An introduction to the electric conduction in crystals

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1 Velocity of band electrons

The electronic states of crystals are described by the band structure $E_n(\mathbf{k})$, where n is the discrete band index and $\mathbf{k}$ the continuous Bloch vector restricted to the first Brillouin zone.[1] In a single-particle description these energies $E_n(\mathbf{k})$ are the eigenvalues of the crystal Hamiltonian

$$\hat{H}(\mathbf{r})\Psi_{n\mathbf{k}}(\mathbf{r}) = E_n(\mathbf{k})\Psi_{n\mathbf{k}}(\mathbf{r}) \tag{1}$$

Being stationary states, the time and space dependence of the Bloch functions $\Psi_{n\mathbf{k}}(\mathbf{r},t)$ is just given by

$$\Psi_{n\mathbf{k}}(\mathbf{r},t) = \mathrm{e}^{\mathrm{i}(\mathbf{k}\cdot\mathbf{r}-\omega_n(\mathbf{k})t)}u_{n\mathbf{k}}(\mathbf{r}) \quad \text{with} \quad \omega_n(\mathbf{k}) = \frac{1}{\hbar}E_n(\mathbf{k}) \tag{2}$$

where $u_{n\mathbf{k}}(\mathbf{r}+\mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r})$ is a lattice-periodic function. The plane waves $\mathrm{e}^{\mathrm{i}(\mathbf{k}\cdot\mathbf{r}-\omega_n(\mathbf{k})t)}$ provide a constant probability density over the entire crystal. Localized states (with an extension still much larger than the unite cell) can be described by wave packages containing k-values from a small interval around $\mathbf{k}_0$ and a fixed band. Then this wave package moves with the group velocity[2] $\mathbf{v}_n(\mathbf{k}_0) = \frac{\partial\omega_n(\mathbf{k})}{\partial\mathbf{k}}_{|\mathbf{k}=\mathbf{k}_0}$. Thus we find:

Bloch states with Bloch vector $\mathbf{k}_0$ in band n provide moving electrons with velocity

$$\mathbf{v}_n(\mathbf{k}_0) = \frac{1}{\hbar}\frac{\partial E_n(\mathbf{k})}{\partial\mathbf{k}}_{|\mathbf{k}=\mathbf{k}_0} \tag{3}$$

This velocity is also called the band velocity of the electron.

2 Kinetics in an electric field

If a force $\mathbf{F}$ is acting on a moving particle with velocity $\mathbf{v}$ the power $P = \mathbf{F}\cdot\mathbf{v}$ is the energy transferred to the particle per time. For electrons in a crystal this change in energy, means that another state in the band structure with a different energy has to be taken. As the band structure is continuous in the Bloch vector this means, that the change in energy is associate with a change in Bloch vector. For a localized wave packet around $\mathbf{k}_0$ this means

$$\mathbf{v}_n(\mathbf{k}_0)\cdot\mathbf{F} = P = \frac{\mathrm{d}E_n(\mathbf{k}_0)}{\mathrm{d}t} = \frac{\partial E_n(\mathbf{k})}{\partial\mathbf{k}}_{|\mathbf{k}=\mathbf{k}_0}\dot{\mathbf{k}}_0 = \mathbf{v}_n(\mathbf{k}_0)\hbar\dot{\mathbf{k}}_0$$

[1] See notes http://www.matfys.lth.se/Andreas.Wacker/Scripts/bandstructure_intro.pdf
[2] See notes http://www.matfys.lth.se/Andreas.Wacker/Scripts/wavepacket.pdf

where Eq. (3) was used. This equation is satisfied if $\hbar\dot{\mathbf{k}}_0 = \mathbf{F}$ holds (note that this is only necessary to hold in the direction of $\mathbf{v}_n(\mathbf{k}_0)$, a full proof goes far beyond these notes). The force on electrons results from electric ($\mathbf{E}$) and magnetic ($\mathbf{B}$) fields as given by the Lorentz force $\mathbf{F} = -e(\mathbf{E} + \mathbf{v} \times \mathbf{B})$ providing

In the presence of electric and magnetic fields the Bloch vector $\mathbf{k}$ of a Bloch state changes according to

$$\hbar\dot{\mathbf{k}} = -e\left[\mathbf{E} + \mathbf{v}_n(\mathbf{k}_0) \times \mathbf{B}\right] \tag{4}$$

The electric and magnetic field break the translational invariance of the Hamiltonian. Thus the Bloch states are no longer eigenstates but change in time according to Eq. (4). At the same time the band index is conserved unless the the fields are strong.[3] Note that the proof of Eq. (4) for the magnetic field is far from trivial and its validity is debated.

For free particles the de Broglie relation ($p = h/\lambda$) reads $\mathbf{p} = \hbar\mathbf{k}$ in vector notation. Thus Newton's law $\dot{\mathbf{p}} = \mathbf{F}$ directly transfers to $\hbar\dot{\mathbf{k}} = \mathbf{F}$ in full analogy for the situation of electrons in crystals discussed above. Therefore the quantity $\hbar\mathbf{k}$ is often called *quasimomentum* for Bloch electrons.

3 Effective mass

The acceleration of Bloch electrons in x direction is given by

$$\dot{v}_x = \frac{\mathrm{d}}{\mathrm{d}t}\frac{1}{\hbar}\frac{\partial E_n(\mathbf{k})}{\partial k_x} = \frac{1}{\hbar}\sum_{j=x,y,z}\frac{\partial^2 E_n(\mathbf{k})}{\partial k_x \partial k_i}\dot{k}_j = \frac{1}{\hbar^2}\sum_{j=x,y,z}\frac{\partial^2 E_n(\mathbf{k})}{\partial k_x \partial k_j}F_j$$

where Eqs. (3,4) were used. The accelerations in y and z direction are analogously. In classical physics the ratio between force and acceleration is the mass m of the particle. In our case the acceleration is not necessarily parallel to the force and thus the mass has to be replaced by a matrix $\mathcal{M}$.

The effective mass of a Bloch electron is given by the matrix $\mathcal{M}_n(\mathbf{k})$ where the elements of inverse matrix are given

$$[\mathcal{M}_n(\mathbf{k})]^{-1}_{ij} = \frac{1}{\hbar^2}\frac{\partial^2 E_n(\mathbf{k})}{\partial k_i \partial k_j} \tag{5}$$

For free electrons with $E_n(\mathbf{k}) = \hbar^2\mathbf{k}^2/2m$ we find $\mathcal{M}^{-1}_{ij} = \delta_{ij}/m$ or $\mathcal{M} = m\mathcal{I}$, where $\mathcal{I}$ is the unit matrix.

For one-dimensional structures with period d, the Brillouin zone extends from $-\pi/d$ to π/d. Then we find

$$\int_{-\pi/d}^{\pi/d}\mathrm{d}k\frac{1}{m_n(k)} = \frac{1}{\hbar^2}\left(\frac{\partial E_n(\pi/d)}{\partial k} - \frac{\partial E_n(-\pi/d)}{\partial k}\right)$$

As the Bloch vectors k and $k + 2\pi/d$ are equivalent, we have $E_n(k + 2\pi/d) = E_n(k)$ and correspondingly, both terms in the bracket cancel each other. Similarly one can show in three dimensions

$$\int_{\text{first Brillouin zone}}\mathrm{d}^3k\left[\mathcal{M}_n(\mathbf{k})\right]^{-1} = 0 \tag{6}$$

and the average (inverse) mass in a band is zero. This will be used to study the conduction properties of solids in the subsequent section.

[3] Zener tunneling is a typical example where the electrons are transferred from the valence to the conduction band at a high electric field

4 Conductance of crystals

If a moderate electric field is applied to a crystal, the Bloch vector changes in each band according to Eq. (4). This goes in hand with an acceleration

$$\dot{\mathbf{v}} = \mathcal{M}_n^{-1}(\mathbf{k})(-e\mathbf{E})$$

Now the total acceleration of a band n is given by the sum of accelerations of the occupied individual Bloch states

$$N_n\langle\dot{\mathbf{v}}\rangle = \sum_{\mathbf{k}} f_{n\mathbf{k}}\mathcal{M}_n^{-1}(\mathbf{k})(-e\mathbf{E})$$

where $f_{n\mathbf{k}}$ is the occupation probability of the Bloch state $(n\mathbf{k})$ and $N_n = \sum_{\mathbf{k}} f_{n\mathbf{k}}$ is the total number of electrons in the band and $\langle\dot{\mathbf{v}}\rangle$ is the average acceleration per electron in the band. Replacing the sum by an integral we obtain

$$n_n\langle\dot{\mathbf{v}}\rangle = \frac{1}{(2\pi)^3}\int_{\text{first Brillouin zone}} \mathrm{d}^3k\, f_{n\mathbf{k}}\mathcal{M}_n^{-1}(\mathbf{k})(-e\mathbf{E}) \tag{7}$$

where n_n is now the electron density in the band (in units 1/volume, the prefactors are not explained here).

For a full band, we have $f_{n\mathbf{k}} = 1$ for all $\mathbf{k}$ and thus Eq. (6) provides a zero net acceleration. Thus the average velocity remains zero and there is no current flowing in the presence of an electric field. For an empty band there is obviously neither any contribution to the electrical current. We conclude:

For moderate electric fields only partially filled bands contribute to the electric conduction.

Due to the Pauli principle each level can be occupied by a single electron (or two in the common case of spin degeneracy). Then the energetically lowest state is obtained by subsequently occupying the levels with increasing energy until the number of electrons matches the ionic charges to guarantee charge neutrality. The energy of the uppermost occupied level is called the Fermi level E_F. Thus for zero temperature the occupation probability becomes $f_{n\mathbf{k}} = 1$ for $E_n(\mathbf{k}) \leq E_F$ and $f_{n\mathbf{k}} = 0$ for $E_n(\mathbf{k}) > E_F$. If the Fermi level is located within an energy gap (of width E_g) in the bandstructure all bands are either entirely filled or empty and the conductance vanishes in an ideal case. As thermal excitations always provide a few carriers in the empty bands, there is some residual conductivity for *semiconductors*, unless $E_g \gg k_BT$, which is the case for *insulators*. The differentiation between semiconductors and insulators is however not sharp. On the other hand, a much higher conductance is found for *metals*, where the Fermi level is within the conduction band.

4.1 Metals with free electron behavior

Metals are characterized by the fact that the Fermi level is within a band, of which the lower part is filled with an electron density n_c (typically being of the order of the density of atoms), while the upper part is empty. Being the curvature of the band, the inverse effective mass $\mathcal{M}_n^{-1}(\mathbf{k})$ is positive for $\mathbf{k}$ values around the minimum of the band $E_n(\mathbf{k})$ and negative around the maximum. As the lower energy states of the band are occupied, we thus we expect that $\int_{\text{first Brillouin zone}} \mathrm{d}^3k\, f_{n\mathbf{k}}\mathcal{M}_n^{-1}(\mathbf{k}) > 0$ and Eq. (7) provides a positive net acceleration. In a free electron model, which is good for many metals, we simply get $\langle\dot{\mathbf{v}}\rangle = -e\mathbf{E}/m_e$. Now scattering processes tend to restore the equilibrium situation and thus provide an effective friction term $\langle\dot{\mathbf{v}}\rangle = -\langle\mathbf{v}\rangle/\tau$, where a finite average velocity decays on the time scale of the scattering time τ (typically tens or hundreds of femtoseconds). In the steady state the electric force and the friction compensate each other, providing $\langle\mathbf{v}\rangle = -e\mathbf{E}\tau/m$. Multiplying the average velocity by the density and the electron charge, we obtain the current density $\mathbf{j} = -en_c\langle\mathbf{v}\rangle$ and the

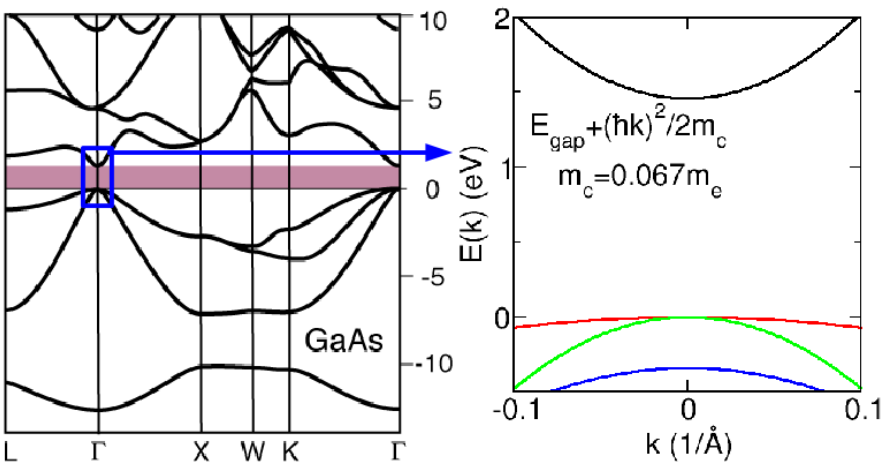

Figure 1: Band structure close the minimum of the conduction and maximum of the valence band of GaAs.

Electric conductivity of simple metals

$$\sigma = \frac{n_c e^2 \tau}{m_e}$$

Assuming that the electron density matches the atomic density of about $(3\text{Å})^{-3} \approx 4\times 10^{22}/\text{cm}^3$ and $\tau \sim 10$ fs we obtain $\sigma \sim 10^7$ A/Vm. This matches measured conductivities of iron and platinum at room temperature. The conductivities of copper and silver are six times larger.

4.2 Semiconductors with some electrons in the conduction band

The energetically lowest state of an ideal semiconductor has no electrons in the lowest empty band called *conduction band*. However due to thermal excitations, doping, irradiation, or charges electrically induced at interfaces there may be a few electrons with density n_c in the conduction band. Typical values for n_c vary between $10^{15}/\text{cm}^3$ and $10^{19}/\text{cm}^3$ which is several orders of magnitudes lower than in metals. Thus only the energetically lowest states of the conduction band close to its minimum are occupied. Close to its minimum the conduction band energies $E_c(\mathbf{k})$ are quadratic in $\mathbf{k}$, see Fig. 1. If the minimum is at the Γ point, which is the case for several III/V semiconductors such as GaAs[4], we may write

$$E_c(\mathbf{k}) \approx E_c + \frac{\hbar^2 \mathbf{k}^2}{2m_c}$$

where the effective mass of the conduction band m_c is a parameter obtained from the second derivative of the band structure, i.e. $\mathcal{M}_c(\mathbf{k}=0) = m_c \mathcal{I}$. Typical values are of the order of 0.1 m_e. Similar to the case of metals we thus find $\sigma = \frac{n_c e^2 \tau}{m_c}$, where now the effective mass replaces the electron mass. As the electron density can change over a larger range, one typically defines the

Mobility of electrons in the conduction band in a semiconductor

$$\mu_e = \frac{e\tau}{m_c} \quad \text{satisfying} \quad \langle \mathbf{v} \rangle = -\mu_e \mathbf{E}$$

[4]Things are more complicated in silicon, where there are several equivalent minima at finite $\mathbf{k}$.

where the sign results from the electron charge. Typical values for the electron mobility in semiconductors are between $10^3\text{cm}^2/\text{Vs}$ and $10^4\text{cm}^2/\text{Vs}$ at room temperature corresponding to $\tau \sim 0.3ps$. Much larger values can be obtained in clean samples at low temperatures.

4.3 Semiconductors with some holes in the valence band

The energetically lowest state of an ideal semiconductor is achieved if all states of the *valence band* (the uppermost filled band) are occupied. However due to thermal excitations, doping, irradiation, or charges electrically induced at interfaces there may be a few electrons missing. Writing the occupation probability of the valence band as $f_{v\mathbf{k}} = 1 - f_h(\mathbf{k})$, we can interpret $f_h(\mathbf{k})$ as the probability to find a missing electron, called *hole*, at $\mathbf{k}$. The density of holes n_h typically varies between $10^{15}/\text{cm}^3$ and $10^{19}/\text{cm}^3$, which is several orders of magnitudes lower than the total number of states in the valence band. Thus only the energetically highest states of the valence band, close to its maximum are emptied. Close to its maximum the valence band energies $E_v(\mathbf{k})$ are quadratic in $\mathbf{k}$, see Fig. 1. If the maximum is at the Γ point, which is the case for all commonly used semiconductors[5], we may write

$$E_v(\mathbf{k}) \approx E_v - \frac{\hbar^2\mathbf{k}^2}{2m_h}$$

where the *hole mass* m_h of the conduction band is a parameter obtained from the second derivative of the band structure, i.e. $\mathcal{M}_v(\mathbf{k}=0) = -m_h\mathcal{I}$. Note that $\mathcal{M}_v(\mathbf{k}=0)$ is negative as we are at a maximum of the band. Now Eq. (7) becomes

$$\begin{aligned} n_v\langle\dot{\mathbf{v}}\rangle =& \frac{1}{(2\pi)^3}\int_{\text{first Brillouin zone}} \mathrm{d}^3k\ [1-f_h(\mathbf{k})]\,\mathcal{M}_v^{-1}(\mathbf{k})(-e\mathbf{E}) \\ \approx& \frac{1}{(2\pi)^3}\int_{\text{first Brillouin zone}} \mathrm{d}^3k\ f_h(\mathbf{k})\frac{1}{m_h}(-e\mathbf{E}) = n_h\frac{-e\mathbf{E}}{m_h} \end{aligned}$$

where Eq. (6) was used and the approximation $\mathcal{M}_v(\mathbf{k}) \approx -m_h\mathcal{I}$ was applied as $f_h(\mathbf{k})$ is vanishing unless close to the maximum of the valence band. Taking into account the friction $\langle\dot{\mathbf{v}}\rangle = -\langle\mathbf{v}\rangle/\tau$, we find the current of the valence band $\mathbf{j}_v = -en_v\langle\mathbf{v}\rangle = n_h\frac{n_he^2\tau}{m_h}\mathbf{E}$ and the corresponding conductivity $\sigma = \frac{n_he^2\tau}{m_h}$. Note that instead of the electron density, the hole density determines the contribution to the conductance from the valence band. Thus one may say that the current is carried by holes with a charge e and an average velocity $\mu_h\mathbf{E}$ where the hole mobility is given by $\mu_h = e\tau/m_h$ in full analogy to the situation in the conduction band.

[5]The situation is actually more complicated due to the presence of three maxima at the Γ point.