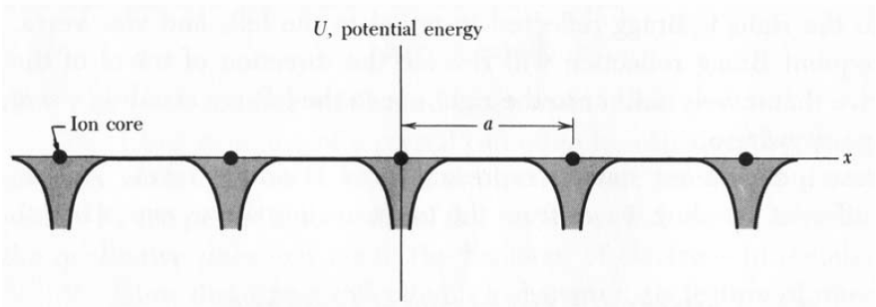
4. Electrons in a solid

Effective one-electron potential



$$U(\vec{r}+\vec{R}) = U(\vec{r})$$

4.1. Bloch - Theorem

Translational symmetry

$$\hat{H}(\vec{r}+\vec{R}) = \hat{H}(\vec{r})$$

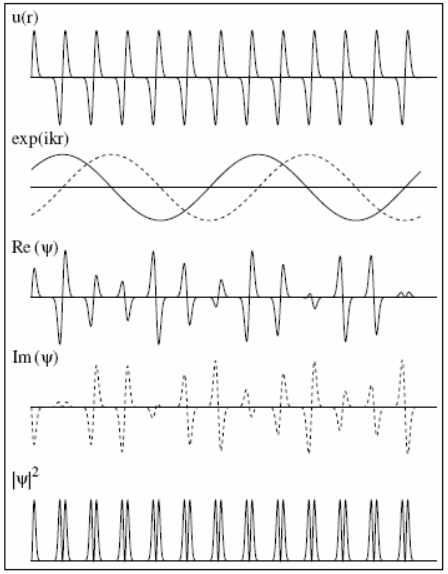
yields Bloch-wave:

$$\Psi(\vec{r}+\vec{R}) = e^{i\vec{k}\vec{R}}\Psi(\vec{r})$$

and therefore:

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

$$\Psi_{\vec{k}+\vec{G}}(\vec{r}) = \Psi_{\vec{k}}(\vec{r})$$
$$E_{\vec{k}+\vec{G}} = E_{\vec{k}}$$



4.2. Free-electron gas

Energy $E = \frac{\hbar^2\vec{k}^2}{2m^*}$

Density $n = \frac{1}{(2\pi)^3}\cdot 2\cdot\int_0^{k_F} 4\pi k^2 dk$

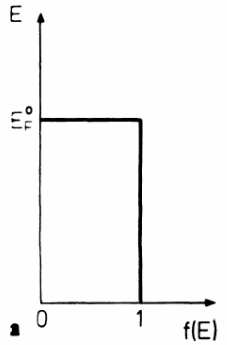
Density of states $D(E) = \frac{1}{2\pi^2}(\frac{\hbar^2}{2m^*})^{2/3}\sqrt{E}$

Fermi-Wellenvektor	$k_F = \sqrt[3]{3\pi^2 n}$	1.75 Å^{-1}
Fermi-Geschwindigkeit	$v_F = \hbar k_F/m$	$0.0068\ c = 2\cdot 10^6$ m/s
Fermi-Energie	$E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m}(3\pi^2 n)^{2/3}$	11.7 eV
Zustandsdichte bei E_F	$D(E_F) = \frac{3}{2}n(E_F)/E_F$	0.38 (eV·Atom)$^{-1}$
Energiedichte	$u = \frac{\hbar^2}{2m}\frac{k_F^5}{5\pi^2} = \frac{3}{5}nE_F$	$2.01\cdot 10^{11}$ J/m^3
Mittlere Energie	$u/n = \frac{3}{5}E_F$	7 eV
Druck	$p = -\frac{\partial E}{\partial V}\vert_N = \frac{2}{3}u$	$1.34\cdot 10^{11}$ Pa
Kompressionsmodul	$\kappa = -V\frac{\partial p}{\partial V} = \frac{5}{3}p$	$2.24\cdot 10^{11}$ Pa

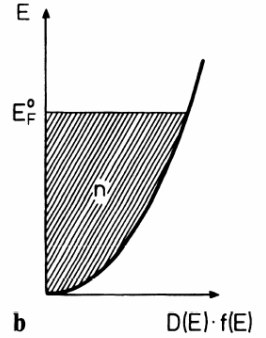
Zahlenwerte: Aluminium mit drei Valenzelektronen $n = \frac{3}{a^3/4}$, $a = 4.05$ Å

4.2. Density of states

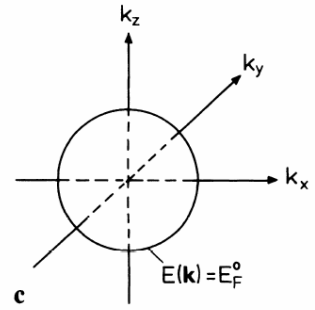
Density of states $D(E) = \frac{1}{2\pi^2}(\frac{\hbar^2}{2m^*})^{2/3}\sqrt{E}$



$T = 0$ K



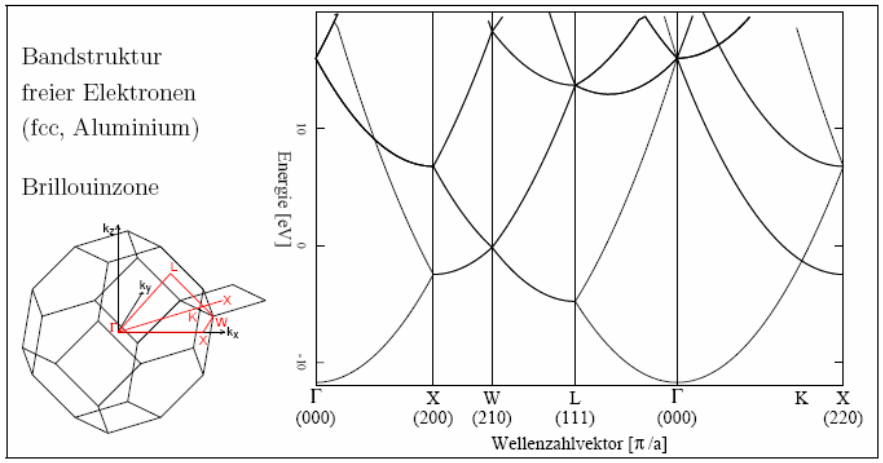
$\propto \sqrt{E}$



Fermi sphere

4.2. Dispersion relation - bandstructure

Energy $E(\vec{k}) = \frac{\hbar^2 \vec{k}^2}{2m^*}$ $\qquad E_{\vec{k}} = E_{\vec{k}+\vec{G}}$

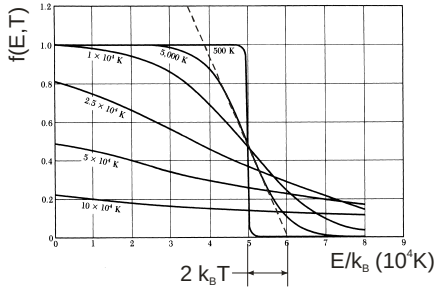


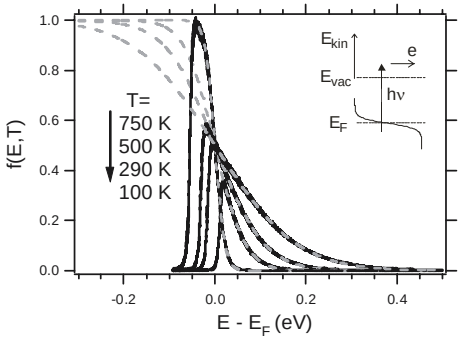
4.3. Fermi distribution-function

$$f(E,T) = \frac{1}{e^{\frac{E-\mu}{k_B T}} + 1}$$

width $\approx 4 k_B T$

$f(E_F, T) = \frac{1}{2}$





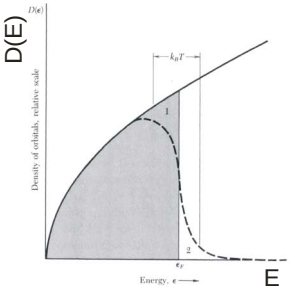
4.4. Specific heat

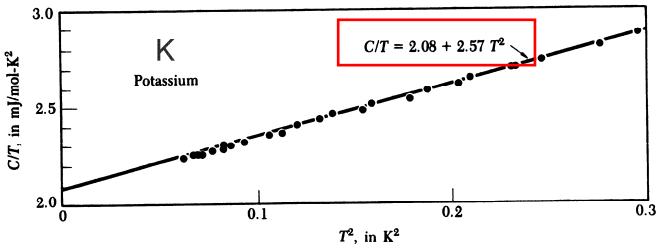
$c_v = c_v^{el} + c_v^{lattice}$

$c_v^{el} = \frac{\pi^2}{3} k_B^2 \cdot D(E_F) \cdot T$

at 300 K: $c_v^{lattice} \approx 1000 \cdot c_v^{el}$

at 10 K: $c_v = \gamma T + \beta T^3$

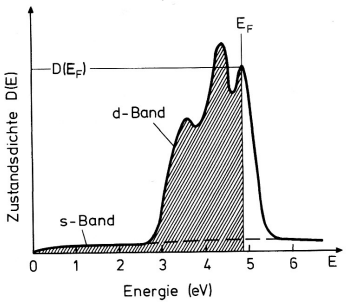




4.4. Specific heat

$$c_v^{el,free} = \frac{\pi^2}{2} k_B^2 \cdot \frac{n}{E_F} \cdot T = \gamma_{theoret.} \cdot T$$

Metall	$\gamma_{exp.}\left(10^{-3}\frac{J}{Mol\,K^2}\right)$	$\gamma_{exp.}/\gamma_{theoret.}$
Li	1.7	2.3
Na	1.7	1.5
K	2.0	1.1
Cu	0.69	1.37
Ag	0.66	1.02
Al	1.35	1.6
Fe	4.98	10.0
Co	4.98	10.3
Ni	7.02	15.3



heavy fermions (e.g. $CeAl_3$): $m_{th} \approx 100 - 1000 \cdot m_e$

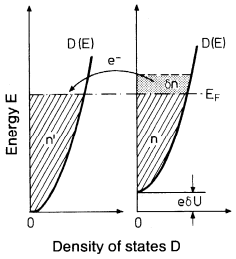
4.5. Electrostatic Screening

for slowly varying potential δU:

$$\delta n = D(E_F) \cdot e\delta U$$

Poisson equation:

$$\nabla^2 \delta U = -\frac{\rho}{\epsilon_0} = \frac{|e|\ \delta n}{\epsilon_0}$$

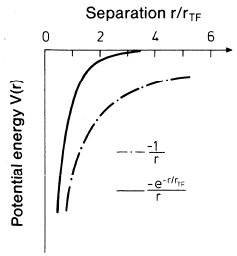


Solution:

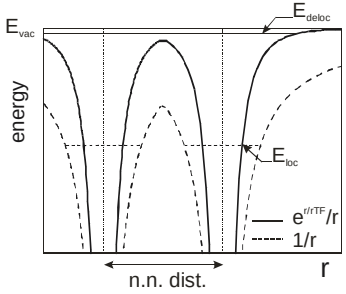
$$\delta U = \frac{e^{-r/r_{TF}}}{r}$$

whereby Thomas-Fermi screening length:

$$r_{TF} = \sqrt{\frac{\epsilon_0}{e^2 D(E_F)}}$$



4.5. Mott insulator

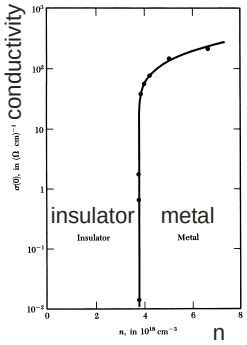


In a shallow potential the number of bound states decreases

$$r_{TF} \propto D(E_F)^{-1/2} \propto n^{-1/2}$$

increase of n ⇒ decrease of r_{TF} ⇒ free electrons

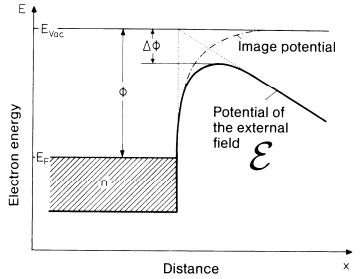
Mott transition: insulator ⇒ metal



4.5. Thermionic emission

$$j = \frac{4\pi me}{h^3}(kT)^2 e^{-\Phi/kT}$$

$$\Phi = \Phi - \sqrt{\frac{e^3\mathcal{E}}{4\pi\epsilon_0}}$$



Work function

Table 6.3. Work functions of elements in eV (polycrystalline samples, after Michaelson [6.5])

Li	Be											B	C		
2.9	4.98											4.45	5.0		
Na	Mg											Al	Si	P	S
2.75	3.66											4.28	4.85	–	–
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
2.30	2.87	3.5	4.33	4.3	4.5	4.1	4.5	5.0	5.15	4.65	4.33	4.2	5.0	3.75	5.9
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
2.16	2.59	3.1	4.05	4.3	4.6	–	4.71	4.98	5.12	4.26	4.22	4.12	4.42	4.55	4.95
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po
2.14	2.7	3.5	3.9	4.25	4.55	4.96	4.83	5.27	5.65	5.1	4.49	3.84	4.25	4.22	–

4.6. Nearly free electrons

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

periodisch: $V(\vec{r}) = V(\vec{r} + \vec{R}) \Rightarrow \vec{G} \cdot \vec{R} = 2\pi n$

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

Potential: $u_{\vec{k}}(\vec{r}) = \sum_{\vec{G}} u_{\vec{G}} e^{i\vec{G}\vec{r}}$

periodisch: $u(\vec{r}) = u(\vec{r} + \vec{R}) \Rightarrow \vec{G} \cdot \vec{R} = 2\pi n$

4.6. Nearly free electrons

Schrödinger: $[\frac{\hbar^2}{2m}\nabla^2 - E + V(\vec{r})]\Psi(\vec{r}) = 0$

...

$$[\frac{\hbar^2}{2m}(\vec{k}+\vec{G})^2 - E]u_{\vec{G}} + \Sigma_{\vec{G}'} V_{\vec{G}'} u_{\vec{G}'} = 0$$

Zweibandnäherung:

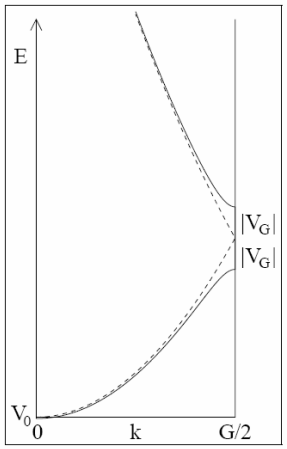
$$\begin{pmatrix} \frac{\hbar^2(\vec{k}+\vec{G}_1)^2}{2m} - E + V_0 & V_{\vec{G}_1-\vec{G}_2} \\ V_{\vec{G}_1-\vec{G}_2} & \frac{\hbar^2(\vec{k}+\vec{G}_2)^2}{2m} - E + V_0 \end{pmatrix} \begin{pmatrix} u_{\vec{G}_1} \\ u_{\vec{G}_2} \end{pmatrix} = 0$$

$\det(\ ) = 0 \ldots$

4.6. Nearly free electrons

$$E(\underline{k}) = V_0 + \tfrac{1}{2}\tfrac{\hbar^2}{2m}(\underline{k}_1^2 + \underline{k}_2^2) \pm \sqrt{\left[\tfrac{1}{2}\tfrac{\hbar^2}{2m}(\underline{k}_1^2 - \underline{k}_2^2)\right]^2 + \left|V_{\underline{G}_1-\underline{G}_2}\right|^2}.$$

$\underline{k}_1 = \underline{k} + \underline{G}_1 \quad \underline{k}_2 = \underline{k} + \underline{G}_2$



"back-folding": $E(k) = E(k+G)$

$$E(G/2) = V_0 + \frac{\hbar^2}{2m}(G/2)^2 \pm |V_G|$$

$$E(k \neq G/2) \approx V_0 + \frac{\hbar^2}{2m}k^2$$

4.6. Nearly free electrons

Extended zone scheme

Reduced zone scheme

Repeated zone scheme

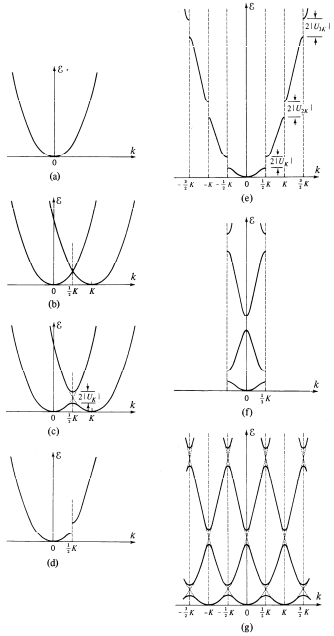


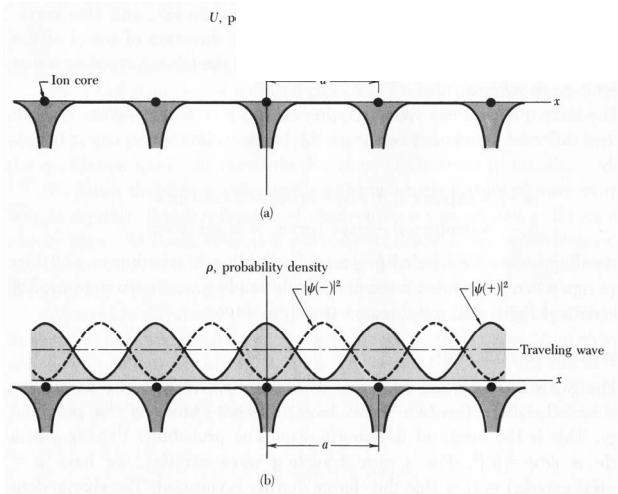
Figure 9.4
(a) The free electron $\mathcal{E}$ vs. k parabola in one dimension. (b) Step 1 in the construction to determine the distortion in the free electron parabola in the neighborhood of a Bragg "plane," due to a weak periodic potential. If the Bragg "plane" is that determined by K, a second free electron parabola is drawn, centered on K. (c) Step 2 in the construction to determine the distortion in the free electron parabola in the neighborhood of a Bragg "plane." The degeneracy of the two parabolas at $K/2$ is split. (d) Those portions of part (c) corresponding to the original free electron parabola given in (a). (e) Effect of all additional Bragg "planes" on the free electron parabola. This particular way of displaying the electronic levels in a periodic potential is known as the *extended-zone scheme*. (f) The levels of (e), displayed in a *reduced-zone scheme*. (g) Free electron levels of (e) or (f) in a *repeated-zone scheme*.

K=2π/a

4.6. Solution at Brillouin zone-boundary

Standing waves: $\Psi_{1/2} = \pm 2u_{g_2} \begin{matrix} i\sin[(\vec{k}+\vec{G}_2)\vec{r}+\varphi/2] \\ \cos[(\vec{k}+\vec{G}_2)\vec{r}+\varphi/2] \end{matrix}$

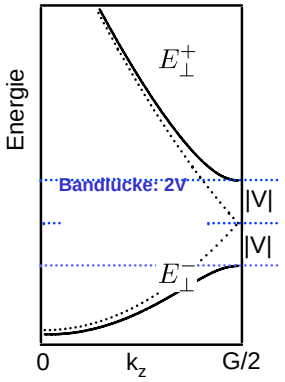
$$e^{i\varphi} = \frac{V_{g_1-g_2}}{|V_{g_1-g_2}|}$$

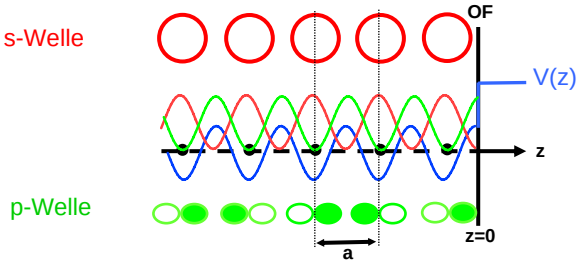


4.6 Standing wave at Brillouin zone-boundary

$$\psi_{\mp}(\vec{r}) \propto e^{i\vec{k}_{\parallel}\vec{r}_{\parallel}} \begin{cases} \cos(\frac{\pi}{a}z + \varphi/2) \\ \sin(\frac{\pi}{a}z + \varphi/2) \end{cases}$$

V reell, $\varphi = 0$

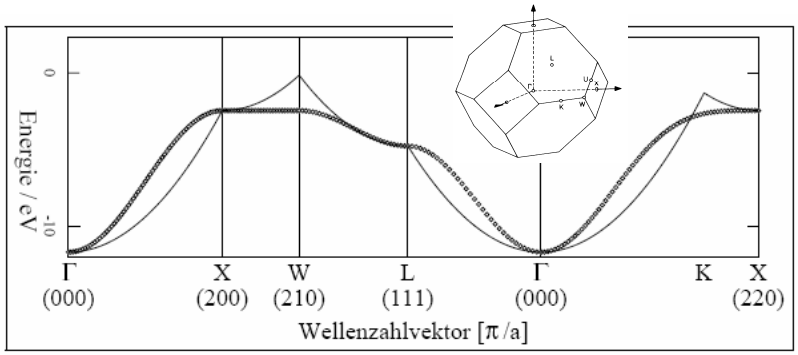




4.7 Tight binding bandstructure

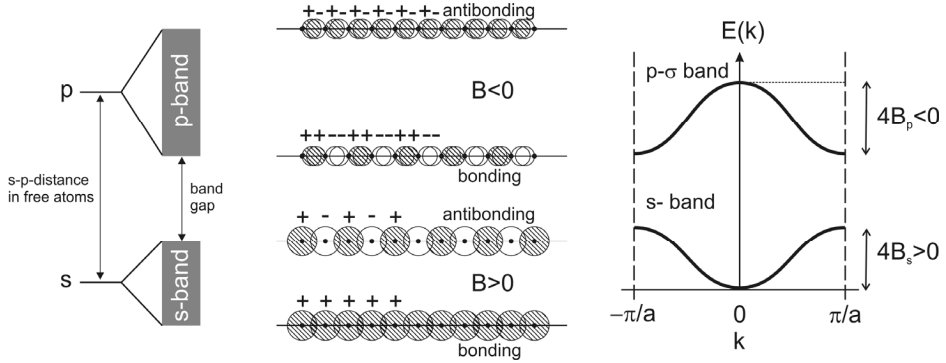
Blochwelle: $\Psi_k(\vec{r}) = \sum_j b_j \sum_{\vec{R}} e^{i\vec{k}\vec{R}} \varphi_j(\vec{r} - \vec{R})$

$$\sum_j [\sum_{\vec{R}} e^{i\vec{k}\vec{R}} \{ \int d^3r \varphi_j^*(\vec{r} - \vec{R}') \, (\frac{\hbar^2}{2m}\nabla^2 - V(\vec{r})) \, \varphi_j(\vec{r} - \vec{R}) - E \int d^3r \varphi_j^*(\vec{r} - \vec{R}') \varphi_j(\vec{r} - \vec{R}) \} \,] \, b_j = 0$$

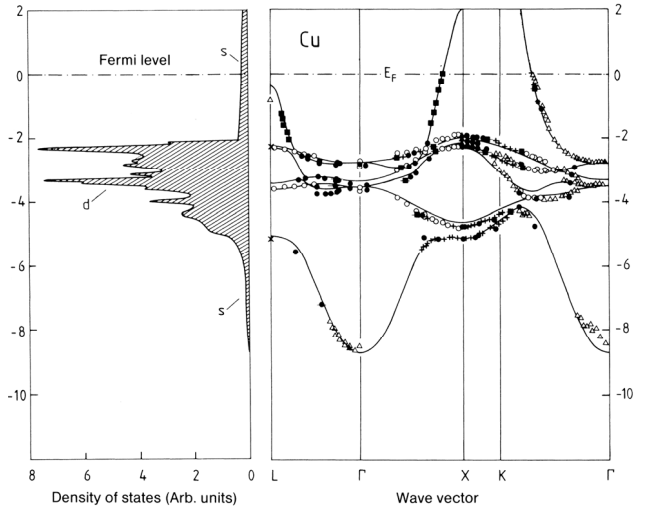


Aluminium-Bandstruktur mit 1 s-artigen, 3 p-artigen und 5 d-artigen Basisfunktionen (j = 1 . . . 9)
nach: D. A. Papaconstantopoulos,
Handbook of the band structure of elemental solids, Plenum Press (New York) 1986.

4.7 s- and p_z- waves

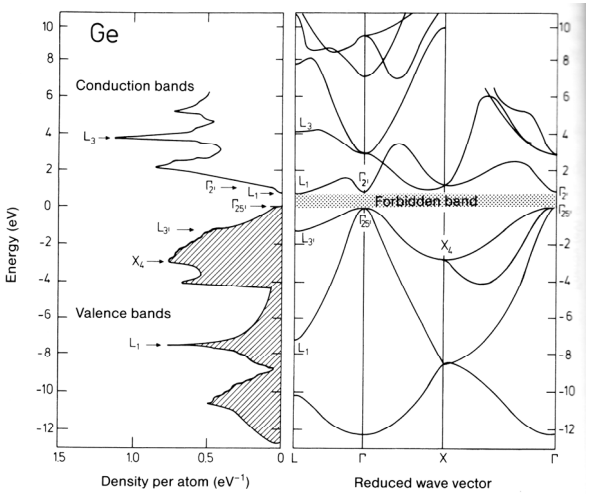


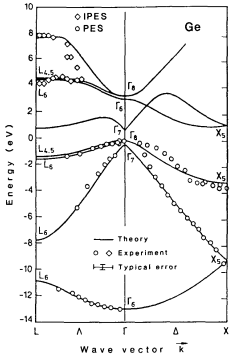
4.8 Examples - metall



Cu, fcc: 3s2 3p6 3d10 4s1, s(p) and d bands, **metal**

4.8 Examples - semiconductor

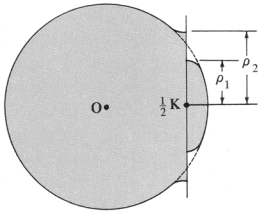


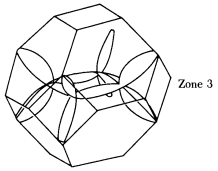


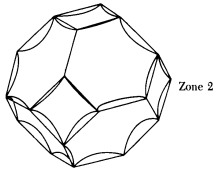
Ge, 4s2 4p2, → sp3 hybridized, absolute band gap, **semiconductor**

4.8 Examples – Fermi surfaces

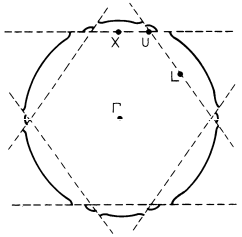
Fermi surfaces

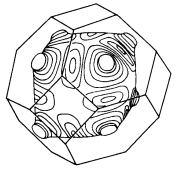


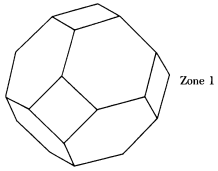




Al

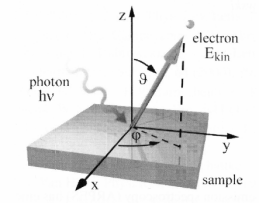



Copper

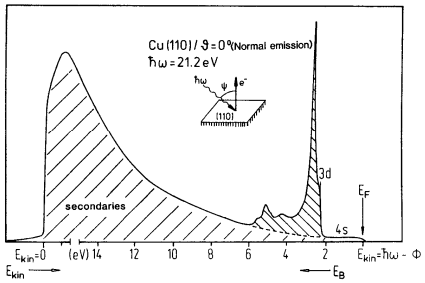


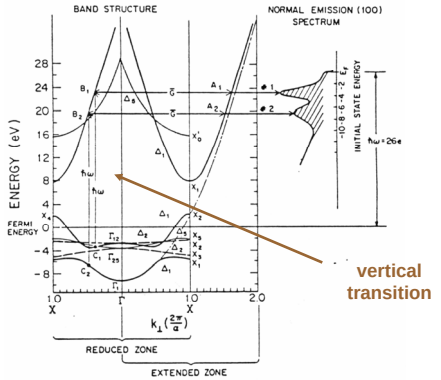
Aluminum

4.8 Occupied states – photoelectron spectroscopy



$$k_{\parallel} = |k| \cdot \sin\vartheta = \frac{\sqrt{2mE_{kin}}}{\hbar}\sin\vartheta = 0.511\sqrt{E_{kin}[\mathrm{eV}]}\sin\vartheta\ [\mathrm{\AA}^{-1}]$$





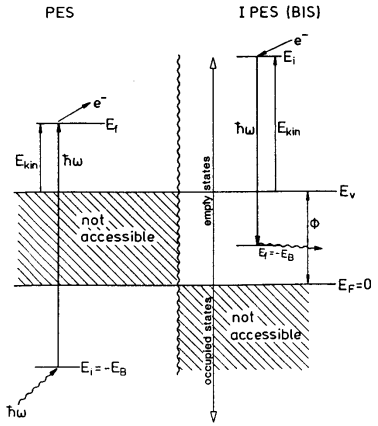
$$E_{kin}(k_{\parallel}, k'_{\perp}) = E_B(k_{\parallel}, ?) + h\nu - \Phi$$

Annahme: freier Endzustand:

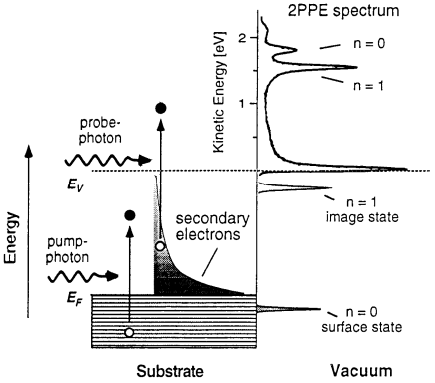
$$k_{\perp} = \sqrt{2m^*(E_{kin} + \Phi - E_0)/\hbar^2 - k_{\parallel}^2}$$

4.8 Unoccupied states

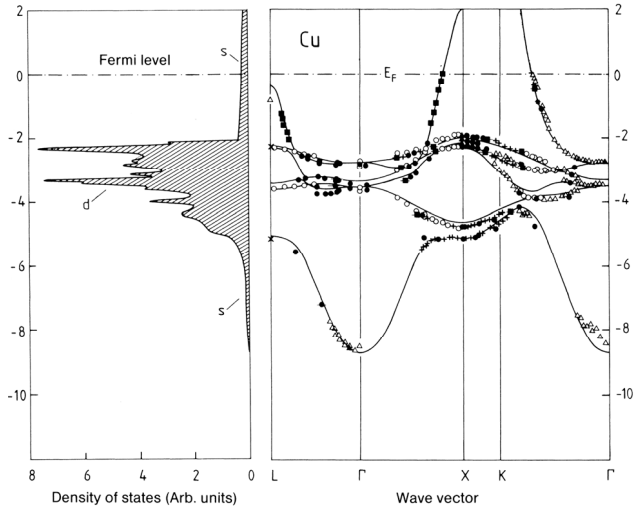
Inverse photoemission (IPES)



Two-photon photoemission (2PPE)

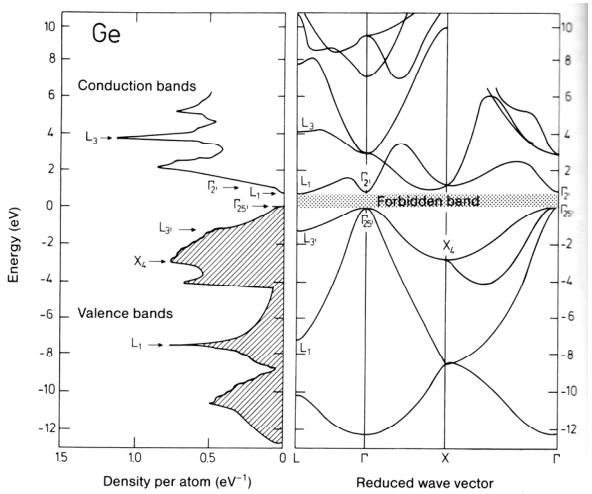


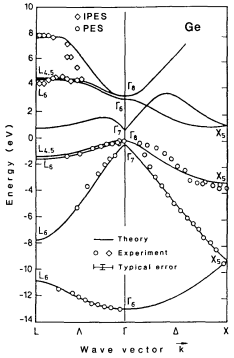
4.8 Examples - metall



Cu, fcc: 3s2 3p6 3d10 4s1, s(p) and d bands, **metal**

4.8 Examples - semiconductor

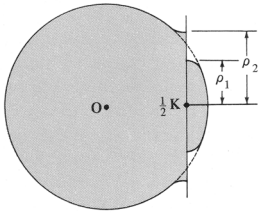


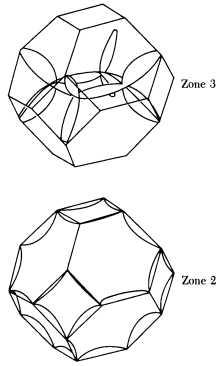


Ge, 4s2 4p2, → sp3 hybridized, absolute band gap, **semiconductor**

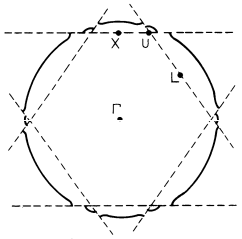
4.8 Examples – Fermi surfaces

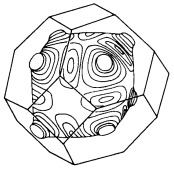
Fermi surfaces

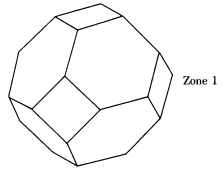




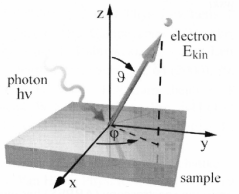
Al




Copper


Aluminum

4.8 Occupied states – photoelectron spectroscopy



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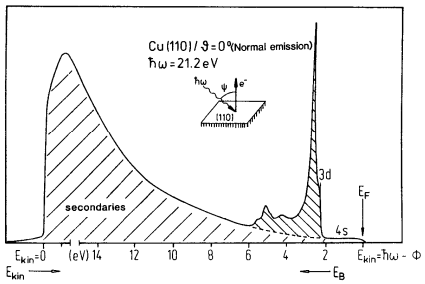

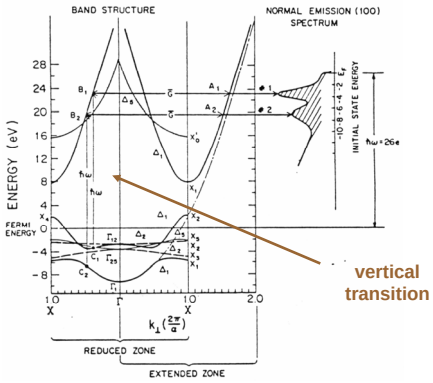

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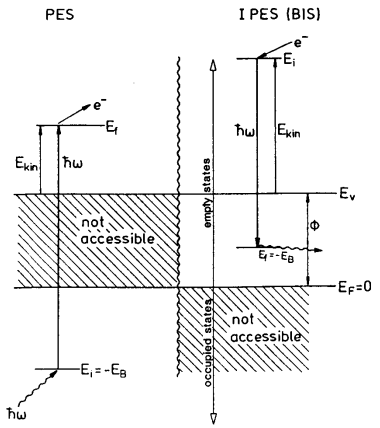

Two-photon photoemission (2PPE)