\right]^{1/2} \begin{matrix} +\frac{1}{2}\Delta n \\ -\frac{1}{2}\Delta n \end{matrix}$$

Extrinsic case

$$n_c = e^{\beta(\mu-\mu_i)} n_i \qquad p_v = e^{-\beta(\mu-\mu_i)} n_i$$

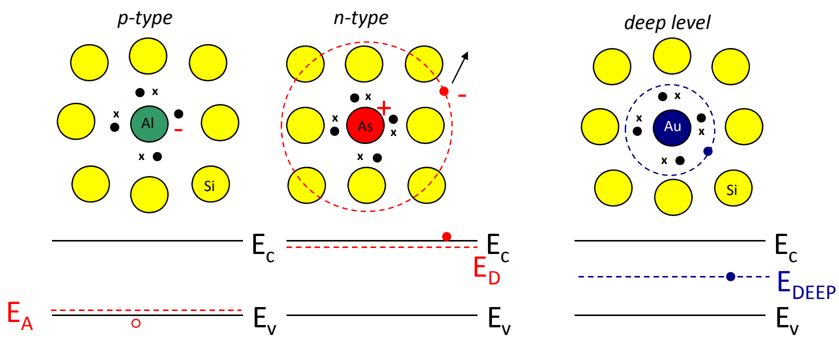
$$\frac{\Delta n}{n_i} = \frac{e^{\beta(\mu-\mu_i)} n_i - e^{-\beta(\mu-\mu_i)} n_i}{n_i} = $$

$$= 2 \sinh \beta(\mu-\mu_i)$$

Impurity levels

- Adding impurities can lead to controlled domination of one carrier type
  - n-type is dominated by electrons
  - p-type is dominated by holes
- Adding other impurities can degrade electrical properties

Impurities with close electronic structure to host | Impurities that create deep levels



Impurity states as "embedded" hydrogen atoms

- Consider the weakly bound 5th electron in Phosphorus as a modified hydrogen atom
- For hydrogenic donors or acceptors, we can think of the electron or hole, respectively, as an orbiting electron around a net fixed charge
- We can estimate the energy to free the carrier into the conduction band or valence band by using a modified expression for the energy of an electron in the H atom

$$E_n = \frac{me^4}{8\varepsilon_o^2 h^2 \mathrm{n}^2} = -\frac{13.6}{\mathrm{n}^2} \text{ (eV)}$$

$$E_n = \frac{me^4}{8\varepsilon_o^2 h^2 n^2} \xrightarrow{\frac{e^2}{\varepsilon_r}=e^2} \frac{m^* e^4}{8\varepsilon_o^2 h^2 n^2}\frac{1}{\varepsilon_r^2} = -\frac{13.6}{n^2}\frac{m^*}{m}\frac{1}{\varepsilon^2}$$

- Thus, for the ground state n=1, we can see already that since e is on the order of 10, the binding energy of the carrier to the impurity atom is <0.1eV
- Expect that many carriers are then ionized at room T
  - B acceptor in Si: 0.046 eV
  - P donor in Si: 0.044 eV
  - As donor in Si: 0.049

Temperature dependence of majority carriers

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Please see Fig. 2.22 in Pierret, Robert F. *Semiconductor Device Fundamentals*. Reading, MA: Addison-Wesley, 1996.

(Inverse temperature plot)

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Please see: Fig. 6.12 in Singleton, John. *Band Theory and Electronic Properties of Solids.* Oxford, England: Oxford University Press, 2001.