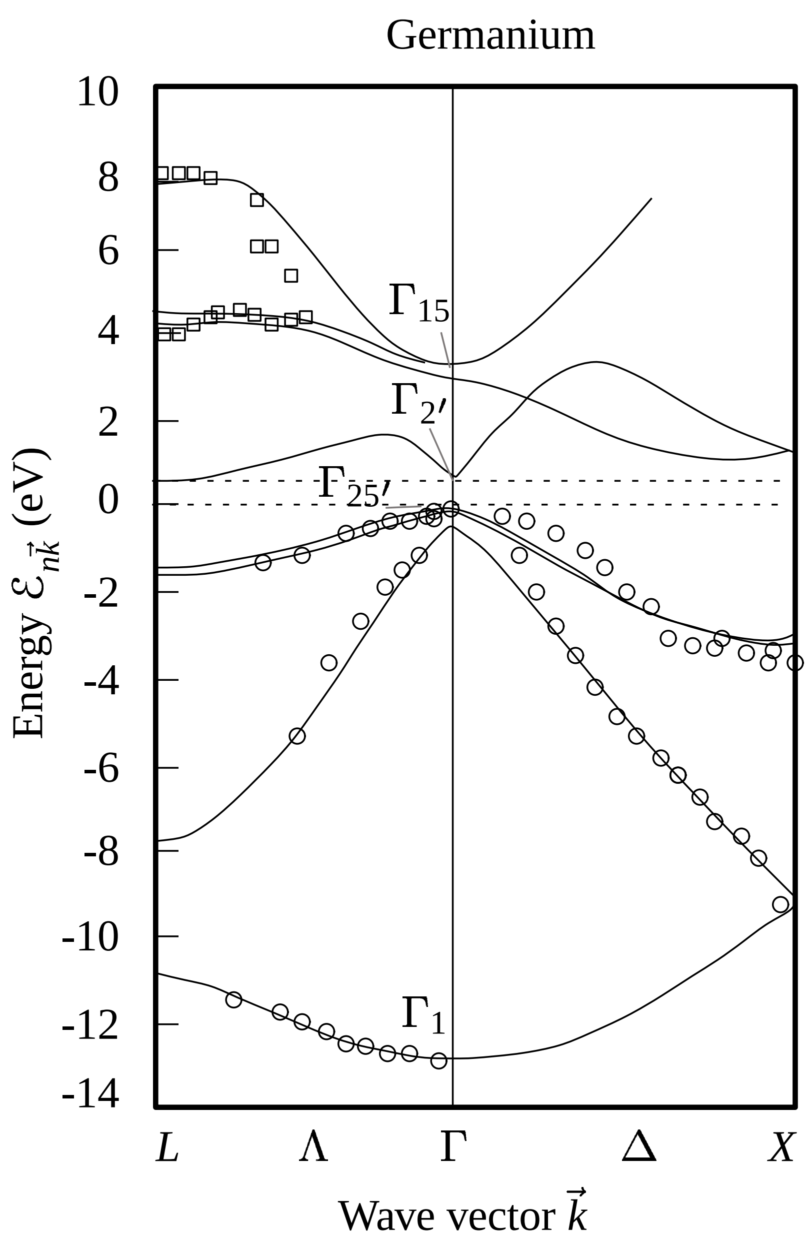
Optical Properties of Metals



Definitions

- ☞ Phenomenology of Metals
- ☞ Anomalous Skin Effect
- ☞ Plasmons
- ☞ Interband Transitions
- ☞ Brillouin and Raman Scattering
- ☞ Photoemission
- ☞ Work Function
- ☞ Angle–Resolved Photoemission Spectroscopy (ARPES)
- ☞ Charge–Transfer Insulators

Plasma Frequency

$$1\,\mathrm{eV} \Rightarrow \omega \sim 10^{15}\,\mathrm{Hz} \Rightarrow \lambda \sim 1\,\mu\mathrm{m}. \tag{L1}$$

$$\epsilon(\omega) = 1 - \frac{\omega_{\mathrm{p}}^2}{\omega(\omega + i/\tau)} \tag{L2}$$

$$\omega_{\mathrm{p}} = \sqrt{\frac{4\pi n e^2}{m}} = 5.64 \cdot 10^{15}\ \mathrm{Hz}\ \left[\frac{n}{10^{22}\mathrm{cm}^{-3}}\right]^{1/2}. \tag{L3}$$

Plasma Frequency

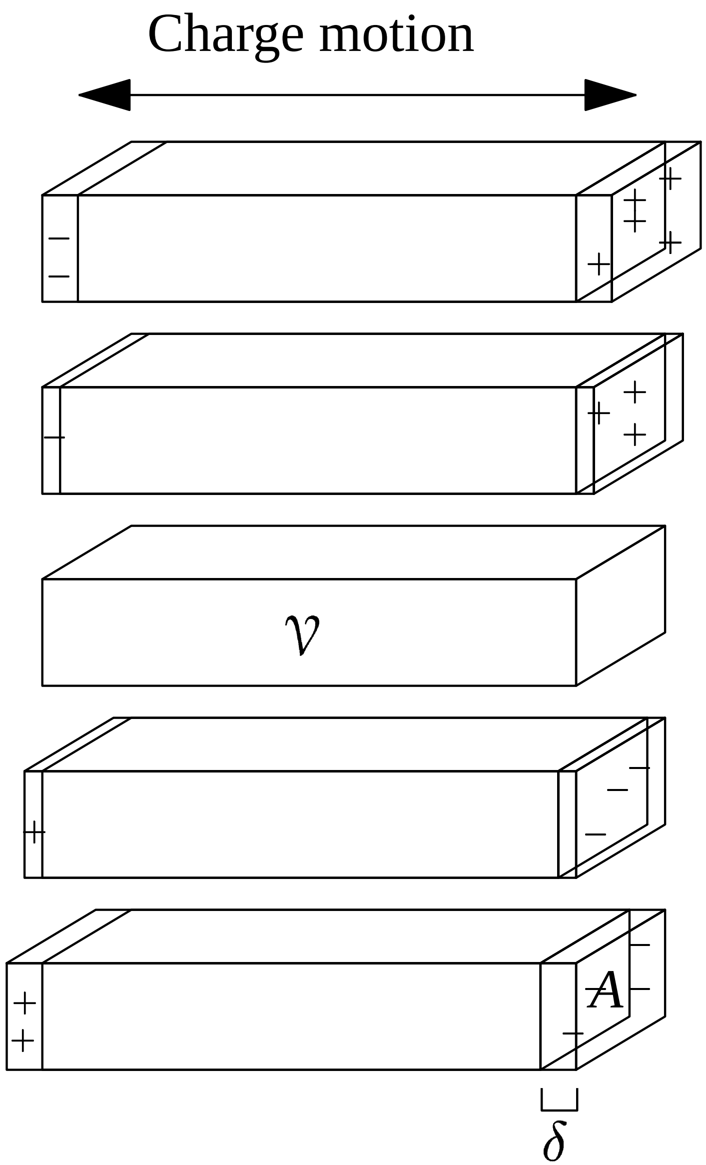


Figure 1: Plasma oscillations

Plasma Frequency

$$\epsilon(\omega) = 1 - \left(\frac{\omega_{\rm p}}{\omega}\right)^2. \tag{L4}$$

$$en\mathcal{V}E = ? \qquad\qquad ?. \tag{L5}$$

$$\ddot{\delta} = -? \qquad\qquad ? \tag{L6}$$

$$\omega_{\rm p}^2 = \frac{4\pi n e^2}{m}. \tag{L7}$$

Plasma Frequency

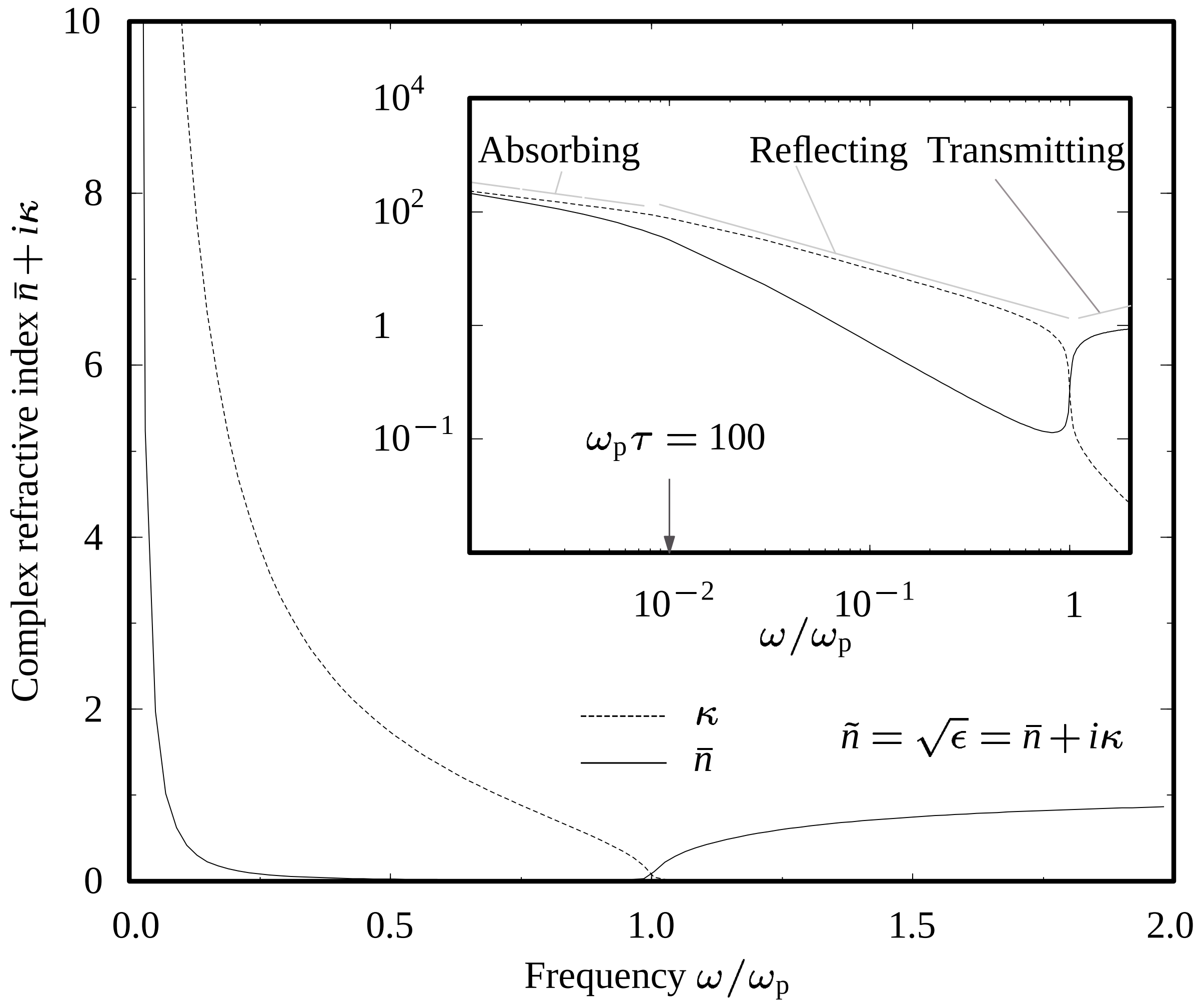


Figure 2: Index of refraction $\bar{n}$ and extinction coefficient κ for metal

Plasma Frequency

$$\epsilon \approx 1 + i\tau \frac{\omega_{\rm p}^2}{\omega}(1 + i\omega\tau) \Rightarrow \bar{n} \approx \kappa \approx \sqrt{\tau\omega_{\rm p}^2/2\omega}. \tag{L8}$$

$$\frac{(\omega^2 - \omega_{\rm p}^2)}{\omega^2} \tag{L9}$$

$$\kappa \approx \sqrt{\omega_{\rm p}^2/\omega^2 - 1} \text{ and } \bar{n} \approx \frac{\omega_{\rm p}^2}{2\tau\omega^2\sqrt{\omega_{\rm p}^2 - \omega^2}}. \tag{L10}$$

$$\bar{n} \approx \sqrt{1 - \omega_{\rm p}^2/\omega^2} \;\; \kappa \approx \frac{\omega_{\rm p}^2}{2\tau\omega^2\sqrt{\omega^2 - \omega_{\rm p}^2}}. \tag{L11}$$

$$\frac{\partial g}{\partial t} = -\vec{v}\cdot\nabla g - e\vec{E}\cdot\vec{v}\frac{\partial g}{\partial \mu} - \frac{g}{\tau}. \tag{L12}$$

$$\vec{E} = \vec{E}(\vec{q},\omega)e^{i\vec{q}\cdot\vec{r}-i\omega t}. \tag{L13}$$

$$g_{\vec{r}\vec{k}} = g_{\vec{k}}(\vec{q},\omega)e^{i\vec{q}\cdot\vec{r}-i\omega t} \tag{L14}$$

$$g_{\vec{k}}(\vec{q},\omega)[-i\omega] = [-i\vec{v}\cdot\vec{q} - 1/\tau]g_{\vec{k}}(\vec{q},\omega) - e\vec{E}\cdot\vec{v}\frac{\partial f}{\partial \mu} \tag{L15}$$

$$\Rightarrow g_{\vec{k}}(\vec{q},\omega) = ? \qquad ?. \tag{L16}$$

$$\vec{j} = -e\int[d\vec{k}]\,\vec{v}g_{\vec{k}} \tag{L17}$$

$$= e^2\int[d\vec{k}]\,\frac{\partial f}{\partial \mu}\frac{\vec{v}[\vec{v}\cdot\vec{E}(\vec{q},\omega)]}{1/\tau - i(\omega - \vec{q}\cdot\vec{v})} \tag{L18}$$

$$\Rightarrow \sigma_{\alpha\beta} = e^2 \int [d\vec{k}] \frac{\partial f}{\partial \mu} \frac{v_\alpha v_\beta}{1/\tau - i(\omega - \vec{q}\cdot\vec{v})} \tag{L19}$$

$$= e^2 \int \frac{d\Sigma}{4\pi^3 \hbar v} \frac{v_\alpha v_\beta}{1/\tau - i(\omega - \vec{q}\cdot\vec{v})} \tag{L20}$$

$$\Rightarrow \epsilon_{\alpha\beta} = \delta_{\alpha\beta} + \frac{4\pi i e^2}{\omega} \int \frac{d\Sigma}{4\pi^3 \hbar v} \frac{v_\alpha v_\beta}{1/\tau - i(\omega - \vec{q}\cdot\vec{v})} \tag{L21}$$

$$q = \frac{\sqrt{\epsilon}\omega}{c} = (\bar{n} + i\kappa)\frac{\omega}{c}. \tag{L22}$$

$$\frac{1}{\tau} - i\omega + i(\bar{n} + i\kappa)\frac{\omega v_F}{c} \approx \frac{1}{\tau} - i\omega \tag{L23a}$$

$$\Rightarrow \frac{\bar{n} v_F}{c} \ll 1 \tag{L23b}$$

and

$$\kappa \omega v_F \tau / c \ll 1 \quad \text{or equivalently} \quad l_T \ll \delta, \tag{L23c}$$

$$\delta \equiv \frac{c}{\kappa\omega} \tag{L24}$$

$$\epsilon = 1 - \frac{\omega_{\rm p}^2}{\omega(\omega + i/\tau)} \tag{L25}$$

with

$$\omega_{\rm p}^2 = \frac{4\pi n e^2}{m_{\rm opt}}, \tag{L26}$$

$$\frac{1}{m_{\rm opt}} = \frac{1}{m} \frac{\int [d\vec{k}]\, \frac{\partial f}{\partial \mu} m v_x^2}{\int [d\vec{k}]\, f_k} = \int \frac{d\Sigma}{12\pi^3 \hbar n}\, v. \tag{L27}$$

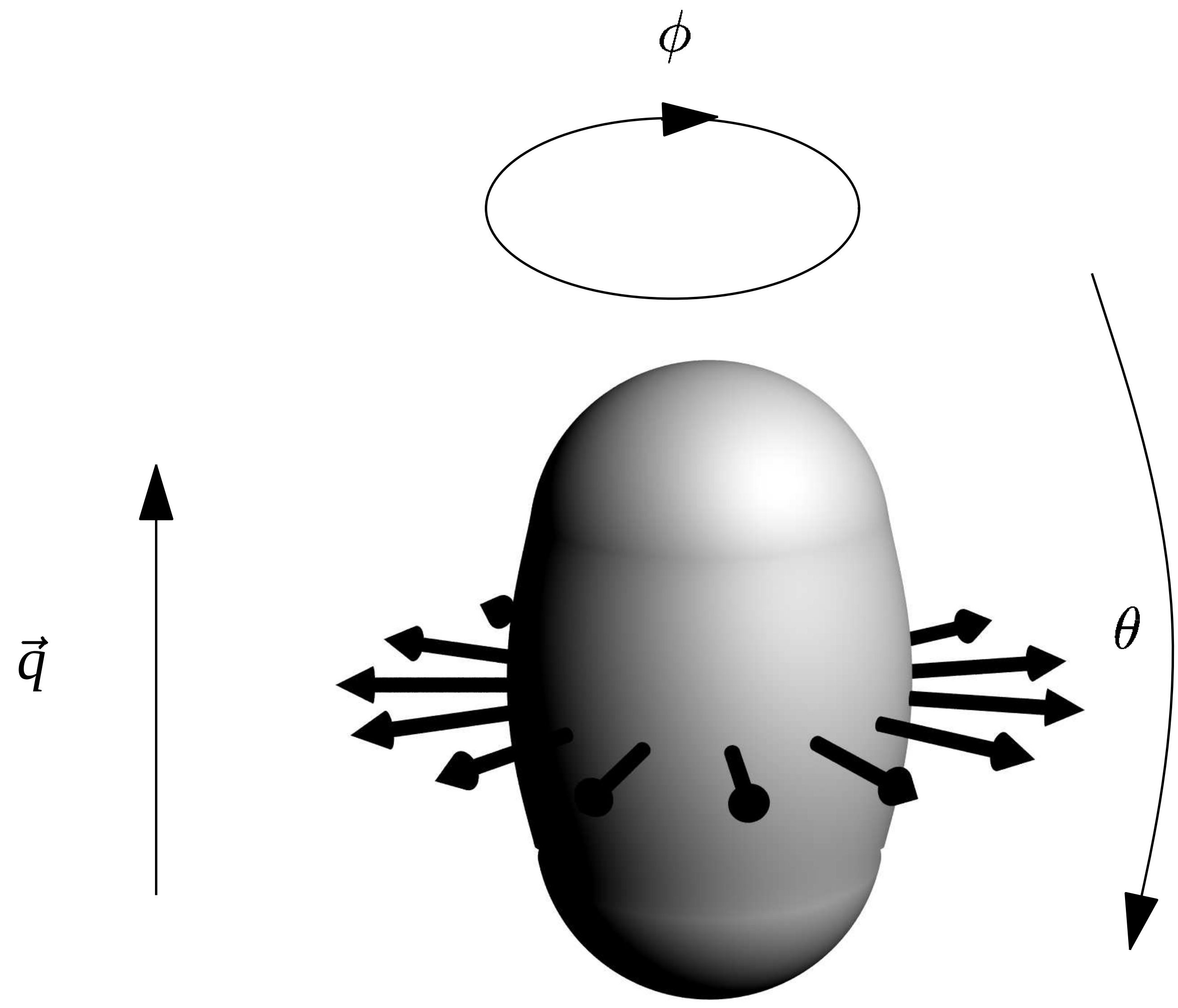


Figure 3: Anomalous skin effect

$$d\Sigma \approx \mathcal{R}_\phi \mathcal{R}_\theta d\theta d\phi, \quad v_x \approx v_F \cos\phi \tag{L28}$$

$$\sigma_{xx} = e^2 \int \frac{\mathcal{R}_\phi \mathcal{R}_\theta d\theta d\phi}{4\pi^3 \hbar v_F} \frac{v_F^2 \cos^2\phi}{1/\tau + iqv_F\theta} \tag{L29}$$

$$= \frac{e^2}{4\pi\hbar q} \mathcal{R}_\phi \mathcal{R}_\theta . \tag{L30}$$

Plasmons

$$\chi_c = \frac{e^2}{\hbar \mathcal{V}} \sum_{\vec{k}} f_{\vec{k}} [\frac{1}{\omega_{\vec{k}} - \omega_{\vec{q}+\vec{k}} - \omega} + \frac{1}{\omega_{\vec{k}} - \omega_{\vec{q}+\vec{k}} + \omega}] \tag{L31}$$

$$= \frac{e^2}{\hbar \mathcal{V}} \sum_{\vec{k}} \frac{2 f_{\vec{k}} (\omega_{\vec{k}} - \omega_{\vec{k}+\vec{q}})}{\left(\omega_{\vec{k}} - \omega_{\vec{k}+\vec{q}}\right)^2 - \omega^2} \tag{L32}$$

$$= \frac{e^2}{\mathcal{V}} \sum_{\vec{k}} \frac{2 f_{\vec{k}} \left[\frac{q^2}{2m} + \frac{\vec{q}\cdot\vec{k}}{m}\right]}{\omega^2 - \hbar^2 \left[\frac{\vec{q}\cdot\vec{k}}{m} + \frac{q^2}{2m}\right]^2}. \tag{L33}$$

$$\chi_c(\vec{q},\omega) \approx \frac{e^2}{\mathcal{V}} \sum_{\vec{k}} \frac{f_{\vec{k}}}{\omega^2} \frac{q^2}{m} \left[1 + \frac{3(\vec{q}\cdot\vec{k})^2 \hbar^2}{m^2 \omega^2}\right]. \tag{L34}$$

$$\chi_c(\vec{q},\omega) = \frac{e^2}{\mathcal{V}} \sum_{\vec{k}} \frac{f_{\vec{k}}}{\omega^2} \frac{q^2}{m} \left[1 + \frac{(qk)^2 \hbar^2}{m^2 \omega^2}\right]. \tag{L35}$$

Plasmons

$$N = \sum_{\vec{k}\sigma} f_{\vec{k}} = \mathcal{V} \int \frac{dk}{4\pi^3} 4\pi k^2 \, f_{\vec{k}}. \tag{L36}$$

$$\sum_{\vec{k}\sigma} f_{\vec{k}} k^2 = \frac{3}{5} N k_F^2. \tag{L37}$$

$$\epsilon(\vec{q},\omega) = 1 - \frac{4\pi n e^2}{m\omega^2}\left[1 + \frac{3}{5}\frac{\hbar^2 k_F^2 q^2}{m^2\omega^2}\right]. \tag{L38}$$

$$1 = \frac{\omega_{\mathrm{p}}^2}{\omega^2}\left[1 + \frac{3}{5}\frac{\hbar^2 k_F^2 q^2}{m^2\omega^2}\right] \tag{L39}$$

$$\Rightarrow \omega^2 = \omega_p^2 + \frac{6}{5}\frac{\mathcal{E}_F q^2}{m}. \tag{L40}$$

Experimental Observation of Plasmons

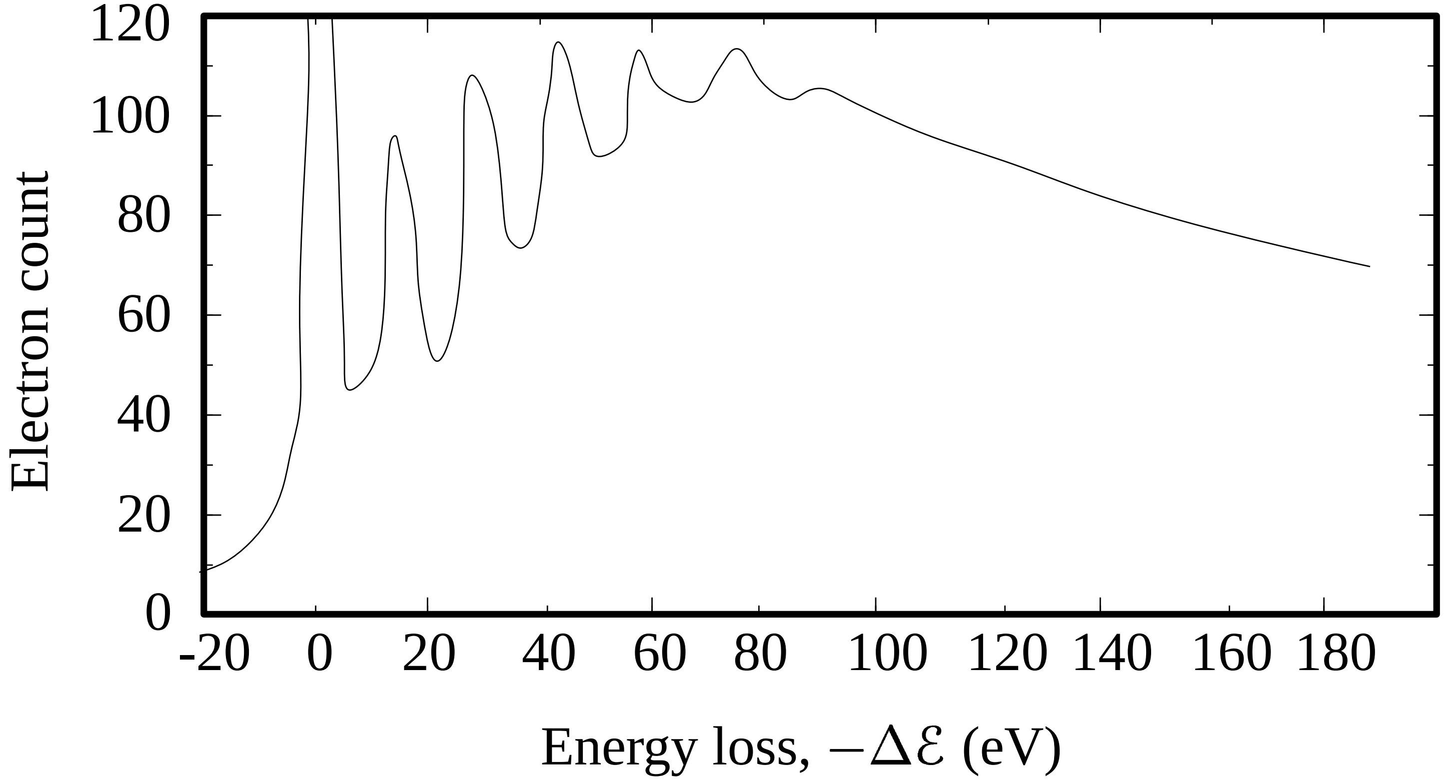


Figure 4: Electron energy loss to plasma oscillations [Lang (1948)]

Experimental Observation of Plasmons

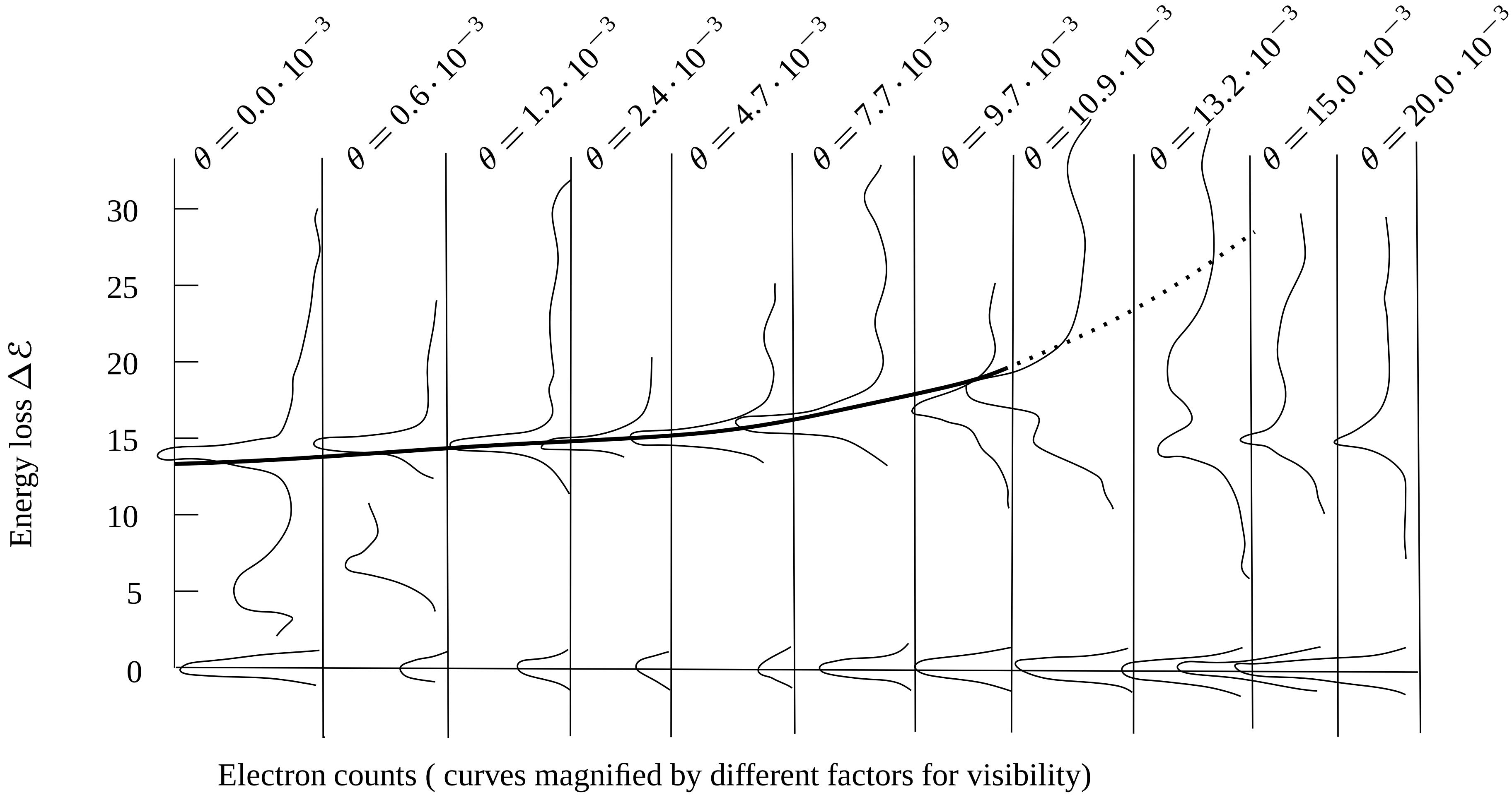


Figure 5: Electron energy loss to plasmons as a function of angle [Kunz (1962)]

$$\hbar\omega(\vec{k}-\vec{k}') = \Delta\mathcal{E} \tag{L41}$$

$$\Rightarrow \hbar\omega(2k\sin\theta/2) \quad \approx \quad \hbar\omega_{\mathrm{p}} + \alpha_{\mathrm{pl}}\frac{\hbar^2 k^2}{m}\theta^2 \tag{L42}$$

$$\alpha_{\mathrm{pl}} = \frac{3}{5}\frac{\hbar^2 k_F^2}{2m\hbar\omega_{\mathrm{p}}}. \tag{L43}$$

Element	Be	Al	Mg	Sb	Na
α_{pl} [from Eq. (L43)]	0.47	0.44	0.39	0.44	0.32
α_{pl} (experiment)	0.42	0.35	0.39	0.37	0.29

Interband Transitions

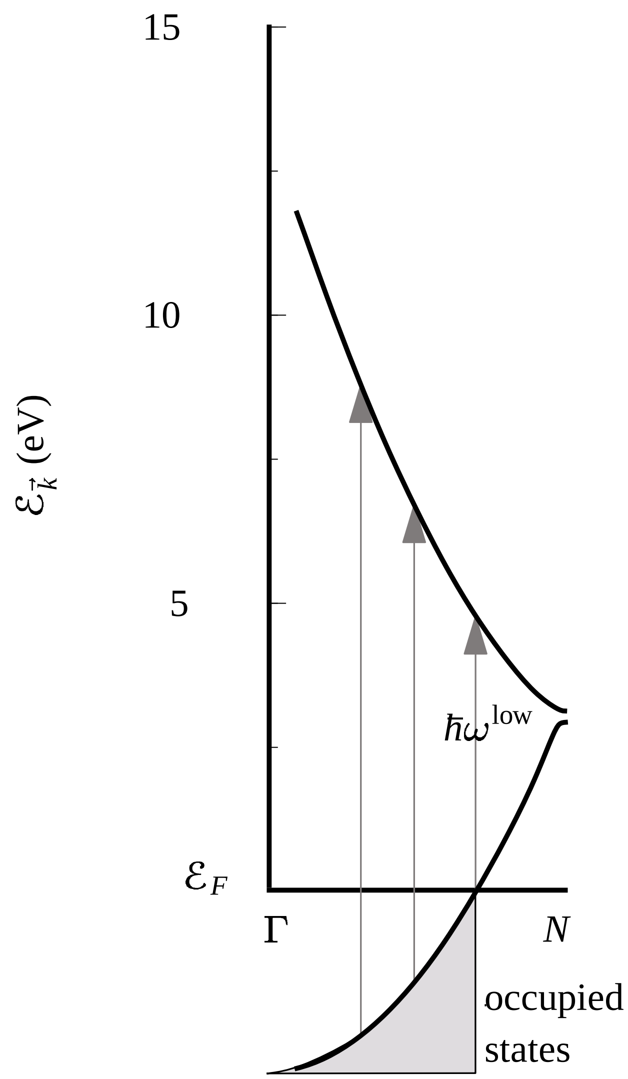


Figure 6: The sodium electron bands.

$$\langle n_1\vec{k}|\hat{P}_\alpha|n_2\vec{k}\rangle. \tag{L44}$$

$$\psi^{\text{low}}_{\vec{k}}(\vec{r}) \approx \frac{1}{\sqrt{\mathcal{V}}}\left[e^{i\vec{k}\cdot\vec{r}} + \frac{e^{i(\vec{k}-\vec{K})\cdot\vec{r}}U_{-\vec{K}}}{\mathcal{E}^0_{\vec{k}} - \mathcal{E}^0_{\vec{k}-\vec{K}}}\right] \tag{L45}$$

$$\psi^{\text{high}}_{\vec{k}}(\vec{r}) \approx \frac{1}{\sqrt{\mathcal{V}}}\left[e^{i(\vec{k}-\vec{K})\cdot\vec{r}} + \frac{e^{i\vec{k}\cdot\vec{r}}U_{\vec{K}}}{\mathcal{E}^0_{\vec{k}-\vec{K}} - \mathcal{E}^0_{\vec{k}}}\right]. \tag{L46}$$

$$\text{Re}[\sigma_{\alpha\beta}](\omega) = \frac{\pi}{\omega}\frac{e^2\hbar^2}{m^2}\frac{1}{\mathcal{V}}\sum_{\vec{k}\vec{K}\in\langle 110\rangle} f_{\vec{k}}\frac{|U_{\vec{K}}|^2K_\alpha K_\beta}{(\mathcal{E}^0_{\vec{k}-\vec{K}} - \mathcal{E}^0_{\vec{k}})^2}\delta(\mathcal{E}^0_{\vec{k}-\vec{K}} - \mathcal{E}^0_{\vec{k}} - \hbar\omega) \tag{L47}$$

$$\Rightarrow \sigma(\omega) = \frac{4e^2\pi}{m^2\omega^3} K^2 |U_{\vec{K}}|^2 D_{\rm j}(\hbar\omega), \tag{L49}$$

$$D_{\rm j}(\hbar\omega) = \frac{1}{\mathcal{V}} \sum_{\vec{k},\vec{K}\in\langle 110\rangle} f_{\vec{k}} \delta(\mathcal{E}^0_{\vec{k}-\vec{K}} - \mathcal{E}^0_{\vec{k}} - \hbar\omega) \tag{L50}$$

$$= \frac{m^3}{4\pi^2\hbar^4 K^3} (\omega^{\rm high} - \omega)(\omega - \omega^{\rm low}) \tag{L51}$$

with

$$\omega^{\rm high} = \frac{\hbar^2 K(K+2k_F)}{2\hbar m} \quad \omega^{\rm low} = \frac{\hbar^2 K(K-2k_F)}{2\hbar m}. \tag{L52}$$

Interband Transitions

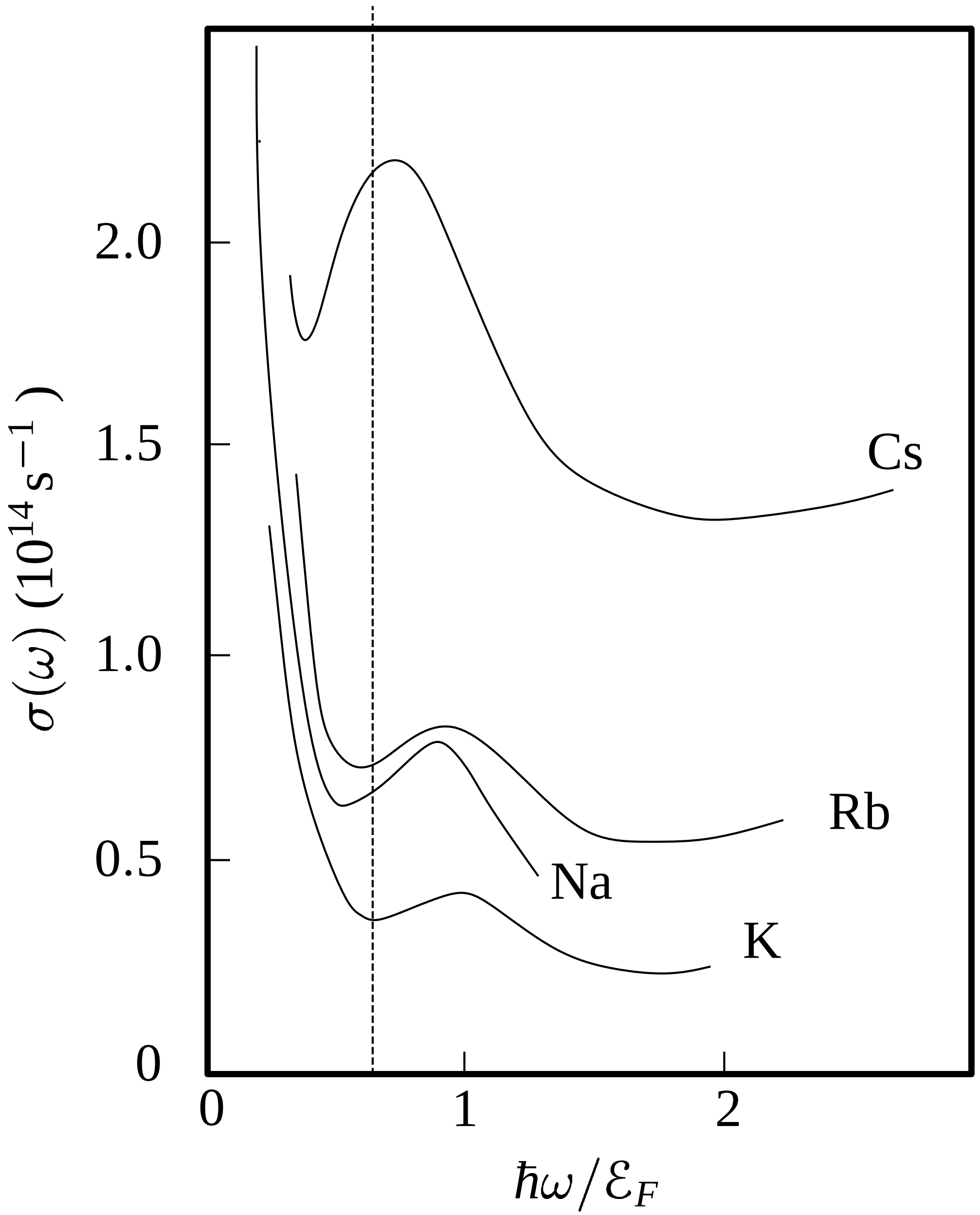


Figure 7: Absorption of alkali metals [Smith (1970)]

Interband Transitions

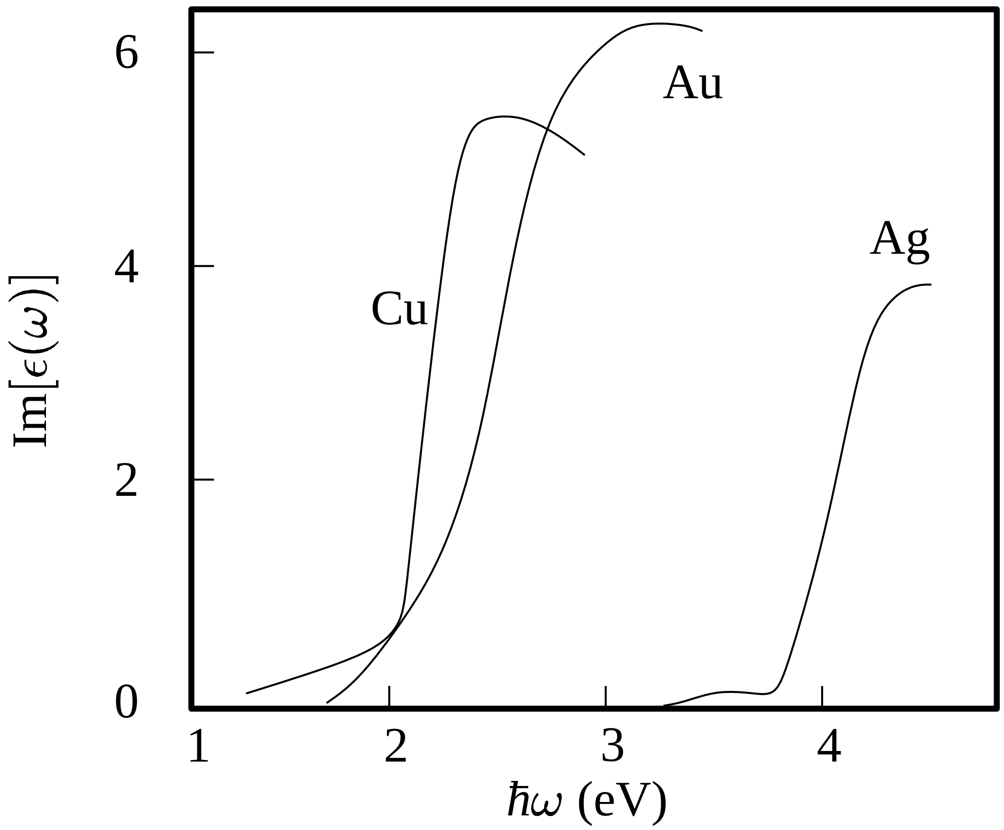


Figure 8: Noble metal absorption [Thèye (1968)]

Conserve (Crystal) Momentum:

$$\vec{k}_f = ? \qquad ? \tag{L53}$$

Conserve Energy:

$$\frac{c}{\bar{n}}(k_f - k_0) = ? \qquad ?. \tag{L54}$$

$$\omega_1 = c_p k. \tag{L55}$$

$$(k_f - k_0) = -\frac{\bar{n} c_p}{c}\sqrt{k_f^2 + k_0^2 - 2k_f k_0 \cos\theta} \tag{L56}$$

$$\Rightarrow k_0 - k_f \approx k_0 \frac{2\bar{n} c_p}{c}\sqrt{\frac{1-\cos\theta}{2}}. \tag{L57}$$

$$\Rightarrow \omega_0 - \omega_f = \frac{2\bar{n}\omega_0 c_p}{c}\sin\theta/2 \tag{L58}$$

Brillouin Scattering

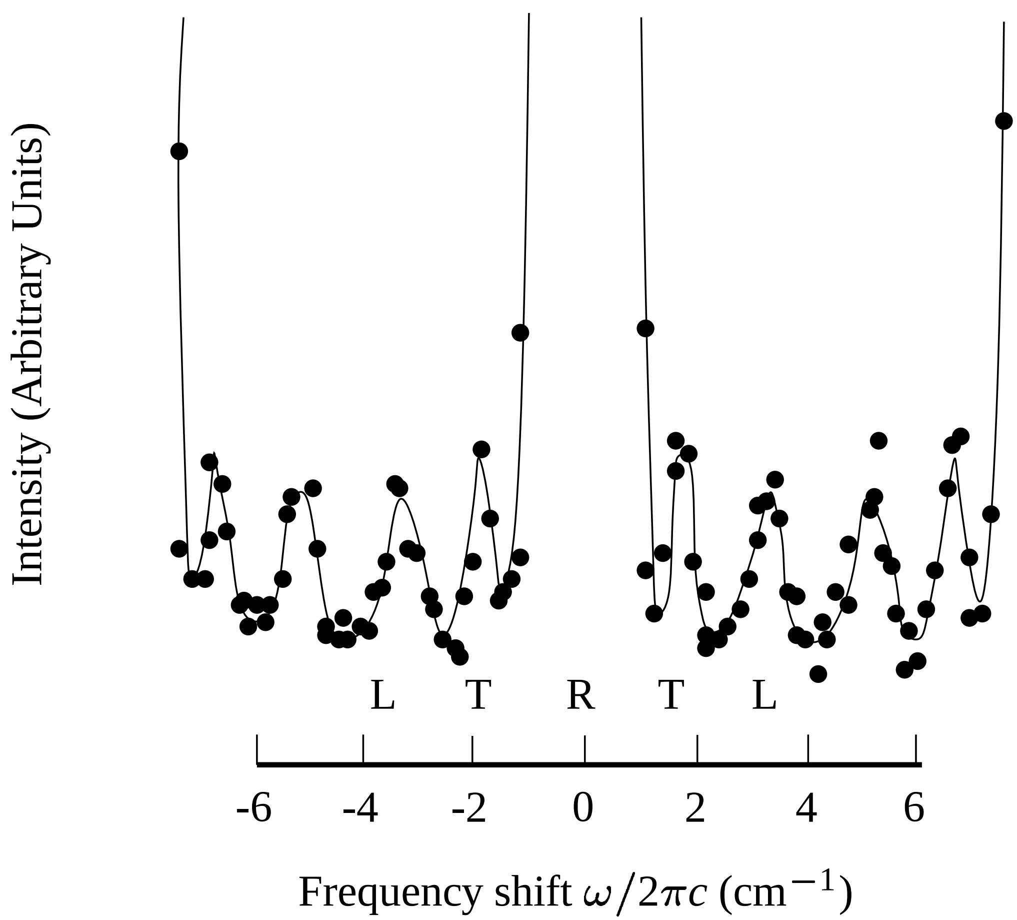


Figure 9: Brillouin scattering from the (111) surface of germanium [Sandercock (1972).]

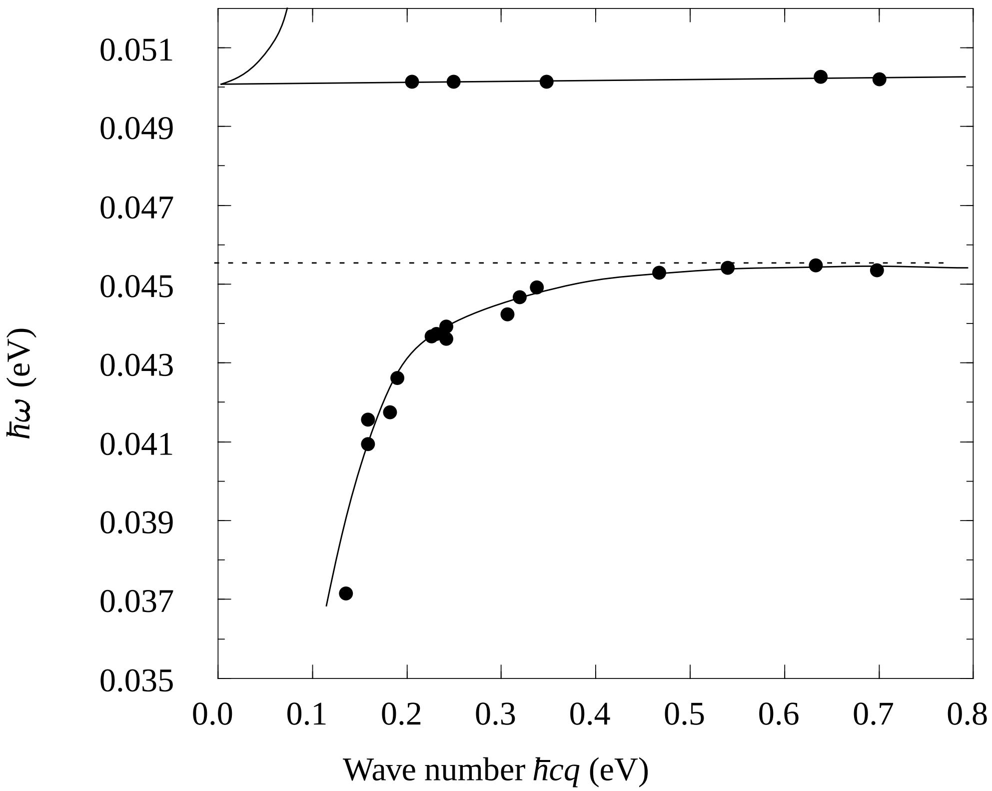


Figure 10: Dispersion relation of polaritons in GaP [Henry and Hopfield (1965)]

Inelastic X-Ray Scattering

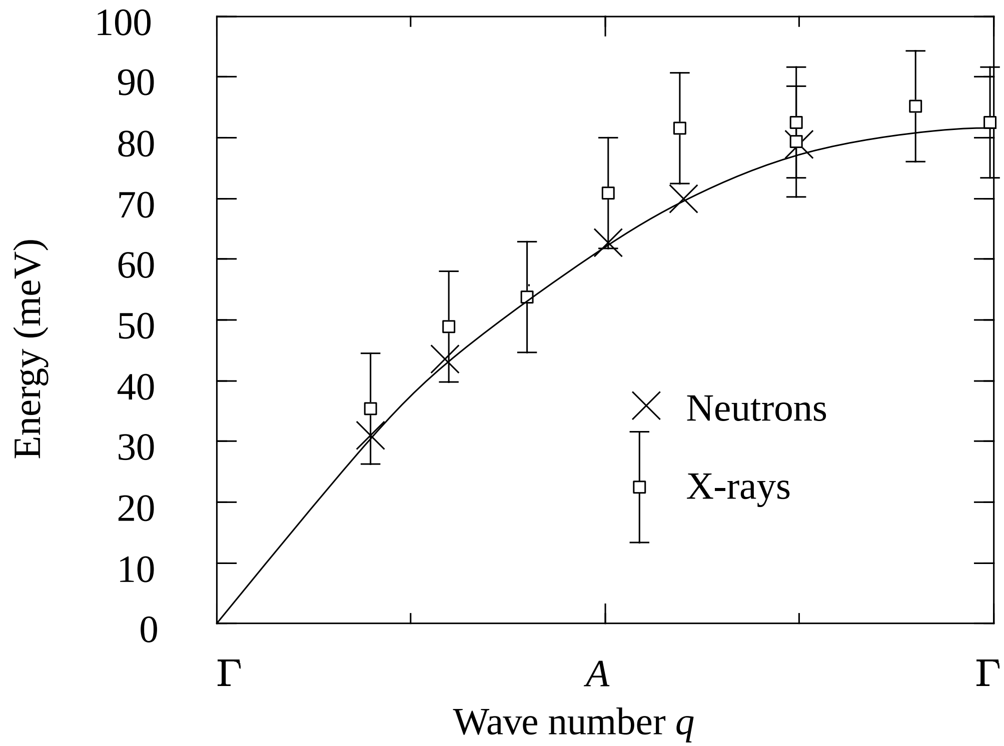


Figure 11: Dispersion relation of longitudinal phonons in beryllium [Dorner et al. (1987).]

Measurement of Work Functions

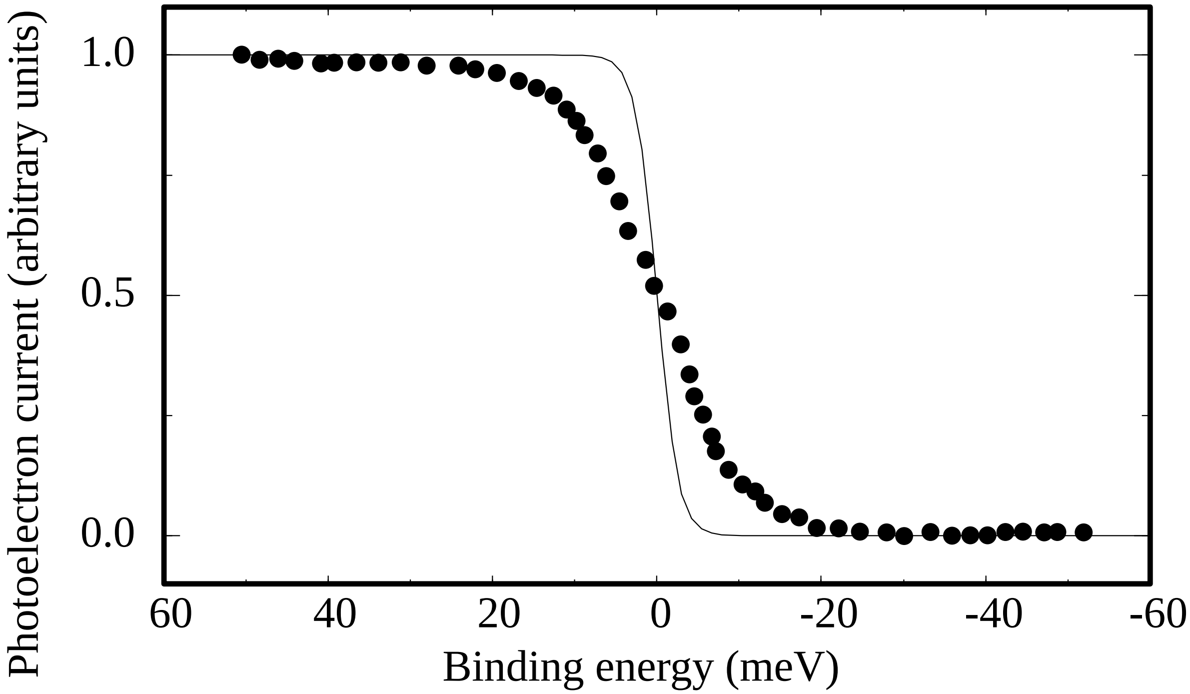


Figure 12: Measurement of Fermi function [Patthey et al. (1990)]

Work Functions

Compound	Surface	ϕ (eV)	Compound	Surface	ϕ (eV)
Ag	(100)	4.64	Na	(110)	2.9
	(110)	4.52	Nb	(100)	4.02
	(111)	4.74		(110)	4.87
Al	(100)	4.20		(111)	4.36
	(110)	4.06	Ni	(100)	5.22
	(111)	4.26		(110)	5.04
Au	(100)	5.47		(111)	5.35
	(110)	5.37	Pt	(100)	5.84
	(111)	5.31	Si	(111) 2×1	4.85
Be	(0001)	5.1		(111) 7×7	4.50
Cu	(100)	5.10		(100) 2×1	4.87
	(110)	4.48	W	(100)	4.63
	(111)	4.94		(110)	5.25
Fe	(100)	4.67		(111)	4.47
Ge	(111) 2×1	4.68	SiC	(0001)	4.6
	(111) 2×8	4.53	AlN	(100)	5.35
K	(110)	2.39	GaAs	(110)	5.56
Mg	(100)	3.71	GaSb	(110)	4.91
Mo	(100)	4.53	InP	(110)	5.85
	(110)	4.95			
	(111)	4.55			

Angle-Resolved Photoemission

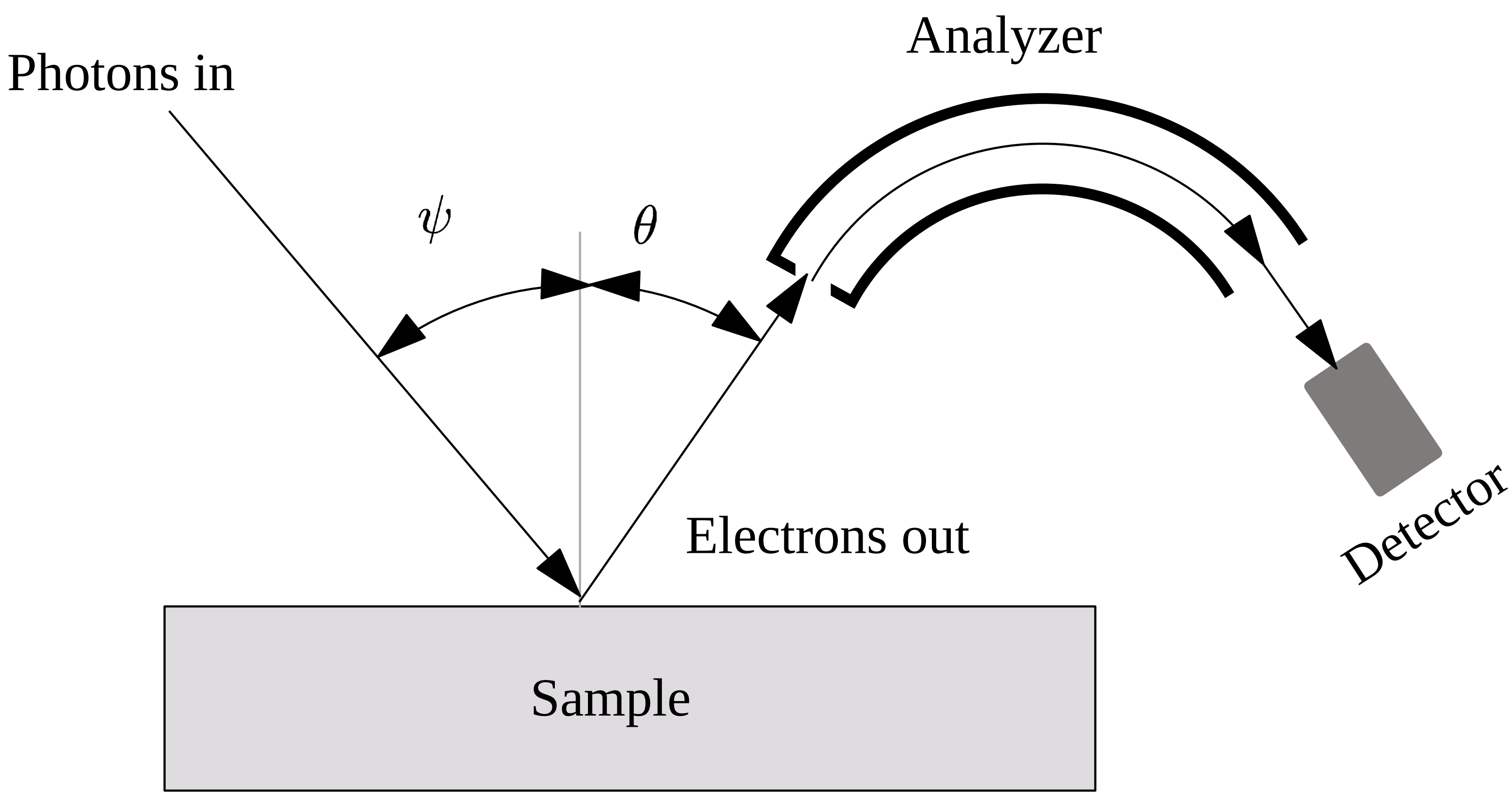


Figure 13: Angle-resolved photoemission experiment.

$$\phi + \mathcal{E}_{\rm kin} - (-\mathcal{E}_B) = \hbar\omega, \tag{L59}$$

$$\mathcal{E}_B(\vec{k}_{\rm final}) = \hbar\omega - \phi - \mathcal{E}_{\rm kin}, \tag{L60}$$

$$\Delta p = \int -\frac{\partial U}{\partial x} dt \approx -\frac{\Delta U}{v}, \tag{L61}$$

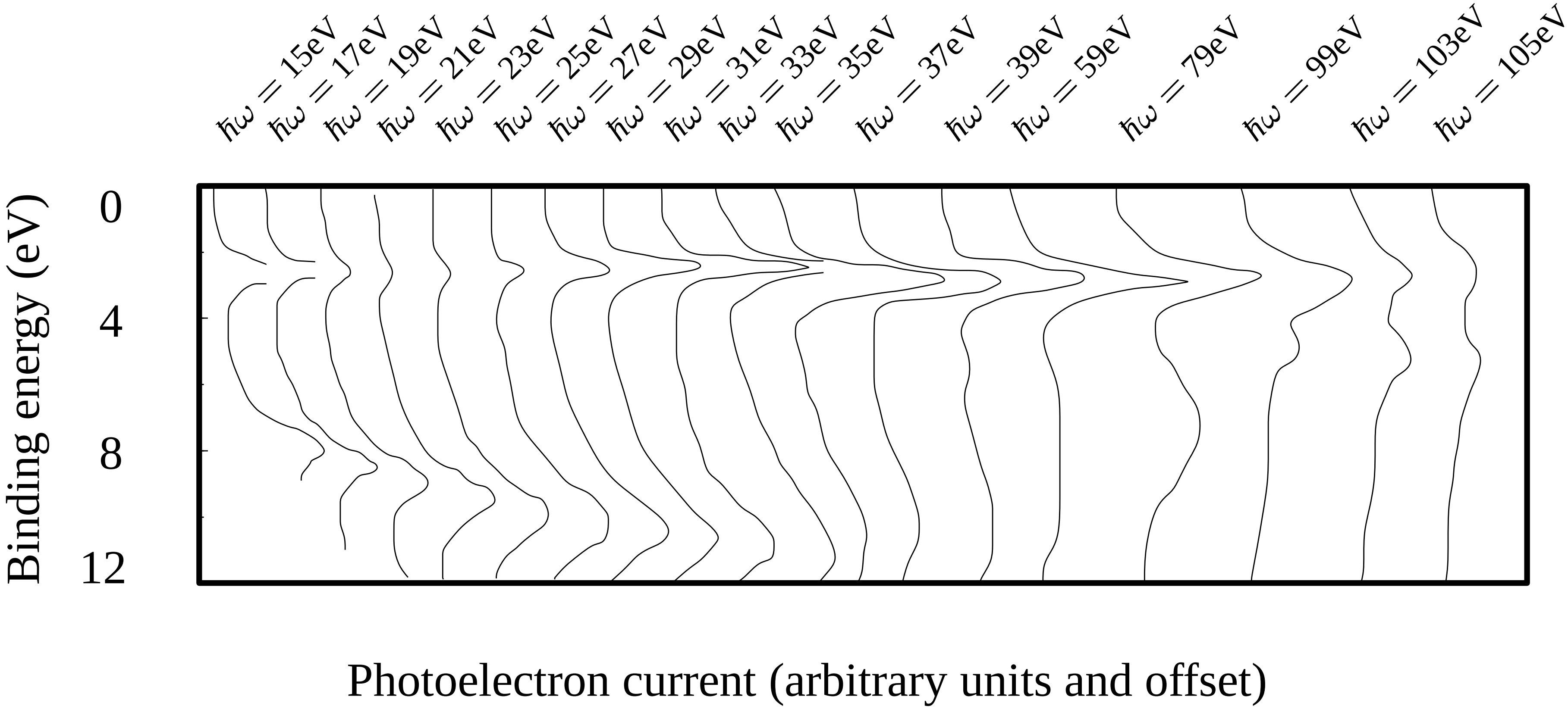


Figure 14: Photon injection and electron emission in beryllium along [0001]. [Jensen et al. (1984)]

Angle-Resolved Photoemission

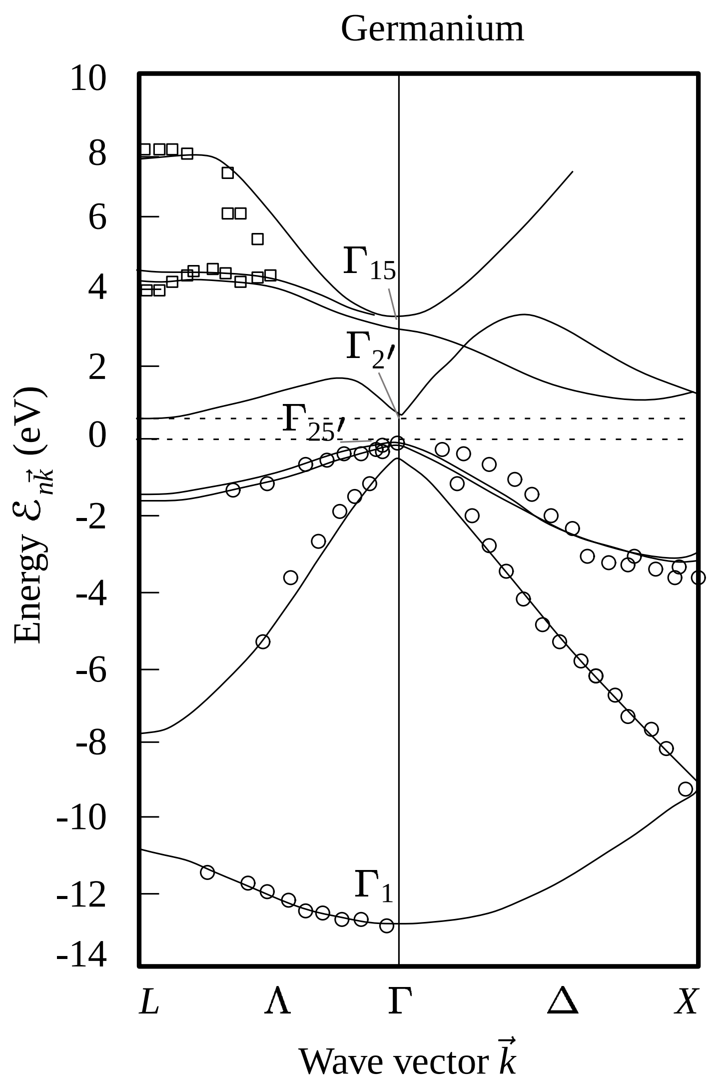


Figure 15: Theoretical calculations of Louie (1992). Experiments of Wachs et al. (1985) and Straub et al. (1986).

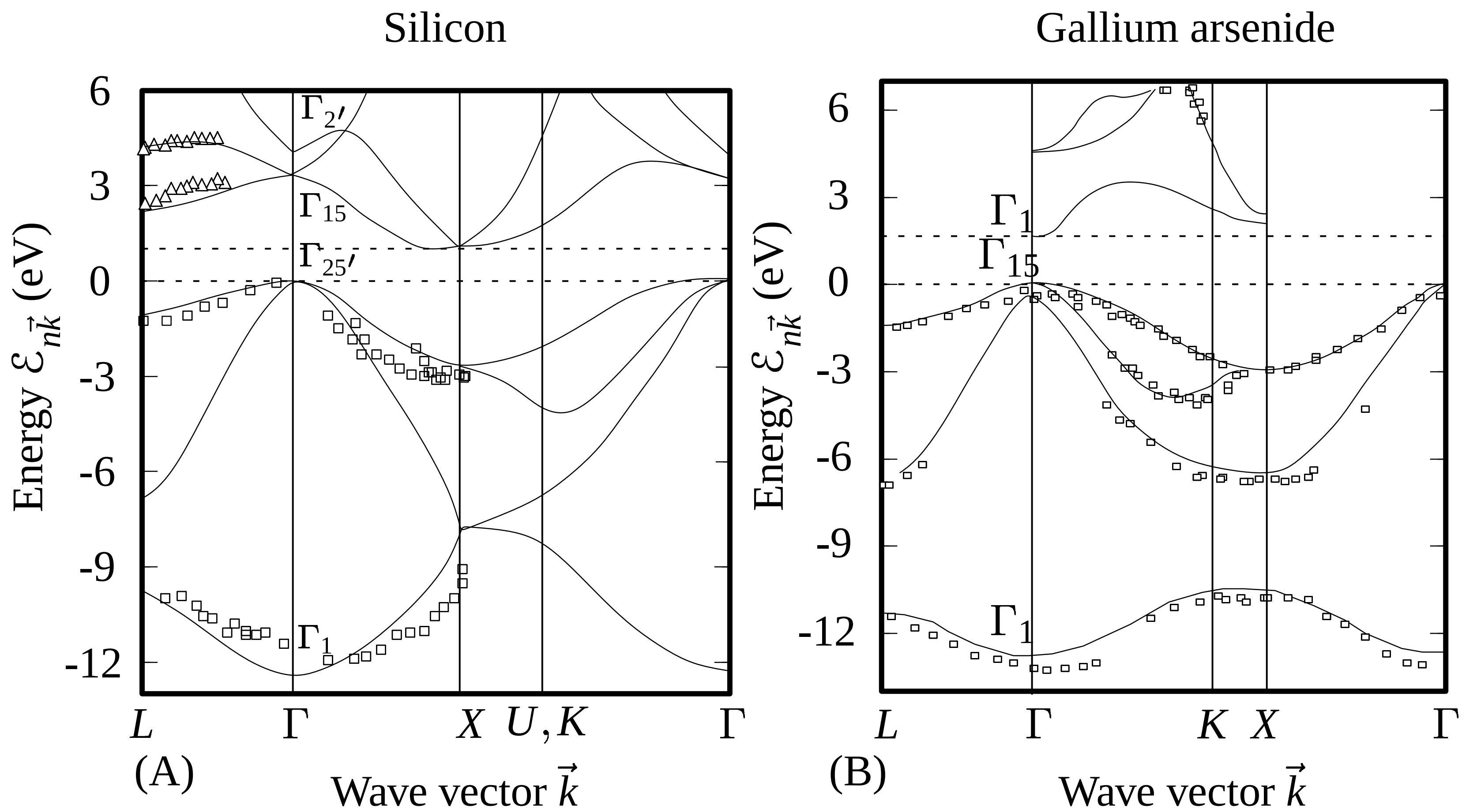


Figure 16: (A) Silicon: theory of Chelikowsky and Cohen (1976), experiments of Straub et al. (1986) and Rich et al. (1989). (B) GaAs: Theory of Pandey and Phillips (1974), experiments of Chiang et al. (1980) and Williams et al. (1986).

Charge-Transfer Insulators

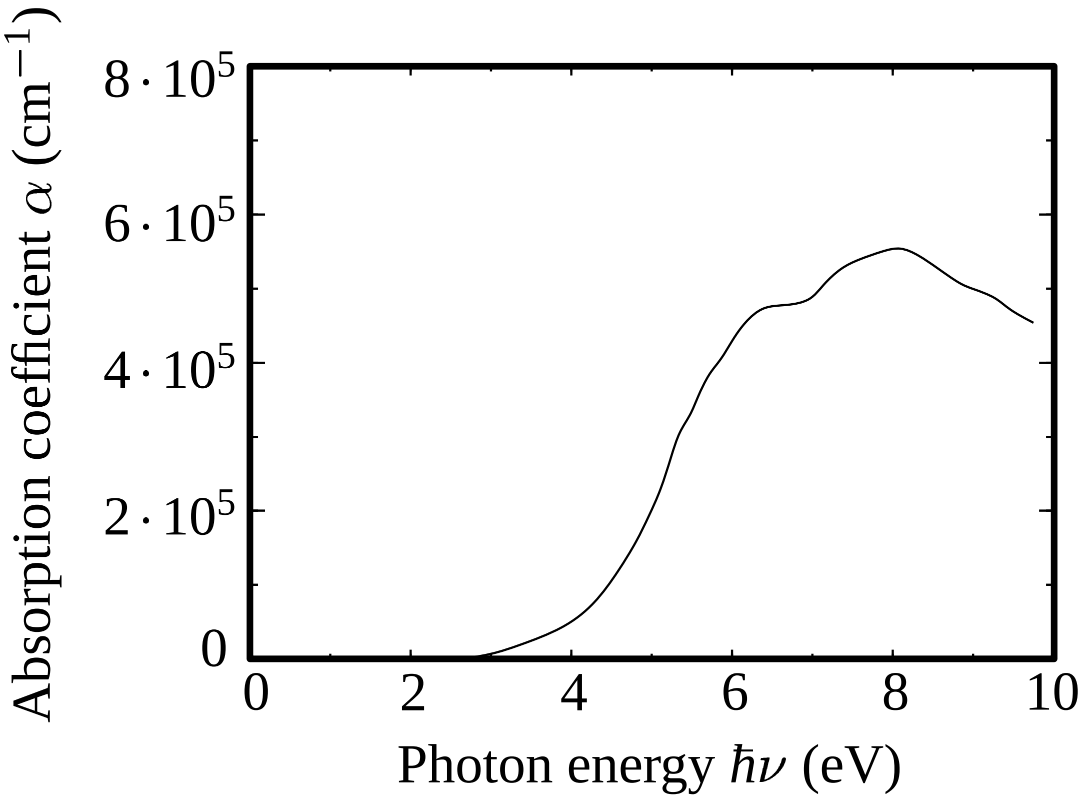


Figure 17: Optical absorption of CoO. [Powell and Spicer (1970).]

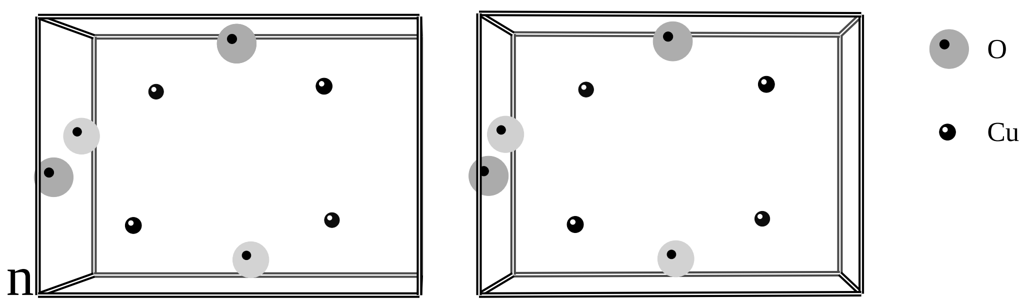


Figure 18: Structure of CuO [Åsbrink and Norrby (1970)].

$$\langle d^9\mathrm{O}^{-\mathrm{II}}|\hat{\mathcal{H}}|d^9\mathrm{O}^{-\mathrm{II}}\rangle \equiv 0 \tag{L62a}$$

$$\langle d^{10}\mathrm{O}^{-\mathrm{I}}|\hat{\mathcal{H}}|d^{10}\mathrm{O}^{-\mathrm{I}}\rangle \equiv \Delta. \tag{L62b}$$

$$\langle d^9\mathrm{O}^{-\mathrm{II}}|\hat{\mathcal{H}}|d^{10}\mathrm{O}^{-\mathrm{I}}\rangle = \langle d^{10}\mathrm{O}^{-\mathrm{I}}|\hat{\mathcal{H}}|d^9\mathrm{O}^{-\mathrm{II}}\rangle \equiv T, \tag{L63}$$

$$\begin{pmatrix} 0 & T \\ T & \Delta \end{pmatrix}. \tag{L64}$$

$$|\Psi_{\mathrm{i}0}\rangle = \cos\theta_i|d^9\mathrm{O}^{-\mathrm{II}}\rangle - \sin\theta_i|d^{10}\mathrm{O}^{-\mathrm{I}}\rangle \tag{L65a}$$

where

$$\tan 2\theta_i = \frac{2T}{\Delta}. \tag{L65b}$$

$$\langle c^{\mathrm{I}}d^9\mathrm{O}^{-\mathrm{II}}|\hat{\mathcal{H}}|c^{\mathrm{I}}d^9\mathrm{O}^{-\mathrm{II}}\rangle \equiv \mathcal{E}_{\mathrm{core}} \tag{L66a}$$

$$\langle c^{\mathrm{I}}d^{10}\mathrm{O}^{-\mathrm{I}}|\hat{\mathcal{H}}|c^{\mathrm{I}}d^{10}\mathrm{O}^{-\mathrm{I}}\rangle = \mathcal{E}_{\mathrm{core}} + \Delta - U_{\mathrm{cd}}. \tag{L66b}$$

Charge-Transfer Insulators

$$\begin{pmatrix} \mathcal{E}_{\rm core} & T \\ T & \mathcal{E}_{\rm core}+\Delta-U_{\rm cd} \end{pmatrix}. \tag{L67}$$

$$|\Psi_{f0}\rangle = \cos\theta_f|c^{\rm I}d^9{\rm O}^{-\rm II}\rangle - \sin\theta_f|c^{\rm I}d^{10}{\rm O}^{-\rm I}\rangle \tag{L68a}$$

$$|\Psi_{f1}\rangle = \sin\theta_f|c^{\rm I}d^9{\rm O}^{-\rm II}\rangle + \cos\theta_f|c^{\rm I}d^{10}{\rm O}^{-\rm I}\rangle, \tag{L68b}$$

where the label f indicates final states of the valence electrons and

$$\tan 2\theta_f = \frac{2T}{\Delta-U_{cd}}. \tag{L68c}$$

$$\langle c^0|\hat{P}|c^{\rm I}\rangle\langle\Psi_{i0}|\Psi_{f\,0,1}\rangle \tag{L69}$$

$$\Delta\mathcal{E} = \sqrt{(\Delta-U_{cd})^2+4T^2}, \tag{L70}$$

$$\frac{|\langle\Psi_{i0}|\Psi_{f1}\rangle|^2}{|\langle\Psi_{i0}|\Psi_{f0}\rangle|^2} = \tan^2(\theta_i-\theta_f). \tag{L71}$$

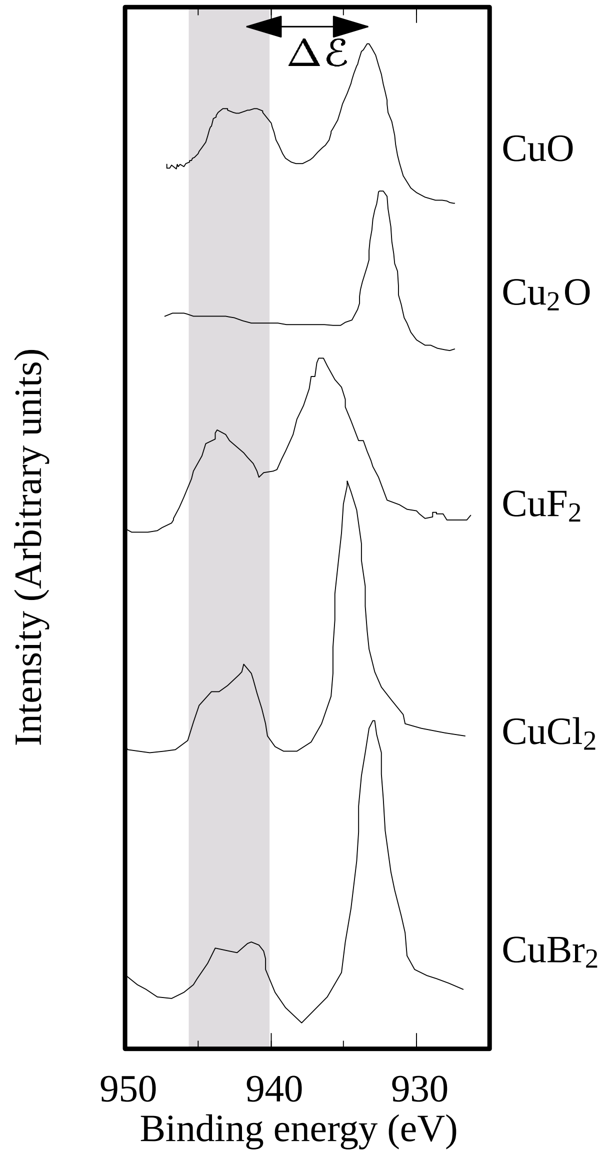


Figure 19: Core-level photoemission from CuO [Ghijsen et al. (1988), and van der Laan et al. (1981) .]