# Condensed Matter Physics I

Prof. Dr. Ir. Paul H.M. van Loosdrecht

II Physikalisches Institut, Room 312

E-mail: pvl@ph2.uni-koeln.de

Website: http:/www.loosdrecht.net/

# Previously

- Free electron model
- Density of states, Fermi-Dirac distribution
- Pressure, Bulk modulus, Heat capacity, Thermal mass
- Charge conductivity

# Today

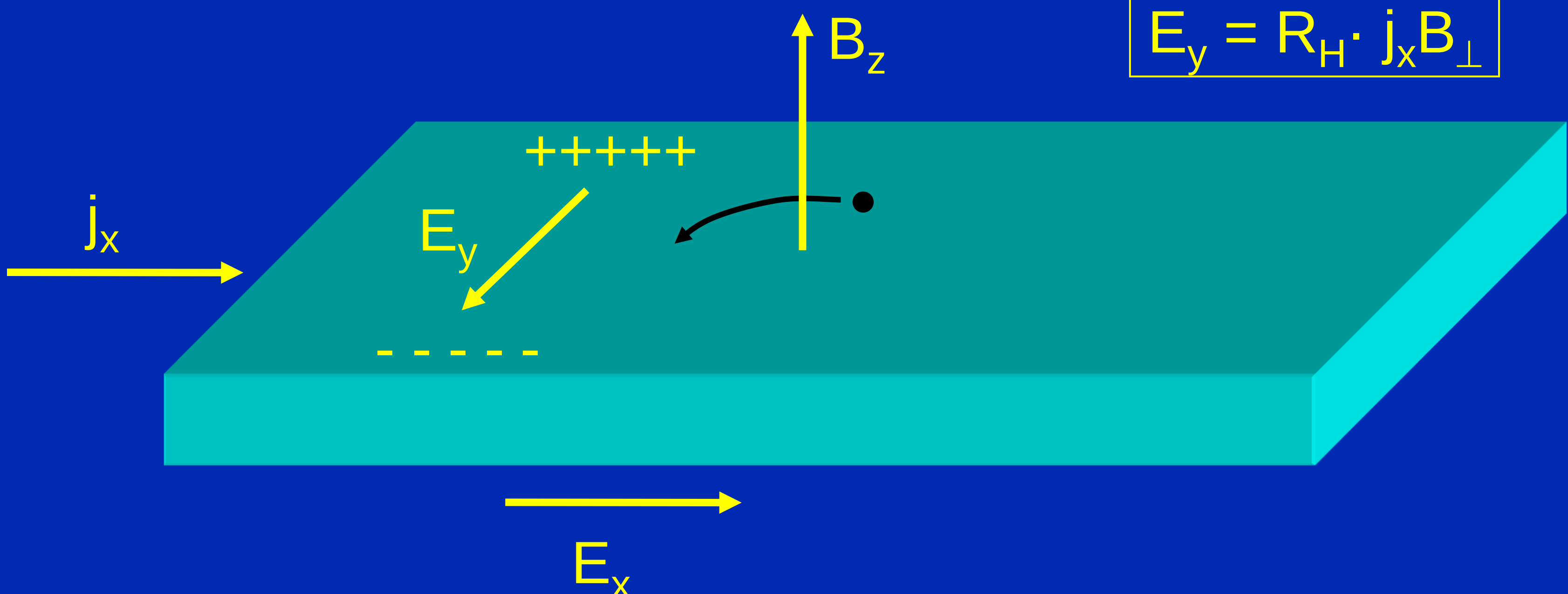
- Transport
- Failures of the free electron model
- Incorporating periodicity

# Classical Hall effect

Transport equation: $\hbar\left(\frac{d}{dt}+\frac{1}{\tau}\right)k = F = q\left(E+\frac{k}{m}\times B\right)$

Steady state: $\hbar\vec{k} = -e\tau\left(\vec{E}+\frac{\hbar}{m}\vec{k}\times\vec{B}\right)$

$E_y = R_H \cdot j_x B_\perp$



# Thermal conductivity

$$J = -K \cdot \nabla T$$

Electronic heat conductivity: $K = \frac{1}{3} C_{el} \cdot v \cdot \ell = \frac{\pi^2 k_B{}^2 n\tau}{3m} T$

Wiedemann-Franz law: $\frac{K}{\sigma} = L \cdot T$

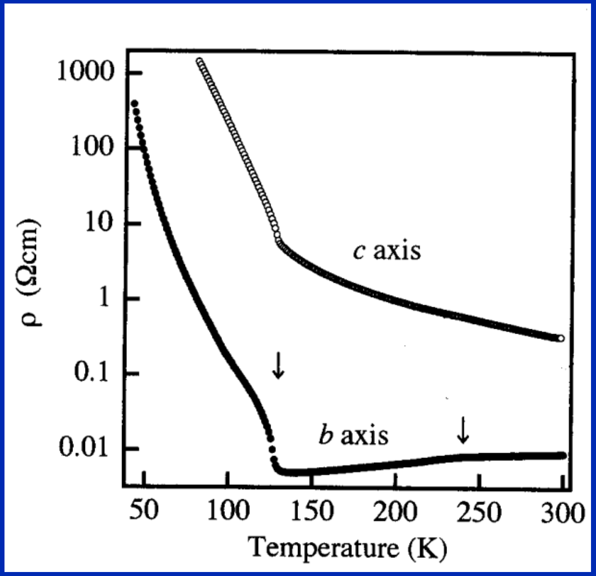
L: Lorenz number = 2.45 $10^{-8}$ W$\Omega$/$K^2$

**Table 10-2** Lorentz number $L = K/\sigma T$ in units of $10^{-8}$ W$\cdot\Omega$/$K^2$, for several metals at 0°C and 100°C

| Metal | 0°C | 100°C | Metal | 0°C | 100°C |
|---|---|---|---|---|---|
| Ag | 2.31 | 2.37 | Pb | 2.47 | 2.56 |
| Au | 2.35 | 2.40 | Pt | 2.51 | 2.60 |
| Cd | 2.42 | 2.43 | Sn | 2.52 | 2.49 |
| Cu | 2.23 | 2.33 | W | 3.04 | 3.20 |
| Mo | 2.61 | 2.79 | Zn | 2.31 | 2.33 |

# Free electron model: failures

- Hall coefficient
- Magnetoresistance
- Wiedemann-Franz law
- T-dependence of conductivity
- Direction dependence of conductivity →
- AC conductivity
- Linear term in specific heat
- Compressibility of metals




$NaV_6O_{15}$

Yamada,Ueda JPSJ **68,** 2735 (1999)

- What determines the electron density
- Why are some materials bad metals or even isolators

# $e^-$ in a periodic potential

- Bragg scattering of free electrons, gaps
- Effect of translational symmetry, Bloch theorem
- Reduced Brillouin zone, Energy bands
- Weak potentials, perturbation theory
- Photo emission

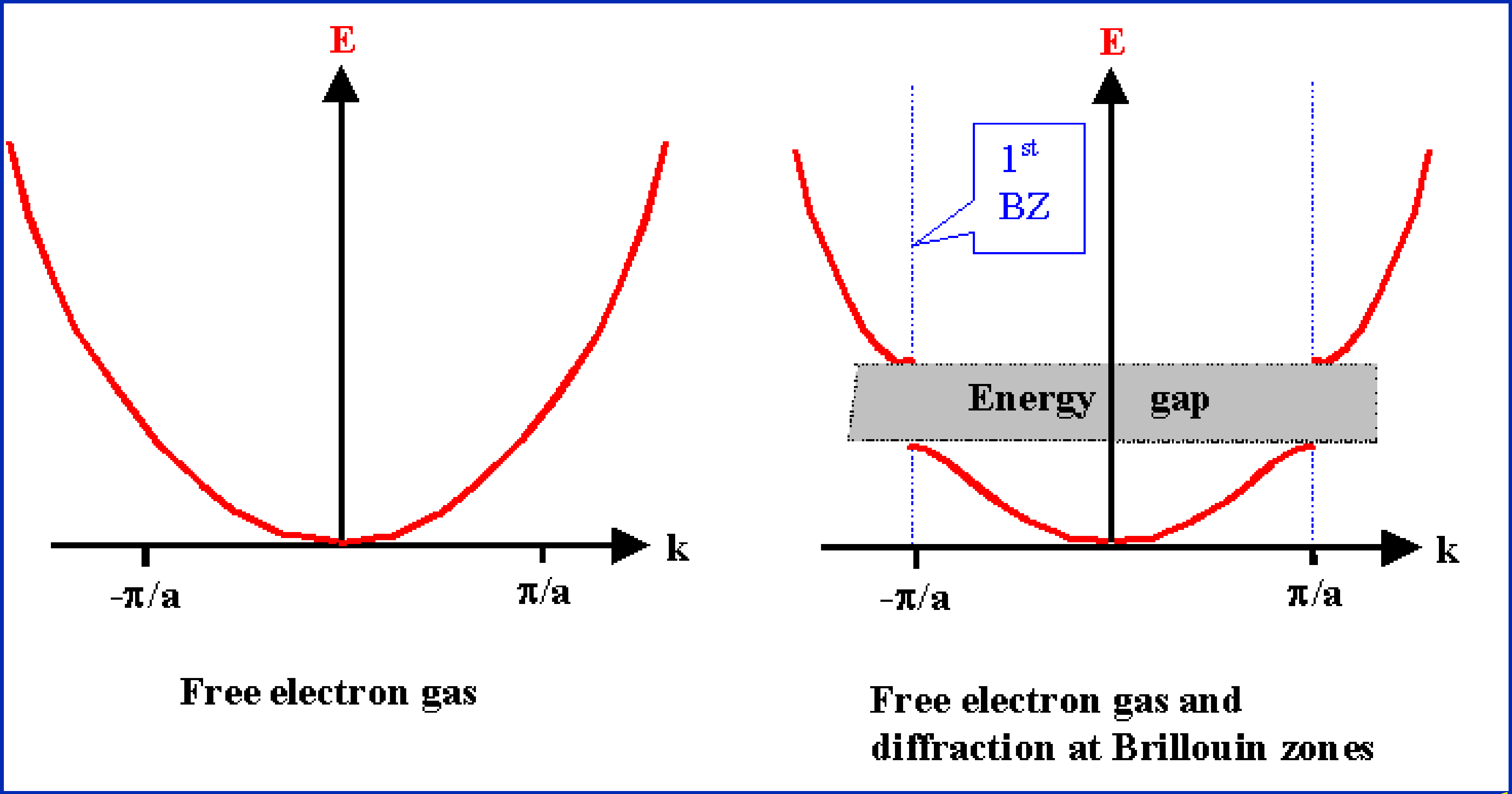
# Incorporating the periodic potential

$$V(\vec{r}) = V(\vec{r} + \vec{R}_{\vec{n}}) \qquad \vec{R}_{\vec{n}} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$$

$$\left( \frac{-\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right) \Psi_\lambda = E_\lambda \Psi_\lambda$$

- Empty lattice
- Weak potential ( nearly free electron model, perturbation )
- Strong potential ( tight binding (LCAO) )

# Bragg scattering



# TRANSLATIONAL SYMMETRY

*When I started to think about it, I felt that the main problem was to explain how the electrons could sneak by all the ions in a metal….
By straight Fourier analysis I found to my delight that the wave differed from the plane wave of free electrons only by a periodic modulation*

*F. BLOCH*

# Translational symmetry

$$V(\vec{r}) = V(\vec{r} + \vec{R}_{\vec{n}}) \qquad \vec{R}_{\vec{n}} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$$

$$\left(\frac{-\hbar^2}{2m}\nabla^2 + V(\vec{r})\right)\Psi_\lambda = E_\lambda \Psi_\lambda$$

Translation operator: $T_{\vec{n}}\psi(\vec{r}) \equiv \psi(\vec{r} + \vec{R}_{\vec{n}})$

Translationally invariant Hamiltonian: $\left[H, T_{\vec{n}}\right] = 0$

$$T_{\vec{n}} \cdot H\Psi_\lambda = H \cdot T_{\vec{n}}\Psi_\lambda = E_\lambda\ T_{\vec{n}}\Psi_\lambda$$

$\Longrightarrow$ If $\Psi_\lambda$ is an eigenstate with energy $E_\lambda$, so is $T_{\vec{n}}\Psi_\lambda$ !

# Bloch theorem

$$T_{100}|\psi_\lambda\rangle = e^{i\phi_{\lambda,1}}|\psi_\lambda\rangle \qquad T_{200}|\psi_\lambda\rangle = e^{i\phi_{\lambda,1}}e^{i\phi_{\lambda,1}}|\psi_\lambda\rangle \; ....$$

$$\Rightarrow T_{nml}|\psi_\lambda\rangle = e^{i(n\phi_{\lambda,1}+m\phi_{\lambda,2}+l\phi_{\lambda,3})}|\psi_\lambda\rangle = e^{i(n\vec{a}_1+m\vec{a}_2+l\vec{a}_3)\cdot\vec{k}}|\psi_\lambda\rangle$$

The vectors *k* label the eigenstates: $|\psi_\lambda\rangle = |\psi_{\vec{k}}\rangle$

<u>Bloch Theorem (form II)</u>

$$T_{\vec{n}}\Psi_{\vec{k}}(\vec{r}) = \Psi_{\vec{k}}(\vec{r}+\vec{R}_{\vec{n}}) = e^{i\vec{k}\cdot\vec{R}_{\vec{n}}}\Psi_{\vec{k}}(\vec{r})$$

# Bloch theorem

<u>Bloch Theorem</u>

$$\Psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}u_{\vec{k}}(\vec{r})$$

$$u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r}+\vec{R})$$

*The eigenstates of a periodic one-electron Hamiltonian can be chosen to have the form of a plane wave times a function with the periodicity of the Hamiltonian*

Bloch: $\Psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r})$

$$u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r} + \vec{R})$$

The functions $u_{\vec{k}}(\vec{r})$ are translational invariant

$\Rightarrow$ 3D fourier expansion of a periodic function

$$u_{\vec{k}}(\vec{r}) = \sum_{\vec{G}} \tilde{u}_{\vec{k},\vec{G}} e^{i\vec{G}\cdot\vec{r}}$$

$$\Rightarrow \boxed{\Psi_{\vec{k}}(\vec{r}) = \sum_{\vec{G}} \tilde{u}_{\vec{k},\vec{G}} \cdot e^{i(\vec{k}+\vec{G})\cdot\vec{r}}}$$

# Electrons in a periodic potential

$$H = \frac{-\hbar^2}{2m}\nabla^2 + V(\vec{r})$$

$$V(\vec{r}) = \sum_{\vec{G}} V_{\vec{G}} e^{i\vec{G}\cdot\vec{r}}$$

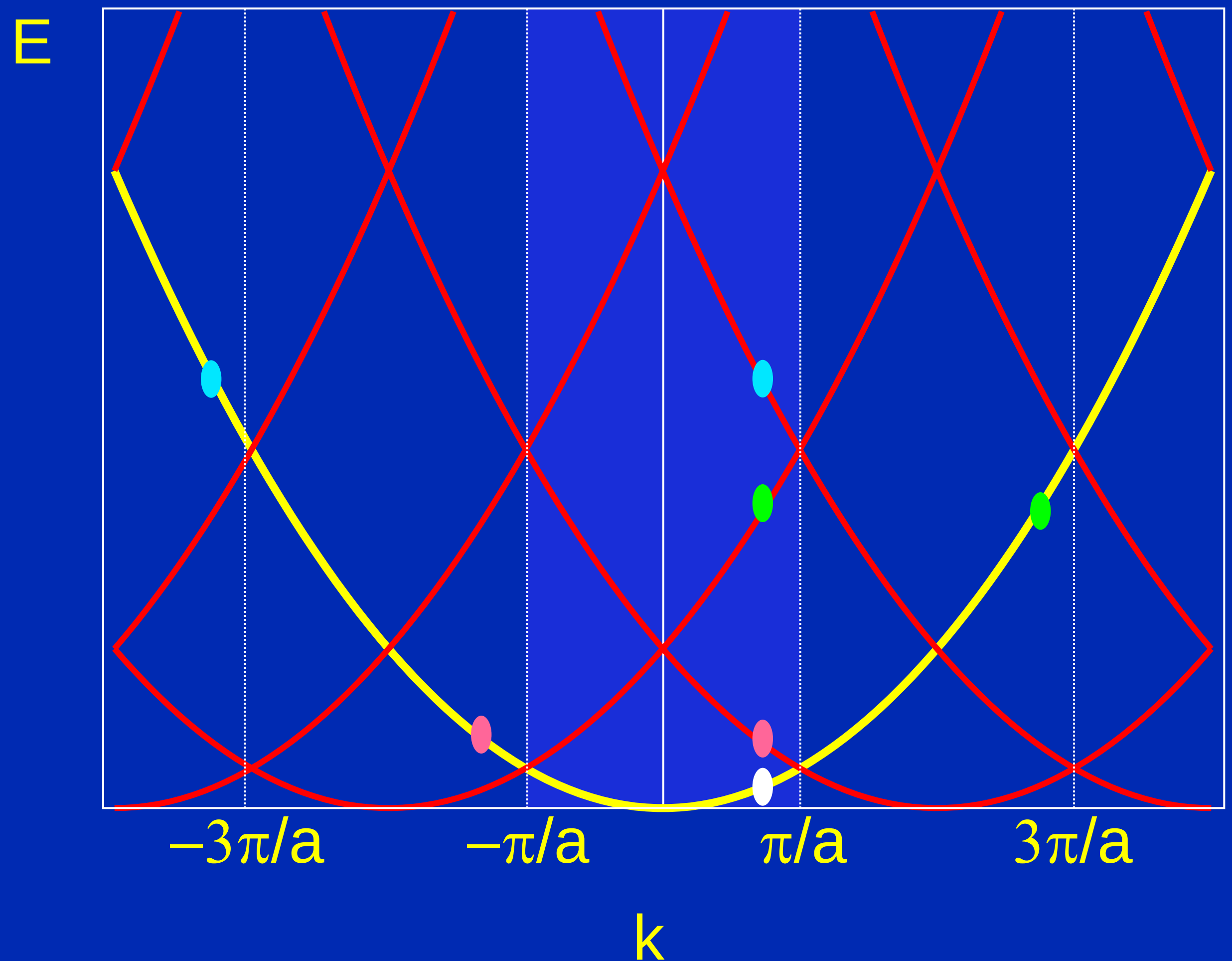
$$\Rightarrow \langle \vec{q} | H | \vec{k} \rangle = \frac{\hbar^2 k^2}{2m}\delta_{\vec{q},\vec{k}} + \sum_{\vec{G}} V_{\vec{G}} \delta_{\vec{q},\vec{k}+\vec{G}}$$

Each free $e^-$ state k couples to all states k+G !

Eigenstates $$|\psi_{\vec{k}}\rangle = \sum_{\vec{G}} \alpha_{\vec{G}} |\vec{k}+\vec{G}\rangle$$

Energies $$E_{\vec{k}} = \frac{\hbar^2}{2m}\sum_{\vec{G}} |\alpha_{\vec{G}}|^2 |\vec{k}+\vec{G}|^2 + \sum_{\vec{G},\vec{Q}} \alpha_{\vec{G}}\alpha^*_{\vec{Q}} V_{\vec{Q}-\vec{G}}$$

# Reduced Brillouin zone



# Perturbation theory

$$\left|\psi_k\right\rangle = \frac{1}{C}\left\{\left|\vec{k}\right\rangle + \sum_{\vec{G}\neq 0} \frac{V_{\vec{G}}}{E_{\vec{k}}^{(0)} - E_{\vec{k}+\vec{G}}^{(0)}} \left|\vec{k}+\vec{G}\right\rangle\right\}$$

$$\left|C\right|^2 = 1 + \sum_{\vec{G}\neq 0} \left|\frac{V_{\vec{G}}}{E_{\vec{k}}^{(0)} - E_{\vec{k}+\vec{G}}^{(0)}}\right|^2$$

$$\left|C\right|^2 E_{\vec{k}} = E_{\vec{k}}^{(0)} + V_{\vec{0}} + \sum_{\vec{G}\neq 0} \frac{\left|V_{\vec{G}}\right|^2}{E_{\vec{k}}^{(0)} - E_{\vec{k}+\vec{G}}^{(0)}}$$

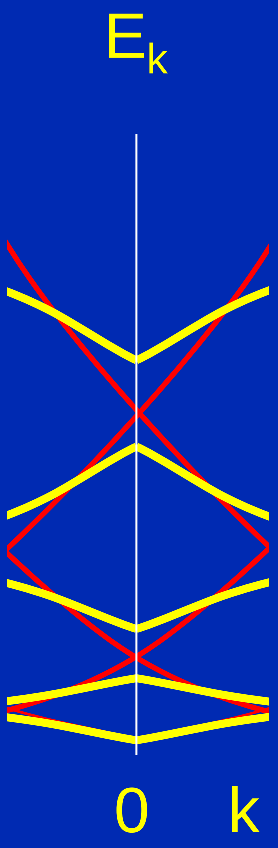
Large contribution when $E^0{}_k \approx E^0{}_{k+G}$

# Near zone boundary

$$|\psi_k\rangle \approx a_0\left|\vec{k}\right\rangle + a_{\vec{b}}\left|\vec{k}+\vec{b}\right\rangle$$

$$H \approx \begin{bmatrix} E_k^{(0)} & V_{\vec{b}} \\ V_{\vec{b}} & E_{k+\vec{b}}^{(0)} \end{bmatrix}$$

$$\Rightarrow E_k = \frac{1}{2}\left[E_k^{(0)} + E_{k+\vec{b}}^{(0)}\right] \pm \frac{1}{2}\sqrt{\left(E_k^{(0)} - E_{k+\vec{b}}^{(0)}\right)^2 + 4V_b^2}$$




If $E^0_k = E^0_{k+b} \;\rightarrow\; E_k = E^0_k \pm V_b$

# Band structure: Approaches

- Empty lattice (only periodicity)
- Perturbation theory (nearly free electrons, weak potential)
- Tight binding method (LCAO)
- Exact models (Kronig-Penney model, see for instance Kittel)
- 'advanced' methods: see for instance
  ashcroft and mermin, chapter 11