Summary Chapter 7.

In Chapter 7 we discussed beyond the free electron model of chapter 6. In particularly we focused on the influence of the periodic potential of the ion cores on the energy level diagram of the outer electrons of the atoms. It will help us better understand why the electric conductivity varies between different materials: note that a good insulator can have a resistivity as high as 10^{22} Ohm.cm while a good conductor has a resistivity of 10^{-10} Ohm.cm. In previous courses you might have been introduced to the energy band diagrams of insulators, metals, and semiconductors (see Fig. 1 of chapter 7). In this chapter we will learn more about the reasons behind the band-diagram.

The energy of a free electron can be found by solving for the Schrodinger equation assuming the potential energy is everywhere zero, i.e.:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}+U\psi=E\psi\Rightarrow-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}=E\psi \qquad [1]$$

In quantum we have learned that the solutions are complex plane waves, i.e.

$$\psi(x)=Ae^{i\vec{k}\bullet\vec{r}} \qquad [2]$$

The free electrons in a piece of copper of size L are no longer free as they are contained in the block of copper, so their wave function is expected to be zero outside the material. Since a good wave-function is continuous, we have to apply the boundary conditions at x=0 and x=L. Similar to the phonon case discussed in chapters 4 and 5, we can apply zero boundary conditions for x=0 and x=L, or better we can apply a periodic boundary condition and assume $\psi(0)$-$\psi(L)$. For the periodic boundary condition, the eigenfunctions are still plane waves as in the completely free electron case, but now not all wave-vectors are allowed, only the following k-values are allowed:

$$k_x,k_y,k_z=0,\ \pm\frac{2\pi}{\mathrm{L}},\ \pm\frac{4\pi}{\mathrm{L}},\ \ldots. \qquad [3]$$

Also the energy values are given by:

$$E_k=\frac{\hbar^2}{2m}\left(k_x^2+k_y^2+k_z^2\right) \qquad [4]$$

Note that the $k=2\pi/\lambda$, and thus is related to the momentum of the free electron ($p=\hbar k$). The relation between the momentum and energy for free electrons is given by a parabola (see also dashed curve in Fig. 4).

Strictly speaking the conduction electrons in a periodic crystal structure are not free but experience the electric potential of the positive ion cores. So the potential at the bottom of the well of length L, where L is the length of the block, is not zero but varies periodically. We expect the potential energy of the electron to be low near the positive ion cores and high in between the ions. A sketch is made in Fig. 3 on page 166. See also the figure 1 below which shows the atomic potential in a solid (near the top), the potential energy of the free electron gas (FEG) of chapter 6 (middle), and the potential energy of the nearly free electron model (bottom).

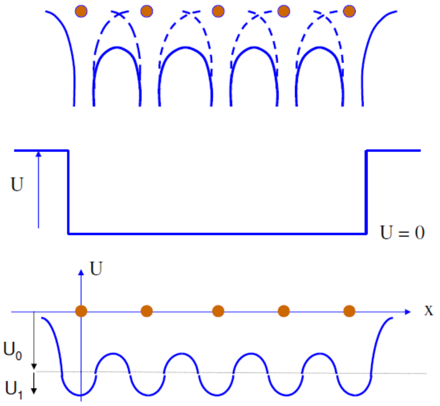


Fig. 1: From top to bottom: atomic potential in a solid (top); potential energy function of conduction electron in the "free electron model" (middle); potential energy function of conduction electron in the "nearly free electron model" (bottom)

Notice that the potential energy of an electron in a hydrogen atom is described by Coulomb's law for V; in SI units:

$$U = qV = -\frac{1}{4\pi\varepsilon_o}\frac{e^2}{r} \tag*{[5]}$$

Since conduction electrons are solutions can be represented by waves (solution of the Schrodinger equation) they can diffract from this periodic potential just like photons did in chapter 2. So we expect that when the wavelength of the conduction electrons is similar to the periodicity of the lattice that diffraction will take place and a electron will be diffracted of the lattice structure (read k-vector of electron will change). I expect strong constructive interference of the waves scattered of two consecutive atoms if the path length difference of the scattered waves is exactly nλ, where n is an integer and λ is the wavelength of the plane wave. This condition is met when the wavelength of the conduction electron is exactly equal to 2a where a is the lattice distance. See also the figure 2 sketched below. So when the wave-vector of the conduction electron is equal to 2π/(2a)=π/a, I expect strong interaction between the electron's wave-function and the crystal lattice. So for k values at the first Brillouin zone boundary a plane wave travelling towards the left will be Bragg reflected towards the right. So I expect that the solution of the Schrodinger equation will consist of a linear combination of both plane wave solutions near the zone boundaries i.e.

$$\psi(+) = e^{i\pi x/a} + e^{-i\pi x/a} \tag*{[6]}$$

Or:

$$\psi(-) = e^{i\pi x/a} - e^{-i\pi x/a} \tag*{[7]}$$

Note that the solution of the Schrodinger equation near the Brillouin zone boundary is no longer a traveling wave but a standing wave.

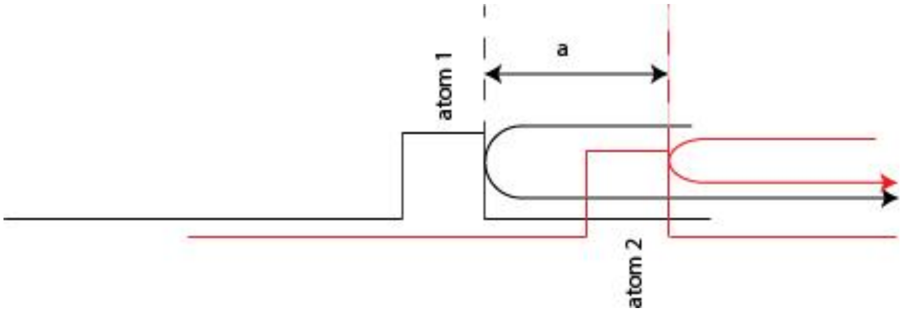


Fig. 2: Interference of two traveling waves reflected of neighboring atoms.

The probability density function of both wave-functions described by equation [6] and [7] can be calculated from $\psi^*\psi=|\psi|^2$ (where the star indicates the complex conjugated), i.e.

$$\begin{aligned}\psi(+)^*\psi(+)&=\left(e^{i\pi x/a}+e^{-i\pi x/a}\right)^*\left(e^{i\pi x/a}+e^{-i\pi x/a}\right)=\left(e^{-i\pi x/a}+e^{i\pi x/a}\right)\left(e^{i\pi x/a}+e^{-i\pi x/a}\right)=\\ 1+e^{i2\pi x/a}&+e^{-i2\pi x/a}+1=2+2\cos(2\pi x/a)=4\cos^2(\pi x/a)\end{aligned} \qquad [8]$$

And for the wave-function of equation [7]:

$$\begin{aligned}\psi(-)^*\psi(-)&=\left(e^{i\pi x/a}-e^{-i\pi x/a}\right)^*\left(e^{i\pi x/a}-e^{-i\pi x/a}\right)=\left(e^{-i\pi x/a}-e^{i\pi x/a}\right)\left(e^{i\pi x/a}-e^{-i\pi x/a}\right)=\\ 1-e^{i2\pi x/a}&-e^{-i2\pi x/a}+1=2-2\cos(2\pi x/a)=4\sin^2(\pi x/a)\end{aligned} \qquad [9]$$

Both solutions are sketched in figure 3 on page 166 of Kittel. The probability density of the $\psi(+)$ solution is maximum near the positive ion cores, while the probability density of the $\psi(-)$ solution is maximum in between the two ion cores (dashed function). The figure also shows the probability density function of a traveling plane wave solution (constant line). The $\psi(+)$ solution has the lowest energy while the $\psi(-)$ solution has the highest energy of the three wave-function. Notice that the plane wave is not a stationary state as it will be immediately Bragg reflected if it tries to propagate through the periodic crystal. Another interesting this about the wave-function of Fig. 3 is that they look the same from any lattice point (makes sense!).

The expectation value of the energy of both states can be calculated using the energy operator and the wave-function, i.e. sandwich the energy operator between ψ^* and ψ and then integrate over all space (0-L). I expect the kinetic energy of both solutions to be comparable as they both have the same wavelength, and the wavelength tells me normally something about the momentum of the particle, which for a free particle is related to the kinetic energy ($KE=p^2/2m$). I expect the potential energy of both wave-functions however to be quite different. The potential energy operator is given by expression [5]. So:

$$\langle U \rangle = \int_{-\infty}^{\infty} \psi^{*}\left(-\frac{1}{4\pi\varepsilon_{o}}\frac{e^{2}}{x}\right)\psi dx = \int_{-\infty}^{\infty} |\psi|^{2}\left(-\frac{1^{2}}{4\pi\varepsilon_{o}}\frac{e^{2}}{x}\right)dx \qquad [10]$$

So the expectation value of the potential energy is a kind of a weighted integral. Since $|\psi(+)|^2$ is large for the areas of low potential energy I expect that the +wave-function to have a low potential energy. On the contrary inspecting Fig. 3 below I see that $|\psi(-)|^2$ is large for the areas where the potential energy is high, so $\psi(-)$ will have a larger potential energy.

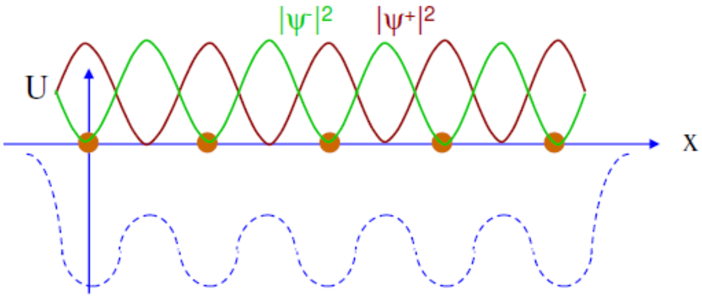


Fig. 3: Potential energy (dashed blue curve) function of conduction electron (nearly free electron model) and probability density function of electrons with a wave-vector at the first zone boundary. The orange dots represent the positive ion cores.

Summarizing: near the Brillouin zone boundaries I expect that the k-ε dispersion of the nearly free electron differs from the k-ε dispersion of a free electron. Both dispersion curves are sketched in figure 2 on page 164 of Kittel. Point A corresponds to ψ(+) and point B corresponds to ψ(-). In between both energies, no stationary states exists. Have also a look at the k-ε dispersion relation sketched in figure 6 on page 170 and in the figure below. Note that the x-axis of figure 6 is not k but ka. You can see that because of the interaction of the electron with the positive nuclei near the zone boundaries bandgaps are introduced in the k-ε dispersion (see also figure below).

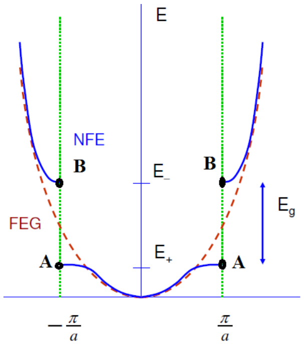


Fig. 4: Energy dispersion for free electron model (FEG: dashed curve) and nearly free electron model (NFE: blue solid line). Note that the quantity along the x-axis is the wave-vector and the quantity along the y-axis is the total energy. The dashed lines at k=p/a and k=-p/a represent the boundaries of the first Brillouin zone.

The larger the variation of the potential energy of the positive ion cores, the larger the bandgap. In class we calculated that for a sinusoidal potential energy with amplitude U, i.e $U(x) = U\cos(2\pi x/a)$, the bandgap is equal to $E_g = U$.

To really understand the electronic bandstructure of a solid we have to solve the Schrodinger equation for a certain periodic potential energy function. In general this requires advanced computer programs to do: Dr. Scolfaro uses Density Functional Theory (DFT) for calculation of the band-structure of solids. DFT is based on the Bloch theorem: The eigenfunctions of the wave equation for a periodic potential are the product of a plane wave $e^{i\mathbf{k}.\mathbf{r}}$ times a periodic function $u_k(\mathbf{r})$ that has the same period as the crystal lattice. Or in other words: if the potential energy is a periodic function with periodicity **T**, the solution of the Schrodinger equation can be written as the product of a complex plane wave and a function $u_k(\mathbf{r})$ which has the same periodicity as the potential energy function, i.e.:

$$\psi_k(\vec{r}) = u_k(\vec{r})e^{i\vec{k}\bullet\vec{r}} \qquad [11]$$

Note that the complex plane wave part of equation [11] is the wave-function of a free particle. So we see that wavefunction is a modulated complex plane wave. Note that $u_k(\mathbf{r})$ in general has a much smaller period than the plane wave (see also the figure below).

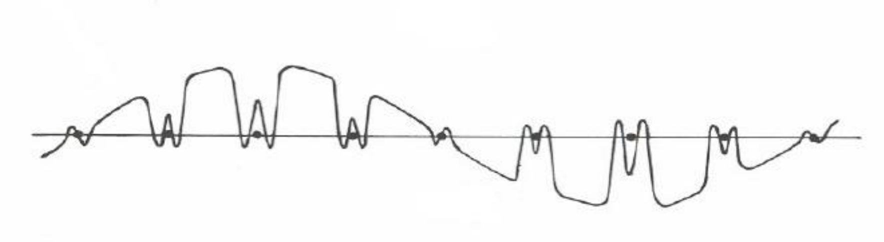


Fig. 5: Bloch function for 3s electron in sodium: notice that the wave-function is product of a plane wave with a long period and a function $u_k(r)$ which has the same periodicity as the lattice. The black dots represent the position of the atoms in the crystal lattice.

We discussed two proofs of Bloch's theorem:

1. Assume that the solution of the Schrodinger equation is given by:

$$\psi(\vec{r}) = \sum_k C_k e^{i\vec{k}\bullet\vec{r}} \qquad [12]$$

Where $\psi(\mathbf{r})$ matches the periodic boundary conditions for a block of material with length L, so $\psi(0)=\psi(L)$ and L=Na, where a is the lattice constant, N is the number of atoms, and L is the total length of the block of material. Note that an electron can be considered to consist of a sum of plane waves each with their own phase and amplitude. Almost any k is allowed but strictly speaking **k** is discretized to 0, $+/-2\pi/L$, $+/- 4\pi/L$, etc. Equation [12] can be considered to be a Fourier series. We can rewrite the sum by splitting the summation in two parts, i.e.

$$\psi(\vec{r}) = \sum_{k \in 1BZ} \sum_{\vec{G}} C_{\vec{k}+\vec{G}} e^{i(\vec{k}+\vec{G})\bullet\vec{r}} \qquad [13]$$

Where the first summation is only over the first Brillouin zone (1BZ), and the 2nd summation is over k-vectors in higher Brillouin zones: note that for each **k** in the first Brillouin zone, there is a point in the 2nd Brillouin zone that differs from **k** by **G**. Let us focus on just one of the plane waves of equation [13]:

$$\psi_k(\vec{r}) = \sum_{\vec{G}} C_{\vec{k}+\vec{G}} e^{i(\vec{k}+\vec{G})\bullet\vec{r}} = e^{i\vec{k}\bullet\vec{r}} \sum_{\vec{G}} C_{\vec{k}+\vec{G}} e^{i\vec{G}\bullet\vec{r}} \qquad [14]$$

Note that the summation on the left is a Fourier series and is thus periodic with the lattice (compare equation [14] with equation [9] of chapter 2). So replacing the summation on the left by $u_k(\mathbf{r})$ gives us Bloch's theorem.

2. Bloch's theorem implies that

$$\begin{aligned} &\psi_k(\vec{r}+\vec{T}) = u_k(\vec{r}+\vec{T})e^{i\vec{k}\bullet\vec{r}}e^{i\vec{k}\bullet\vec{T}} = u_k(\vec{r})e^{i\vec{k}\bullet\vec{r}}e^{i\vec{k}\bullet\vec{T}} = \psi_k(\vec{r})e^{i\vec{k}\bullet\vec{T}} \Rightarrow \\ &\psi_k(\vec{r}+\vec{T}) = \psi_k(\vec{r})e^{i\vec{k}\bullet\vec{T}} \end{aligned} \qquad [15]$$

Or in other words the wave-function at atom position **r**+**T** (where **T** is a crystal lattice vector) can be calculated from the wave-function at **r** by multiplication with a phase factor $e^{i\mathbf{k}.\mathbf{T}}$. So if I can proof 15 I basically proof Bloch's theorem.

Consider N identical lattice points separated by a. The symmetry of the periodic boundary condition implies that we can find a solution to the wave equations that looks like:

$$\psi(x+a) = C\psi(x) \qquad [16]$$

b/c of periodic boundary condition:

$$\psi(x+Na) = C^N\psi(x) \qquad [17]$$

As the wave function is single valued:

$$C^N = 1 = e^{i2\pi n} \Rightarrow C = e^{\frac{2\pi n i}{N}} \qquad [18]$$

If we assume that $k=2\pi n/(Na)$ than we can rewrite [18] as:

$$\psi(x+a) = e^{ika}\psi(x) \qquad [19]$$

Which is the same equation [15].

We discussed in class the Kronig Penney model described on pages 168-169 of Kittel. The model assumes a square potential energy distribution caused by the positive ion cores. It then solves the Schrodinger equation for the two types of areas. The math is similar to the particle in the square box problem that was discussed in quantum. Solutions for the low potential energy regions are complex plane waves traveling in both directions. Solutions for the high potential energy regions are exponential decaying. The constants in the solutions can be found by enforcing the boundary conditions at the interfaces between both regions, i.e. (1) a good wave function is continuous and (2) a good wave-function in an area with finite energy is differentiable. Together with Bloch's theorem this leads to four equations and four unknown. We are looking for the non-trivial solutions, so we set the determinant equal to zero. Please check equation (21a) on page 169 and make sure that you know the origin of K and lower case k, and how they relate to the physical properties of the system. Also check the chapter 7 handout as that contained several pretty slides that might be useful when studying the Kronig-Penney method.

The Kronig Penney model can be used to calculate the band-structure of a periodic crystal. The figure below shows two representations of the band structure calculated with the Kronig-Penney model: the extended zone scheme (black) and the reduced zone scheme (red). The extended zone scheme is a single valued function that stretches from minus infinity to infinity. Along the x-axis is the wave-vector (associated with the momentum but not quite the momentum) and along the y-axis is the energy of the electron. The extended zone scheme shows the k and E combinations of stationary states. The figure shows that there are energy values for which no stationary states exists. The figure also shows the reduced zone scheme. For the reduced zone scheme one plots the k-ε dispersion only for the first Brillouin zone. Parts of the extended zone scheme that fall outside the first Brillouin zone are shifted over one or more reciprocal lattice vectors so their dispersion curve is depicted in the first Brillouin zone. Note that for the reduced zone scheme the dispersion is no longer a single valued function. We use the reduced zone scheme to simplify allowed transitions. An electron that jumps vertically in the reduced zone scheme diagram has the same crystal momentum in the initial and final state. Please see also the discussion below that summarizes wave-vector conservation rules discussed in the first 7 chapters of the book.

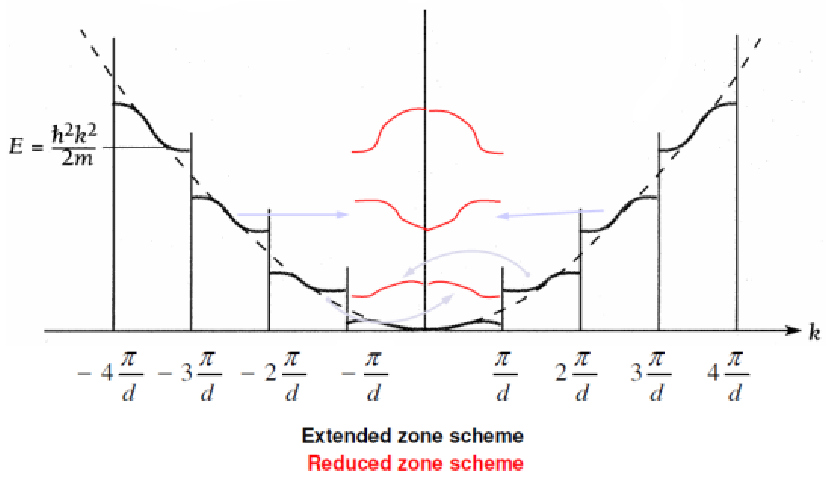


Fig. 6: Extended zone scheme for dispersion relation of free electron (black dashed) and nearly free electron (black solid); Reduced zone scheme for nearly free electron model is sketched in solid red.

Earlier in the book we have noticed that in a periodic lattice the momentum conservation rules can be written as wave vector conservation rules involving the reciprocal lattice vectors:

1. The diffraction condition of electrons, neutrons, or x-ray photons of a periodic crystal could be written as (chapter 2, page 31):

   $$\vec{k}' - \vec{k} = \vec{G} \qquad [20]$$

   Where **k'** is the wave-vector of the scattered particles, **k** the wave-vector of the incident particles and **G** a reciprocal lattice vector. Multiplying both sides of the equation by h bar will result in:

   $$\hbar\vec{k}' - \hbar\vec{k} = \hbar\vec{G} \qquad [21]$$

   Note that the left side is the change off momentum of the incident particles upon diffraction, so the right part should be the recoil of the total crystal. Note also that if the diffraction condition is not met, there will not be a diffracted beam and there is no change of momentum between k' and k as incident wave is not diffracted.

2. Also electrons in the material have to obey equation [20] upon scattering. As the left part of equation [21] is the crystal momentum change of the scattered electron, the right part of equation [22] can be considered to be the momentum change of the rest of the material, i.e. all other electrons and the ion-lattice. Equation [20] is often referred to as the wave-vector selection rule (see also Kittel page 100). Note that when a phonon is involved in the scattering and is absorbed that then the wave-vector selection rule will become:

   $$\vec{k}' = \vec{k} + \vec{G} - \vec{K} \qquad [22]$$

   Where **k'** is the wave-vector of the scattered electron, **k** is the wave-vector of the incident electron, **G** is a reciprocal lattice vector, and **K** is the wave-vector of the absorbed phonon. Reorganizing equation [22] and multiplying by h bar gives:

   $$\hbar\vec{k}' - \hbar\vec{k} = \hbar\vec{G} - \hbar\vec{K} = \hbar\left(\vec{G} - \vec{K}\right) \qquad [23]$$

   The left part of equation [23] is the crystal momentum change of the electron. The right part is the crystal momentum change of all other electrons and the positive ion cores. The phonon can be considered to change the periodicity of the lattice and thus the effective reciprocal lattice vector: so we can consider equation [23] as a diffraction condition similar to equation [20]. Kittel emphasizes that a phonon does not carry physical linear momentum, which is thus different from photons, electrons, and neutrons. The factor $\hbar K$ is referred to as the crystal momentum on the phonon.

3. When two phonons collide and are converted to a single phonon the created phonon has a wave-vector equal to the wave-vector of the two initial phonons (page 123 of Kittel), i.e.

$$\vec{K}_1 + \vec{K}_2 = \vec{K}_3 \qquad [24]$$

We saw that anharmonic effects can cause interaction between two phonons. But also crystal defects can mediate interaction between phonons. Kittel did not proof this equation, it was just presented. It says that crystal momentum is conserved with two phonons interact. Note that phonon modes beyond the first Brillouin zone boundary are identical to modes in the first Brillouin zone. So if $\mathbf{K_1}$+$\mathbf{K_2}$ is in the 2nd Brillouin zone, we can subtract a reciprocal lattice vector to find the identical mode in the first Brillouin zone (see also discussion on page 93 and 94 of Kittel). So:

$$\vec{K}_1 + \vec{K}_2 = \vec{K}_3 + \vec{G} \qquad [25]$$

We referred to this as an umklapp process.

4. In chapter 6 umklapp processes were also introduced for electron phonon interaction to better understand electrical conductivity. See Figure 13 on page 152. Assuming that an electron with a wave-vector **k** absorbs a phonon with a wave-vector **q**. The wave-vector of the scattered electron should be equal to:

$$\vec{k}' = \vec{k} + \vec{q} \qquad [26]$$

If **k'** is situated in the first Brillouin zone we speak of a normal process. If **k'** is situated in k-space beyond the zone boundaries we can consider it to be scattered from a phonon with wave-vector **q**+**G**:

$$\vec{k}' = \vec{k} + \vec{q} + \vec{G} \qquad [27]$$

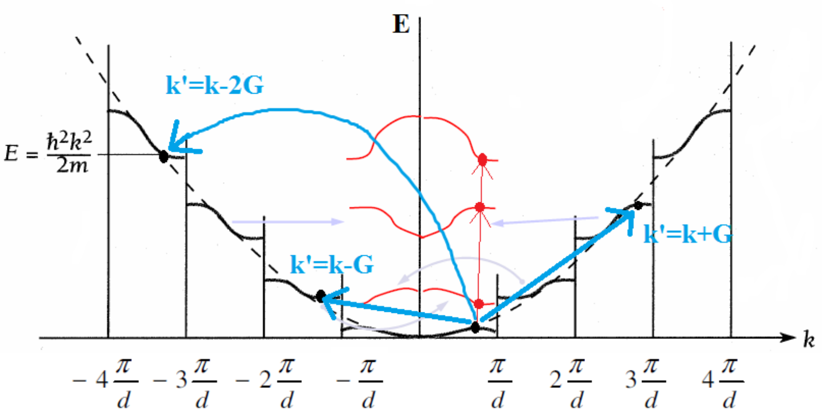
We referred to such process as an umklapp process since direction of **k'** is kind of opposite to **k** (see also Fig. 13 on page 152).

So summarizing, we found that for the interaction of electrons, phonons, and photons in a periodic crystal, wave-vector conservation rules exists: see for example equations [5], [7], and [10] provided above. Note that for a free electron the wave-vector is proportional to the momentum of the electron, so wave-vector conservation rules are similar to momentum conservation rules. So when particles interact in a periodic crystal:

1. Conservation of energy is still valid, so the total energy of the particles before the collision should be equal to the total energy of the particles after the collision.
2. Conservation of momentum is replaced by wave-vector conservation laws involving the reciprocal lattice vector.

The figure below shows a transition that occurs when a conduction electron in a crystal absorbs a photon. Both conservation rules listed above apply. Although photons carry momentum, the momentum of a photon is so small that it can normally be ignored. Considering the conservation rules cited above, after absorption I expect the excited electron to have an energy equal to the sum of its original energy and the energy of the photon. I also expect that “momentum” conservation is obeyed and that the excited electron has a wave-vector that is equal to the wave-vector of the unexcited electron plus or minus a reciprocal lattice vector (see equation [5] above). So only if an unoccupied state exists with that particular energy and that particular wave-vector, the electron can absorb the photon. The figure below shows the transitions for the extended zone scheme (blue arrows) and the transitions for the reduced zone scheme (red). Plotting the dispersion relations in the reduced zone scheme will simplify the indication of transitions that do not involve momentum change. For example the absorption of a photon by an electron will not significantly change the k-vector of the electron as the photon has such small momentum compared to the electron. So these transitions are indicated by vertical lines in the reduced zone scheme.

Note that in most electronics textbooks the k-dependence of the energy is omitted and the band-diagram shows only the available stationary energy state but now as a function of the position in the device (see the plots of Fig. 1 of chapter 7).



Extended zone scheme
Reduced zone scheme

Fig. 7: Allowed transitions for absorption of a photon in extended zone scheme (blue arrows) and reduced zone scheme (red arrows).