Photoemission

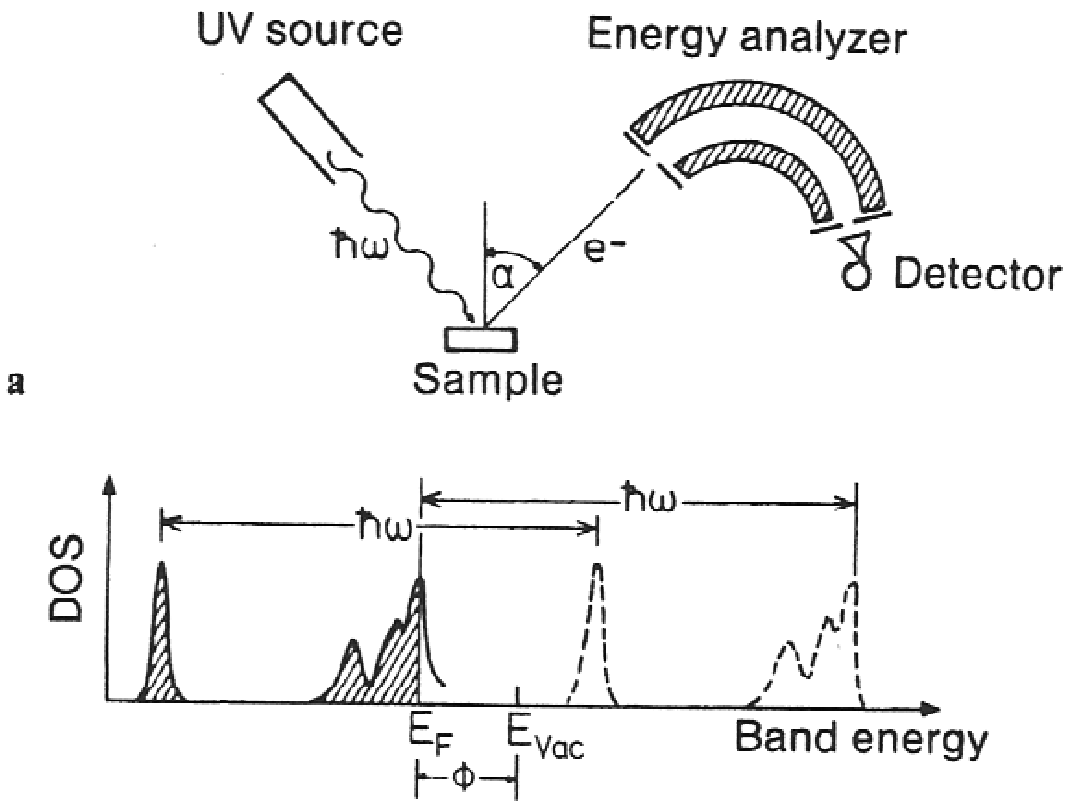
Semiconductors

Photoemission spectroscopy

UPS - Ultraviolet photoemission spectroscopy

XPS - X-ray photoemission spectroscopy

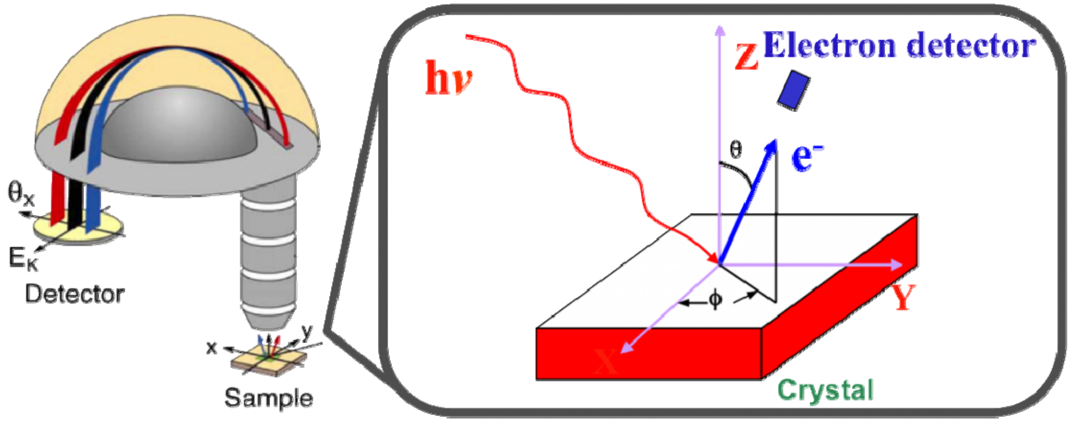
Measure the density of states with photoemission spectroscopy



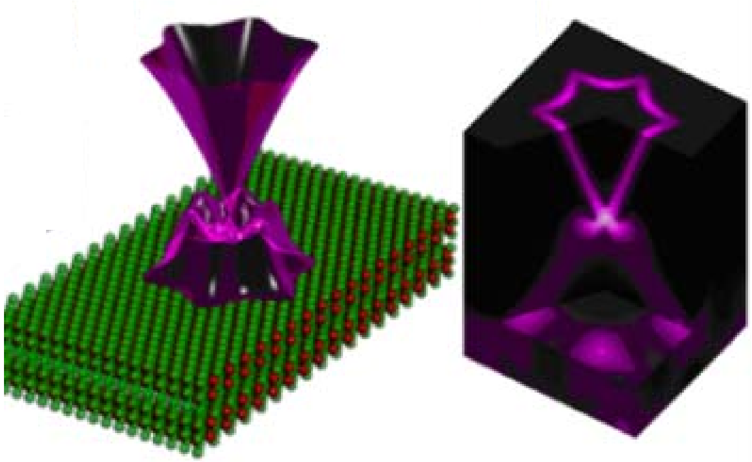
From: Ibach & Lueth

Angle resolved photoemission spectroscopy (ARPES)

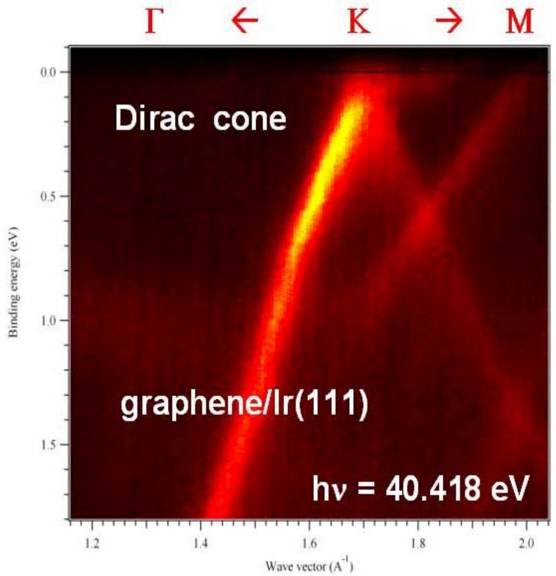
https://arpes.stanford.edu/research/tool-development/angle-resolved-photoemission-spectroscopy



Bi_2Te_3



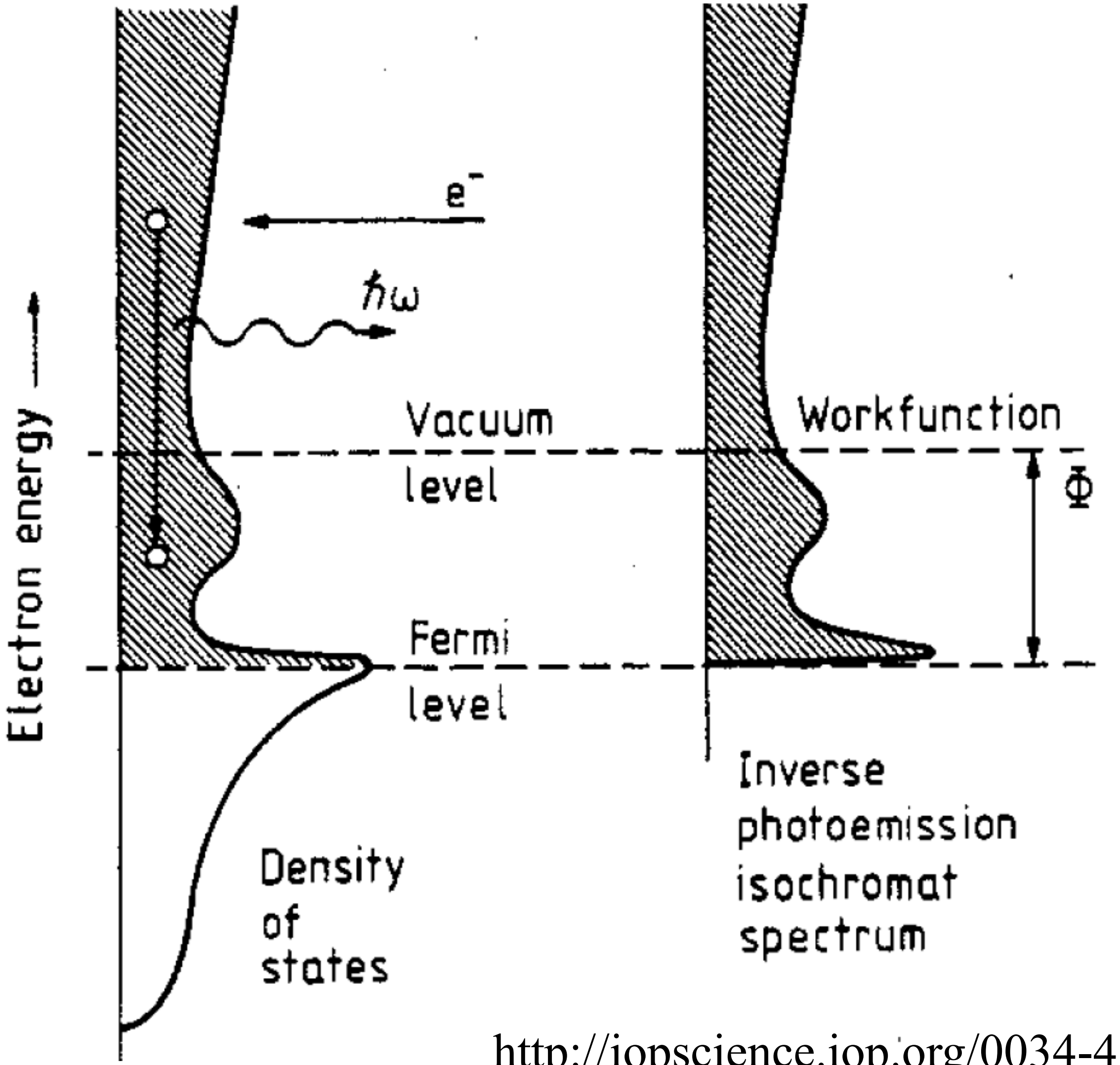
Topological insulator



http://server2.phys.uniroma1.it/gr/lotus/Instrumentation1_M.htm

Measure the dispersion relation with angle resolved photoemission

Inverse photoemission spectroscopy (IPES)



http://iopscience.iop.org/0034-4885/51/9/003

k-resolved Inverse Photoemission Spectroscopy (KRIPES)

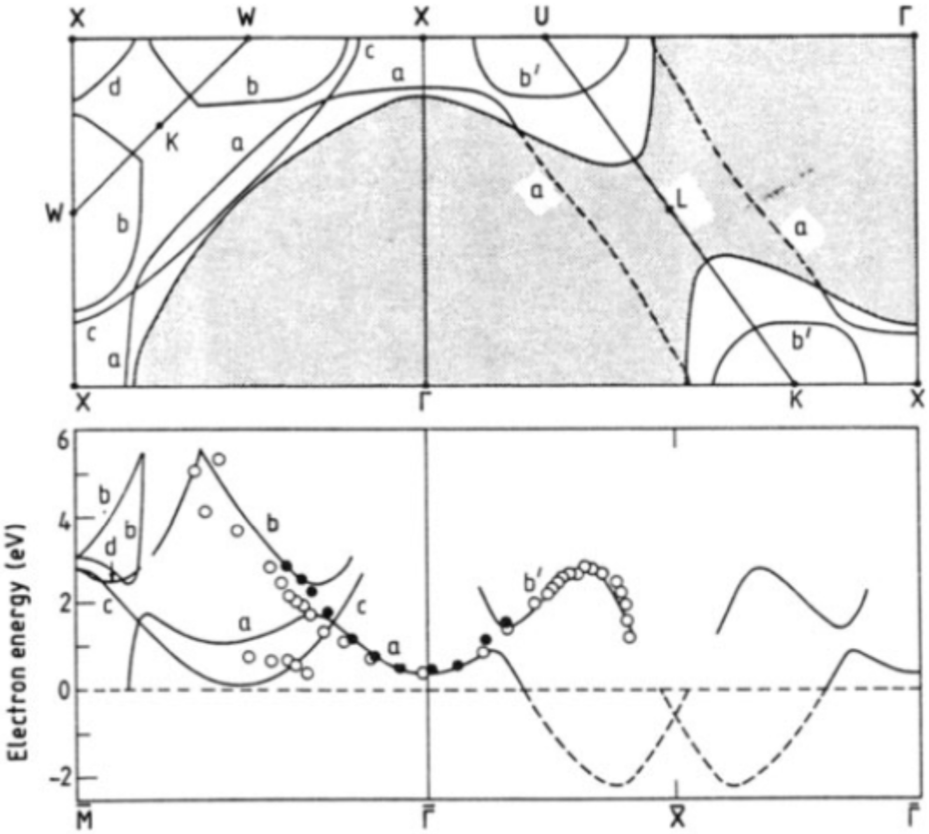
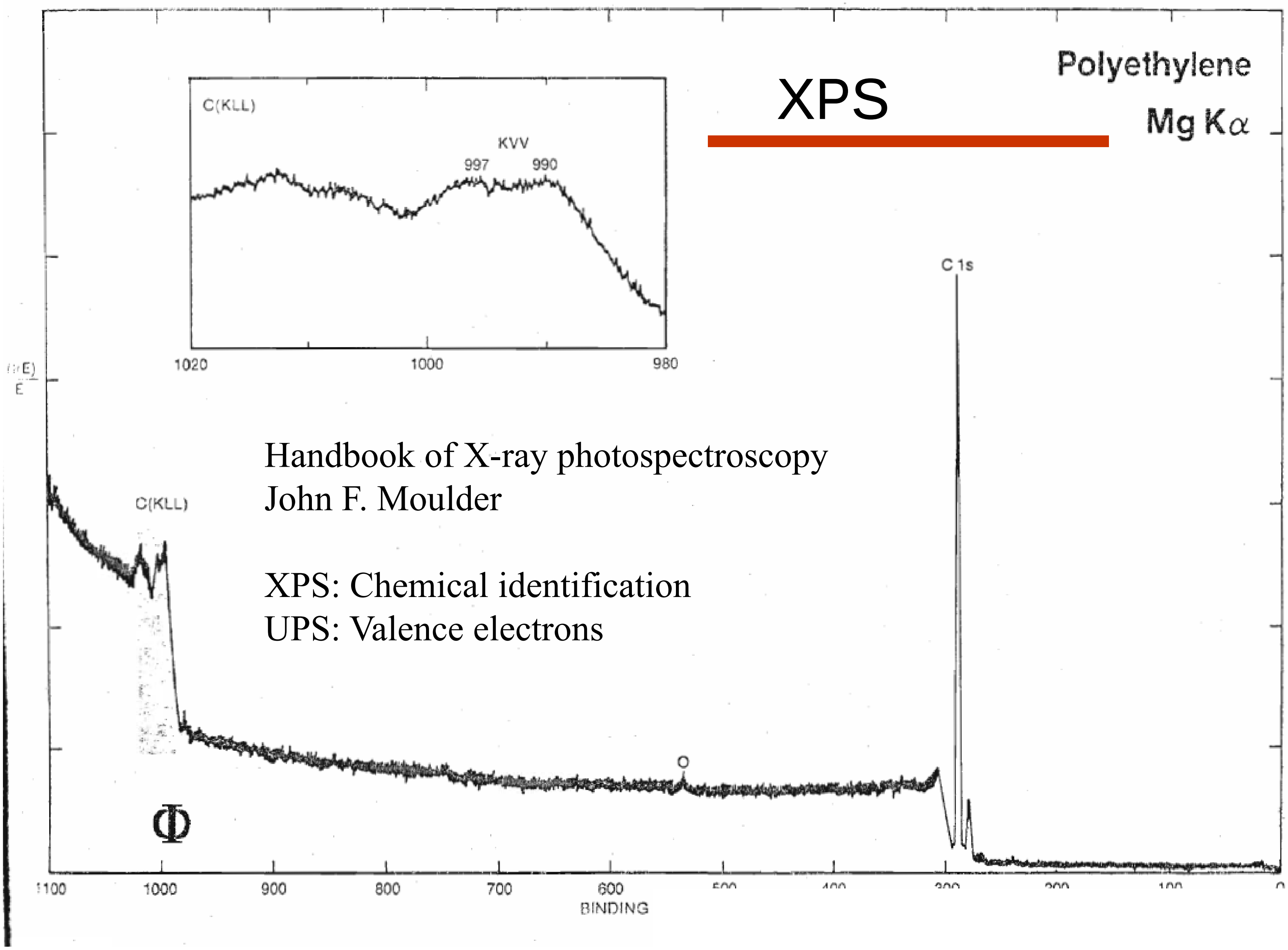


Figure 9. Band calculations and data for bulk direct transitions in the two principal azimuths $\bar{\Gamma}\bar{M}$ and $\bar{\Gamma}\bar{X}$ and Cu(001). Upper panel shows the Fermi surface and isochromat curves at $\hbar\omega = 9.7$ eV for transitions into band 6. Lower panel shows the corresponding $E_f(k_\parallel)$ projections. Computations and filled data circles are from Woodruff *et al* (1982); open circles are data from Jacob *et al* (1986).

http://iopscience.iop.org/0034-4885/51/9/003

XPS



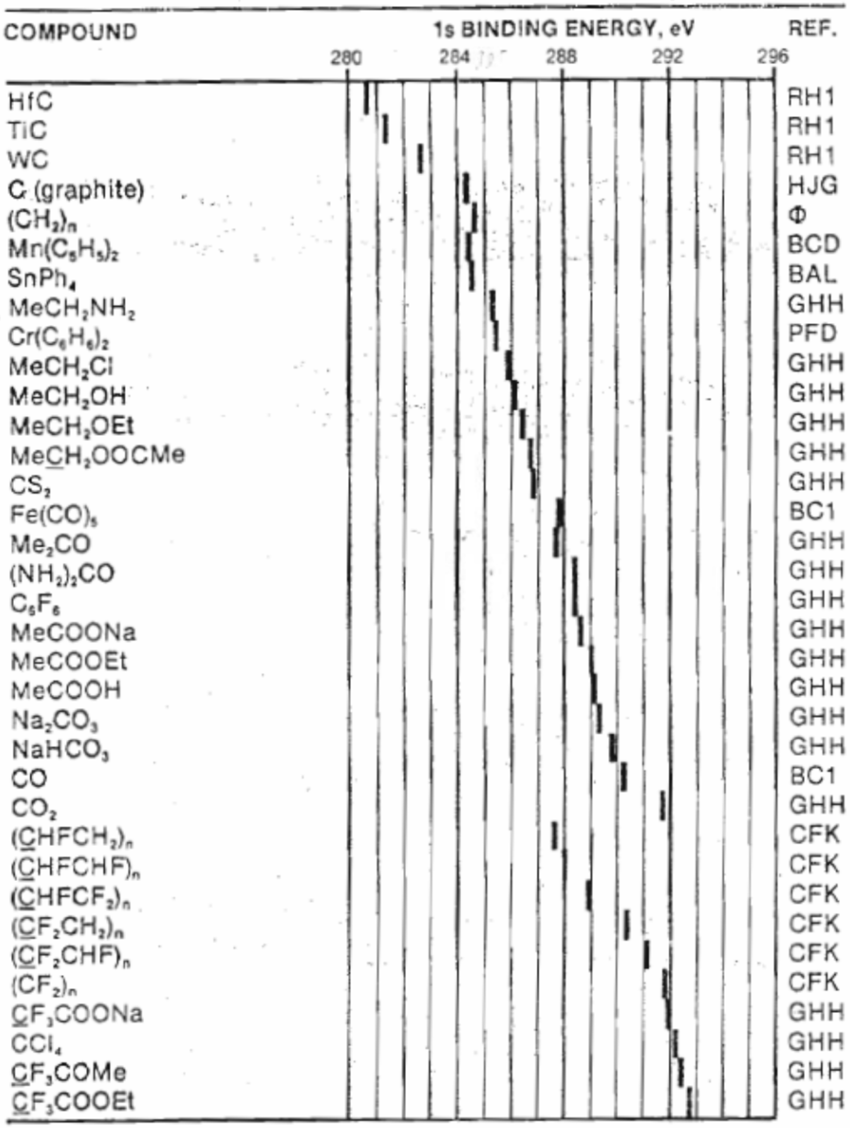
Handbook of X-ray photospectroscopy
John F. Moulder

XPS: Chemical identification
UPS: Valence electrons

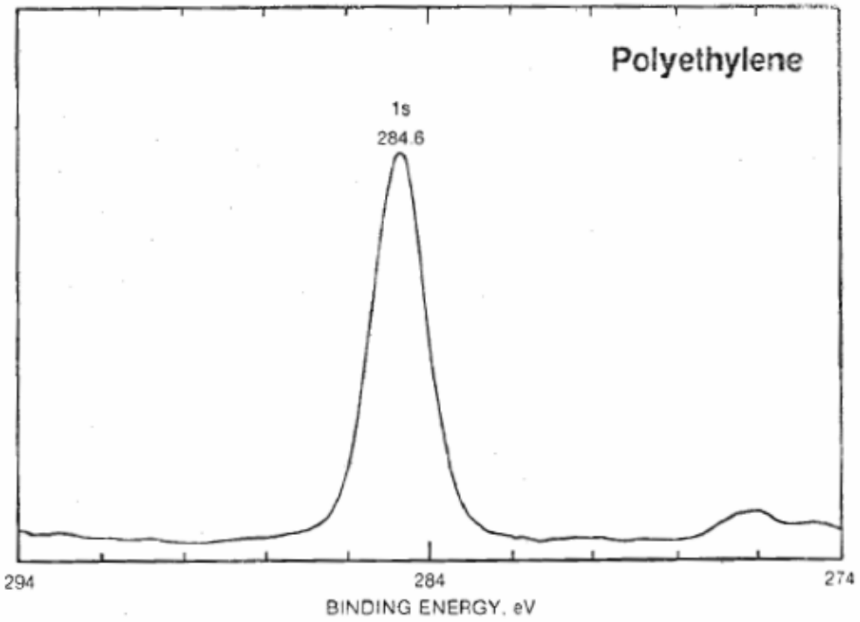
XPS

HANDBOOK OF X-RAY PHOTOELECTRON SPECTROSCOPY

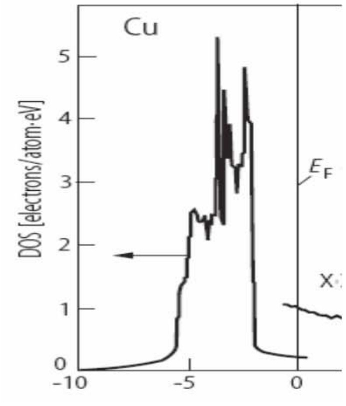
Carbon, C Atomic Number 6

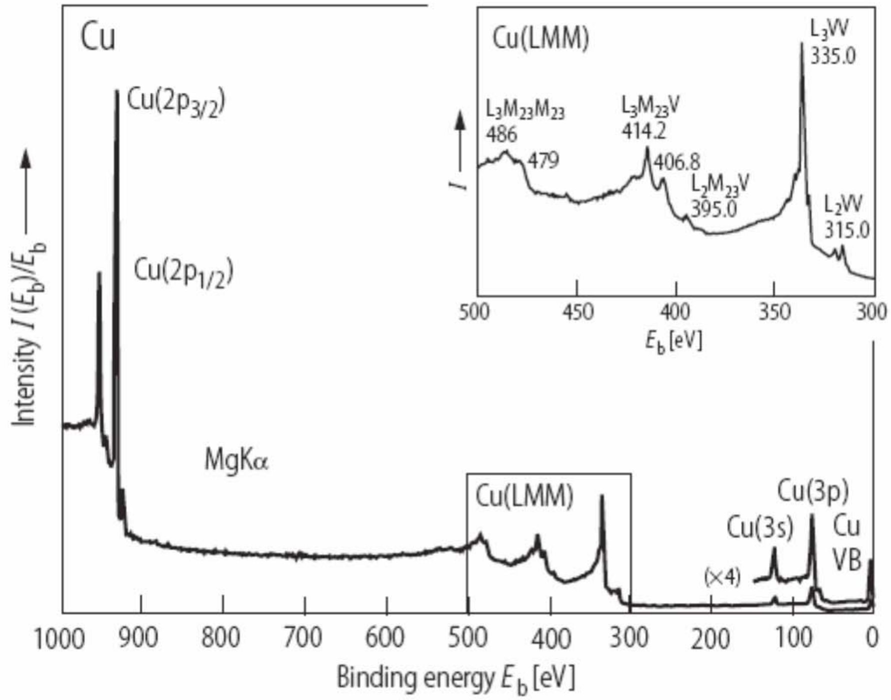


COMPOUND	REF.
HfC	RH1
TiC	RH1
WC	RH1
C (graphite)	HJG
$(CH_2)_n$	Φ
$Mn(C_5H_5)_2$	BCD
$SnPh_4$	BAL
$MeCH_2NH_2$	GHH
$Cr(C_6H_6)_2$	PFD
$MeCH_2Cl$	GHH
$MeCH_2OH$	GHH
$MeCH_2OEt$	GHH
$Me\underline{C}H_2OOCMe$	GHH
CS_2	GHH
$Fe(CO)_5$	BC1
Me_2CO	GHH
$(NH_2)_2CO$	GHH
C_6F_6	GHH
MeCOONa	GHH
MeCOOEt	GHH
MeCOOH	GHH
Na_2CO_3	GHH
$NaHCO_3$	GHH
CO	BC1
CO_2	GHH
$(\underline{C}HFCH_2)_n$	CFK
$(\underline{C}HFCHF)_n$	CFK
$(\underline{C}HFCF_2)_n$	CFK
$(\underline{C}F_2CH_2)_n$	CFK
$(\underline{C}F_2CHF)_n$	CFK
$(CF_2)_n$	CFK
$\underline{C}F_3COONa$	GHH
CCl_4	GHH
$\underline{C}F_3COMe$	GHH
$\underline{C}F_3COOEt$	GHH

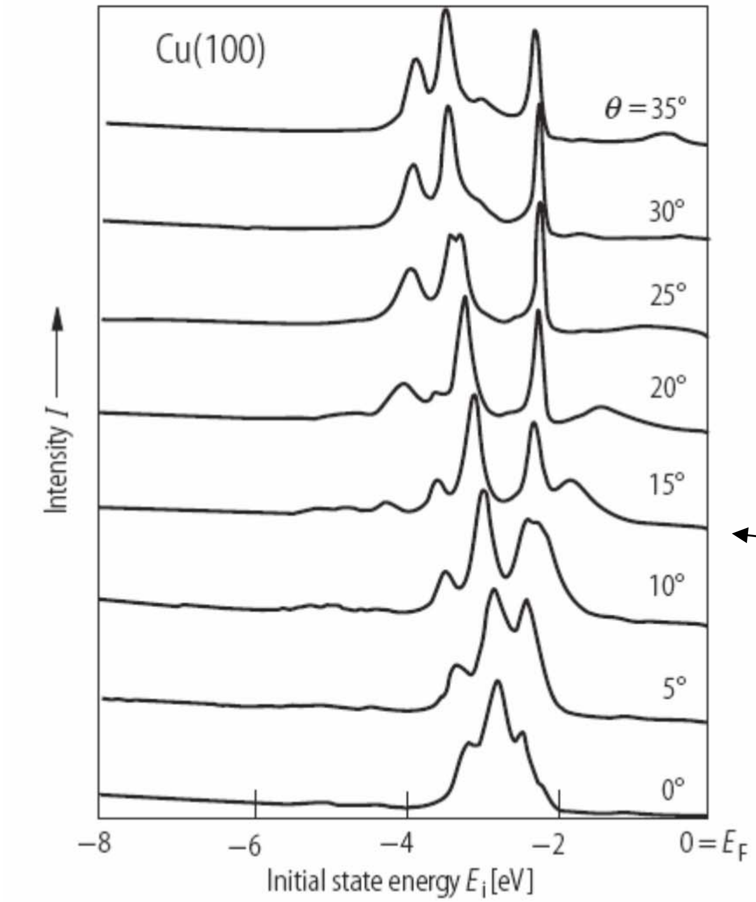


Cu





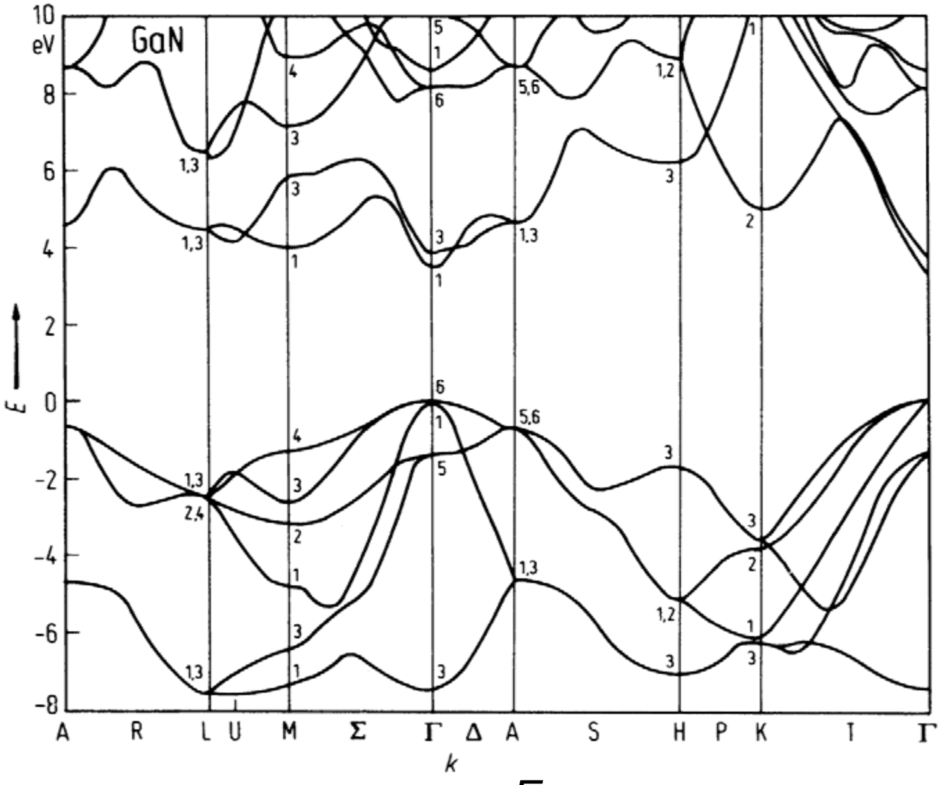
XPS

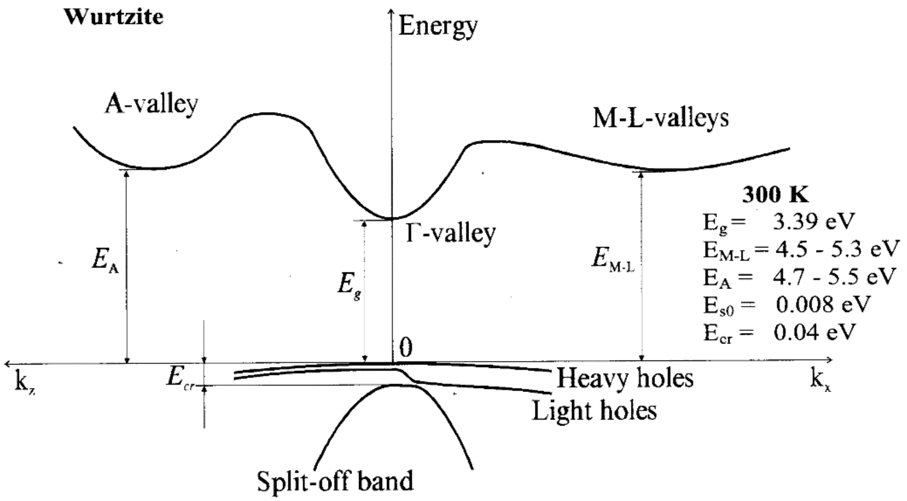


ARPES

Fig. 28. Cu(100). Angle-resolved photoelectron spectra taken at different polar angles θ along the ΓXUL bulk mirror plane. Photon energy $h\nu$ = 21.2 eV, sample temperature T = 50 K [93M1]. For further data taken at room temperature see [79H1]. For data taken with linear-polarized photons at $h\nu$ = 40° see [83G].

GaN





300 K

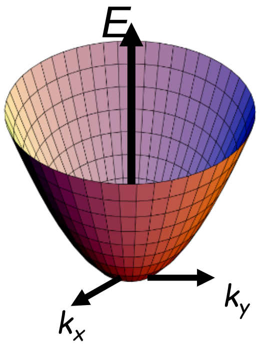
E_g = 3.39 eV

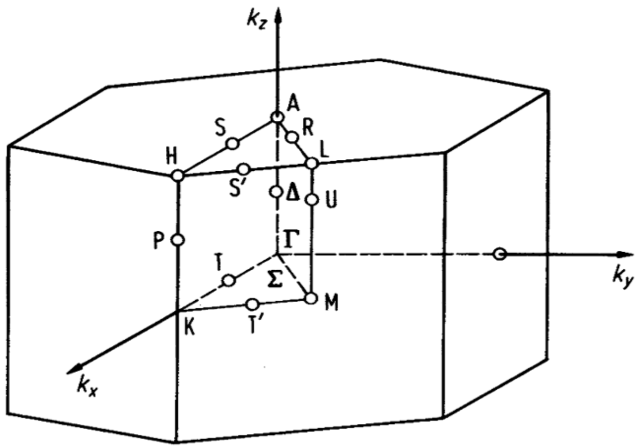
E_{M-L} = 4.5 - 5.3 eV

E_A = 4.7 - 5.5 eV

E_{so} = 0.008 eV

E_{cr} = 0.04 eV





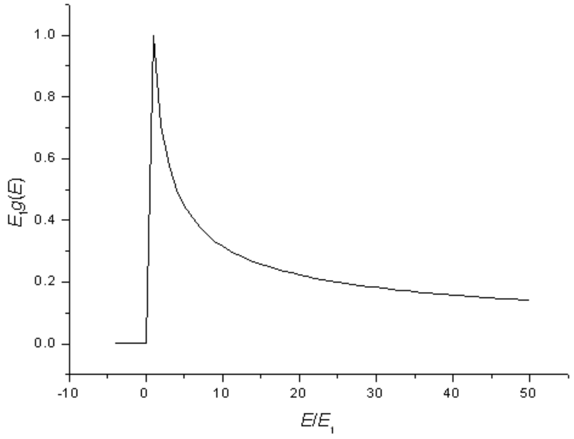
1st Brillioun zone of hcp

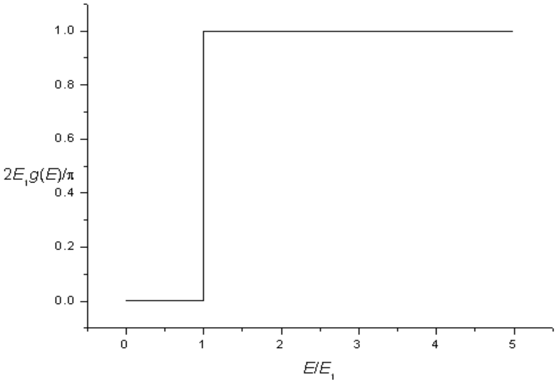
Free electron Fermi gas

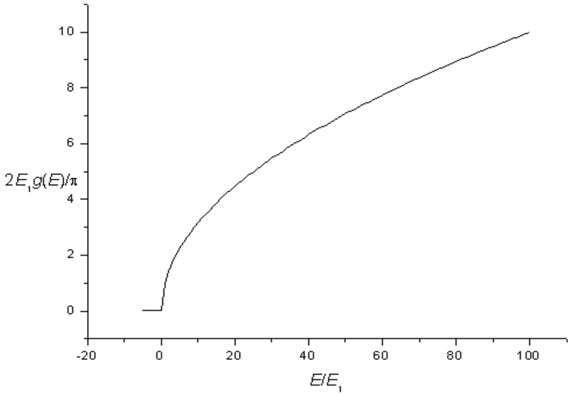
1 - d $$D(E) = \sqrt{\frac{2m}{\hbar^2 \pi^2 E}} = \frac{n}{2\sqrt{E_F E}} \quad \mathrm{J^{-1}m^{-1}}$$

2 - d $$D(E) = \frac{m}{\hbar^2 \pi} = \frac{n}{E_F} \quad \mathrm{J^{-1}m^{-2}}$$

3 - d $$D(E) = \frac{\pi}{2}\left(\frac{2m}{\hbar^2 \pi^2}\right)^{3/2} \sqrt{E} = \frac{3n}{2E_F^{3/2}}\sqrt{E} \quad \mathrm{J^{-1}m^{-3}}$$



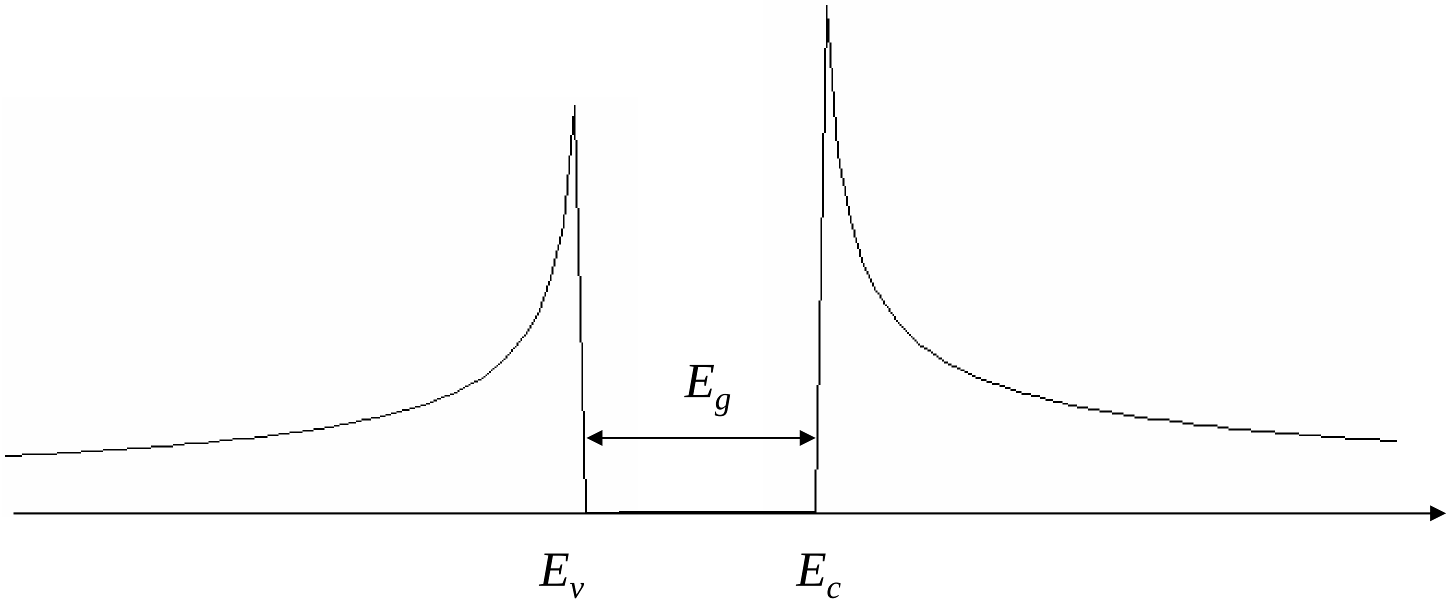




Semiconductors and insulators - 1d

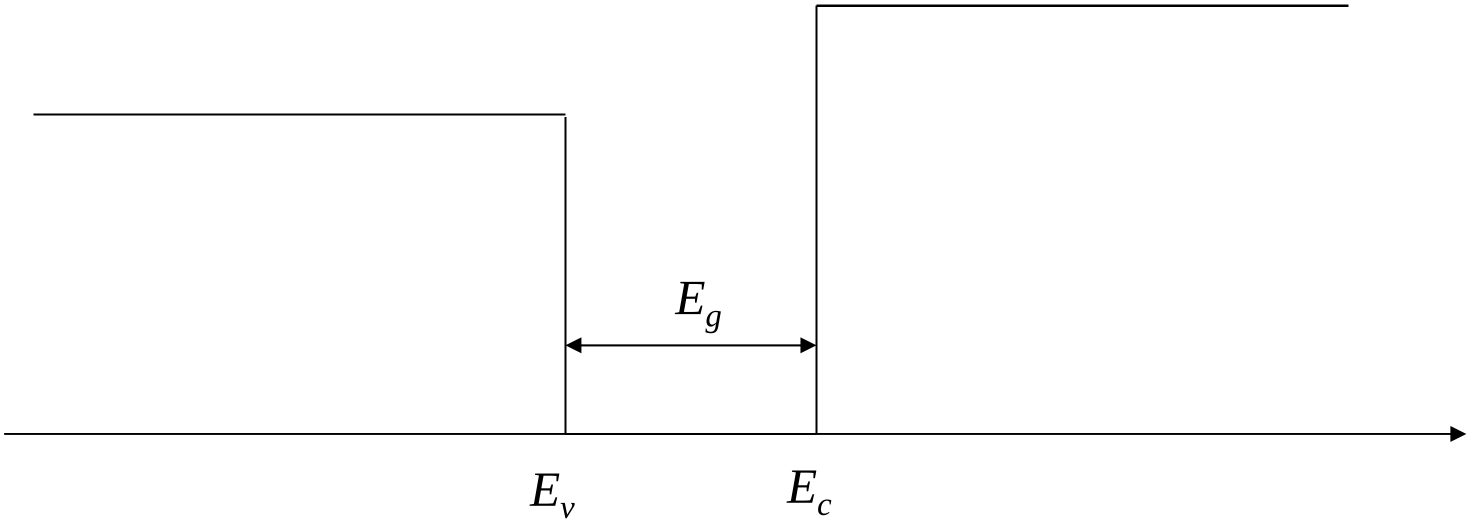
$$E = \frac{\hbar^2(\vec{k} - \vec{k}_0)^2}{2m^*}$$

$$D(E) = \begin{cases} \sqrt{\dfrac{2m_h^*}{\hbar^2\pi^2\left(E_v - E\right)}} & E < E_v \\ 0 & E_v < E < E_c \\ \sqrt{\dfrac{2m_e^*}{\hbar^2\pi^2\left(E - E_c\right)}} & E_c < E \end{cases} \quad \mathrm{J^{-1}m^{-3}}$$



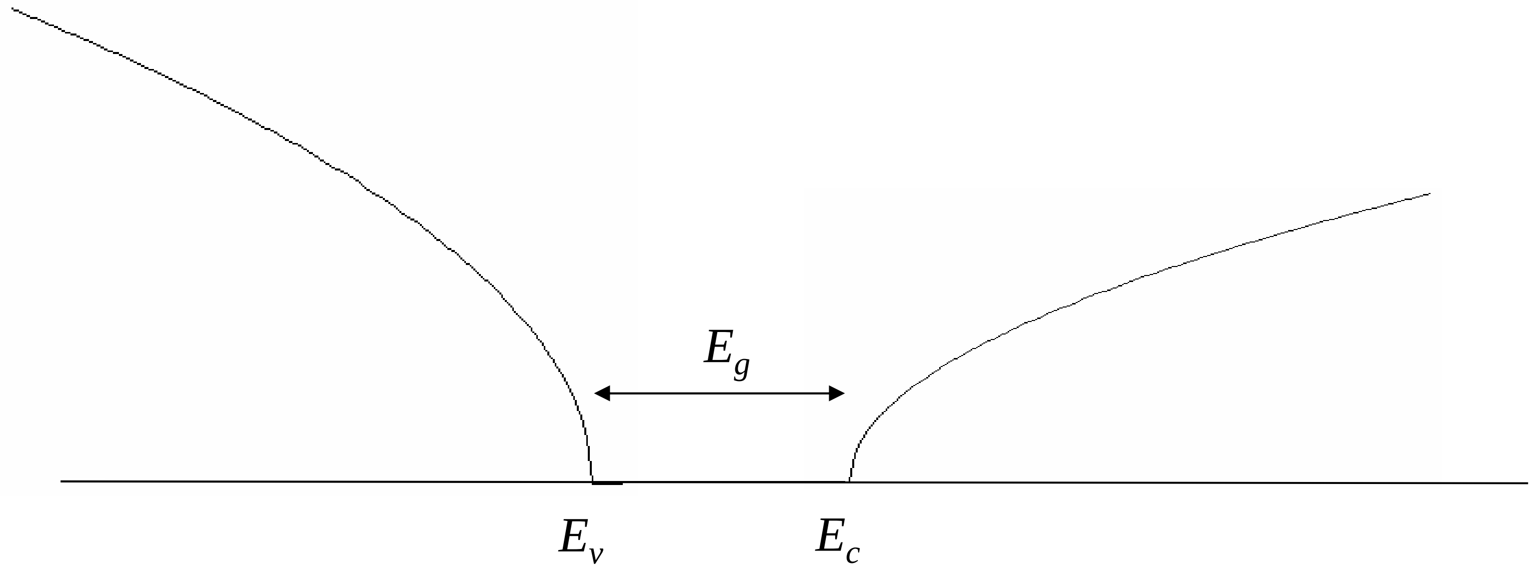
Semiconductors and insulators - 2d

$$D(E) = \begin{cases} \dfrac{m_h^*}{\hbar^2 \pi} & E < E_v \\ 0 & E_v < E < E_c \qquad \mathrm{J^{-1}m^{-3}} \\ \dfrac{m_e^*}{\hbar^2 \pi} & E_c < E \end{cases}$$

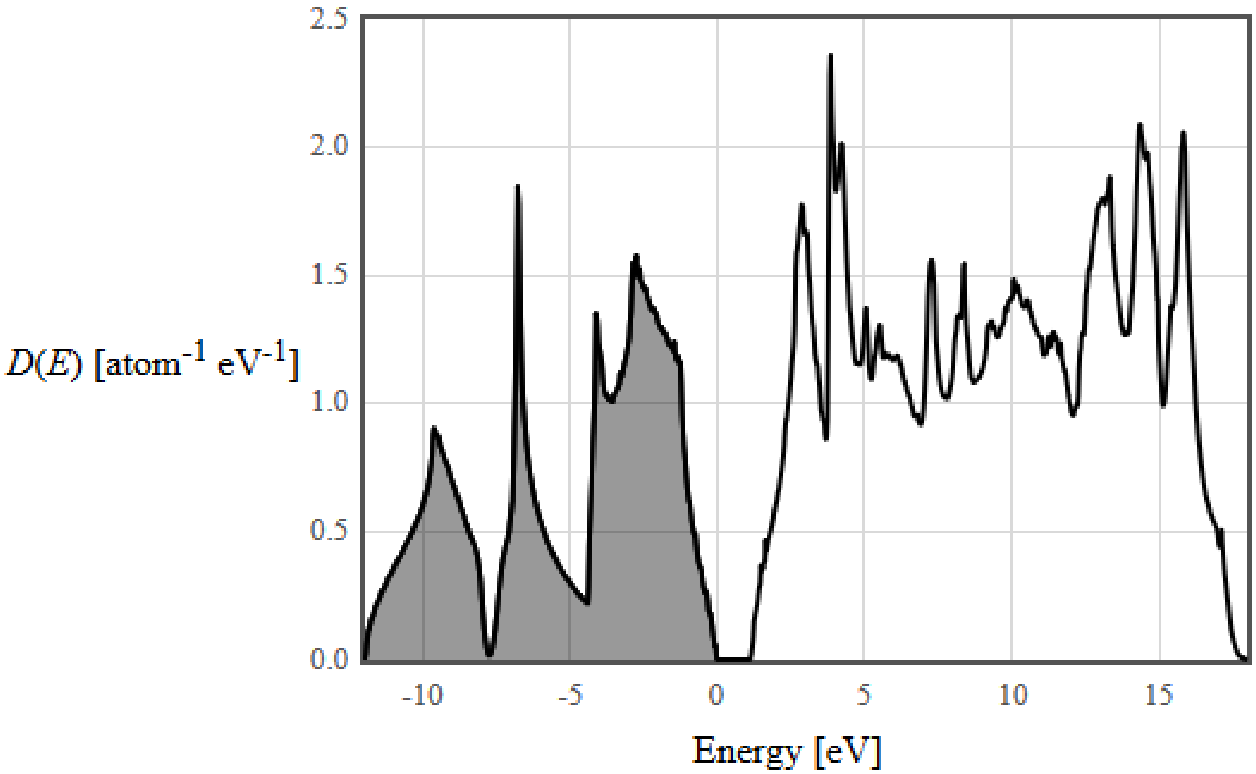


Semiconductors and insulators - 3d

$$D(E) = \begin{cases} \dfrac{\left(2m_h^*\right)^{\frac{3}{2}}}{2\pi^2\hbar^3}\sqrt{E_v - E} & E < E_v \\ 0 & E_v < E < E_c \\ \dfrac{\left(2m_e^*\right)^{\frac{3}{2}}}{2\pi^2\hbar^3}\sqrt{E - E_c} & E_c < E \end{cases} \quad \mathrm{J^{-1}m^{-3}}$$



Electron density of states for silicon



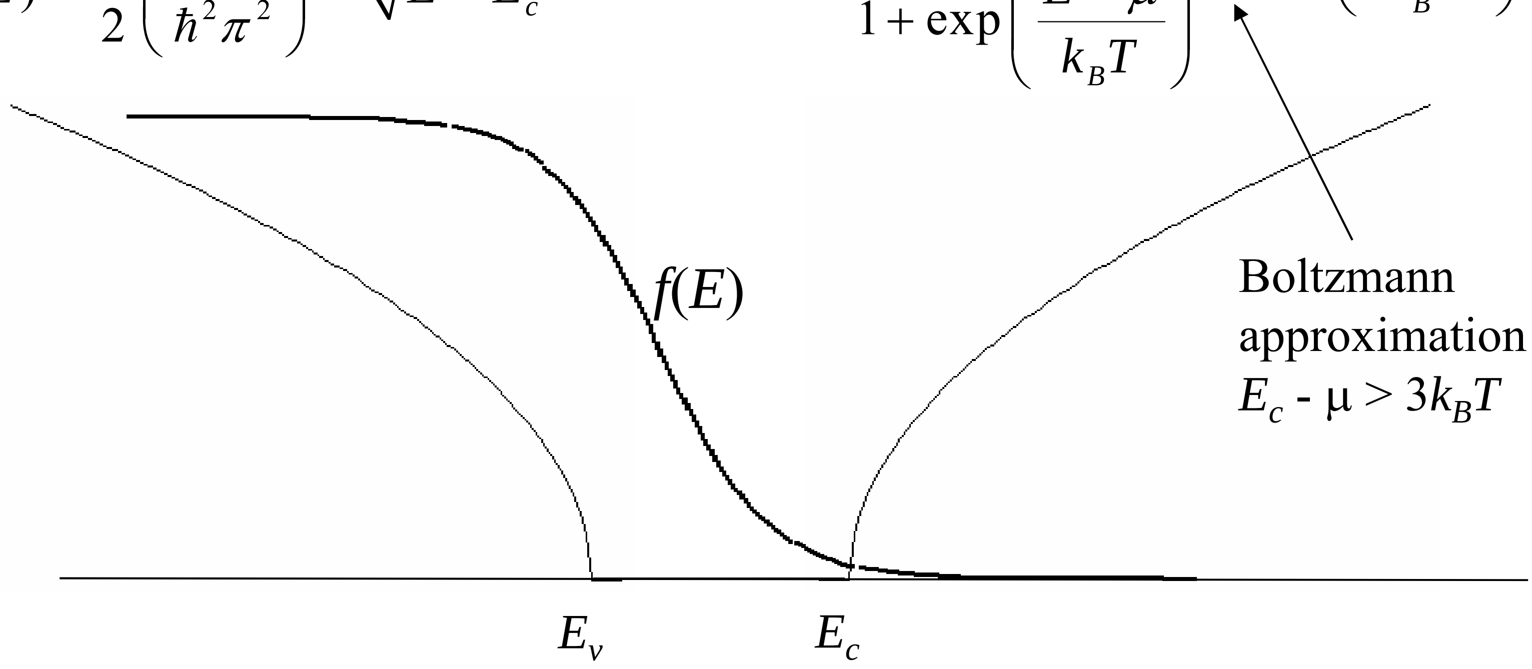
E [eV]	$D(E)$ [eV^{-1} atom^{-1}]	$D(E)$ [eV^{-1} m^{-3}]	$D(E)$ [J^{-1} m^{-3}]
-11.965	0	0	0
-11.935	0.02434	1.2155788844464289e+27	7.586935990802827e+45
-11.905	0.06415	3.203754537273558e+27	1.999597139728847e+46
-11.875	0.0932	4.654558423599309e+27	2.9051044960674754e+46
-11.845	0.117	5.843168836492694e+27	3.6469659446340623e+46
-11.815	0.1204	6.012970324048892e+27	3.752946151572146e+46
-11.785	0.1387	6.926901860013134e+27	4.3233690300918325e+46
-11.755	0.1578	7.88078668716707e+27	4.918728427891068e+46

Density of electrons in the conduction band

The free electron density of states is modified by the effective mass.

$$D(E) = \frac{\pi}{2}\left(\frac{2m^*}{\hbar^2\pi^2}\right)^{3/2}\sqrt{E - E_c}$$

$$f(E) = \frac{1}{1 + \exp\left(\frac{E-\mu}{k_B T}\right)} \approx \exp\left(\frac{\mu - E}{k_B T}\right)$$



Boltzmann
approximation
E_c - μ > 3k_BT

$$n = \int_{E_c}^{\infty} D(E) f(E) dE \approx \frac{\pi}{2}\left(\frac{2m^*}{\hbar^2\pi^2}\right)^{3/2}\int_{E_c}^{\infty}\exp\left(\frac{\mu - E}{k_B T}\right)\sqrt{E - E_c}\, dE$$

Density of electrons in the conduction band

$$n = \int_{E_c}^{\infty} D(E) f(E) dE \approx \frac{\pi}{2}\left(\frac{2m^*}{\hbar^2 \pi^2}\right)^{3/2} \int_{E_c}^{\infty} \exp\left(\frac{\mu - E}{k_B T}\right)\sqrt{E - E_c}\, dE$$

$$\frac{\sqrt{\pi}}{2} = \int_{0}^{\infty} \sqrt{x} e^{-x} dx$$

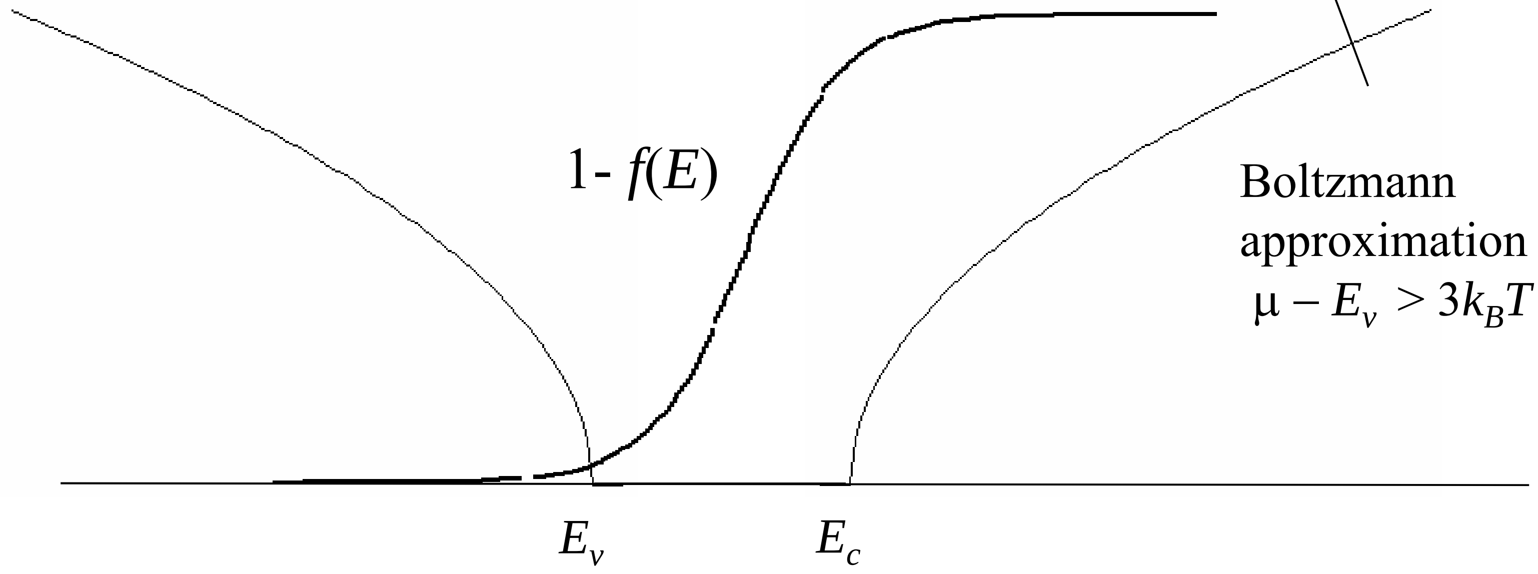
$$\boxed{n = N_c \exp\left(\frac{\mu - E_c}{k_B T}\right)}$$

$$N_c = 2\left(\frac{m^* k_B T}{2\pi\hbar^2}\right)^{3/2} = \text{effective density of states}$$

Density of holes in the valence band

$$D(E) = \frac{\pi}{2}\left(\frac{2m_h^*}{\hbar^2\pi^2}\right)^{3/2}\sqrt{E_v - E}$$

$$1 - f(E) = 1 - \frac{1}{1+\exp\left(\frac{E-\mu}{k_BT}\right)} \approx \exp\left(\frac{E-\mu}{k_BT}\right)$$



Boltzmann
approximation
$\mu - E_v > 3k_BT$

$$p = \int_{-\infty}^{E_v} D(E)\big(1 - f(E)\big)dE \approx \frac{\pi}{2}\left(\frac{2m_h^*}{\hbar^2\pi^2}\right)^{3/2}\int_{-\infty}^{E_v}\exp\left(\frac{E-\mu}{k_BT}\right)\sqrt{E_v - E}\,dE$$

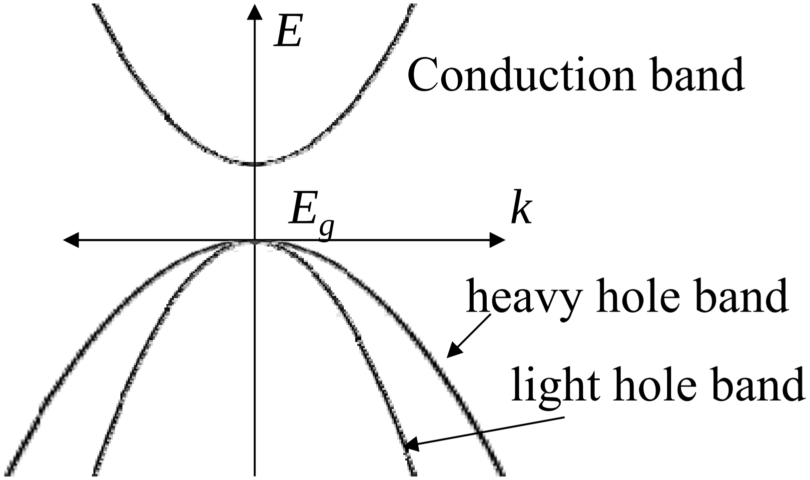
Density of holes in the valence band

$$p = \frac{1}{L^3}\int_{-\infty}^{E_v} N(E)\left(1 - f(E)\right)dE \approx \frac{\pi}{2}\left(\frac{2m_h^*}{\hbar^2\pi^2}\right)^{3/2}\int_{-\infty}^{E_v}\exp\left(\frac{E-\mu}{k_BT}\right)\sqrt{E_v - E}\,dE$$

$$\boxed{p = N_v \exp\left(\frac{E_v-\mu}{k_BT}\right)}$$

$$N_v = 2\left(\frac{m_h^* k_B T}{2\pi\hbar^2}\right)^{3/2}$$ = Effective density of states in the valence band

Semiconductors

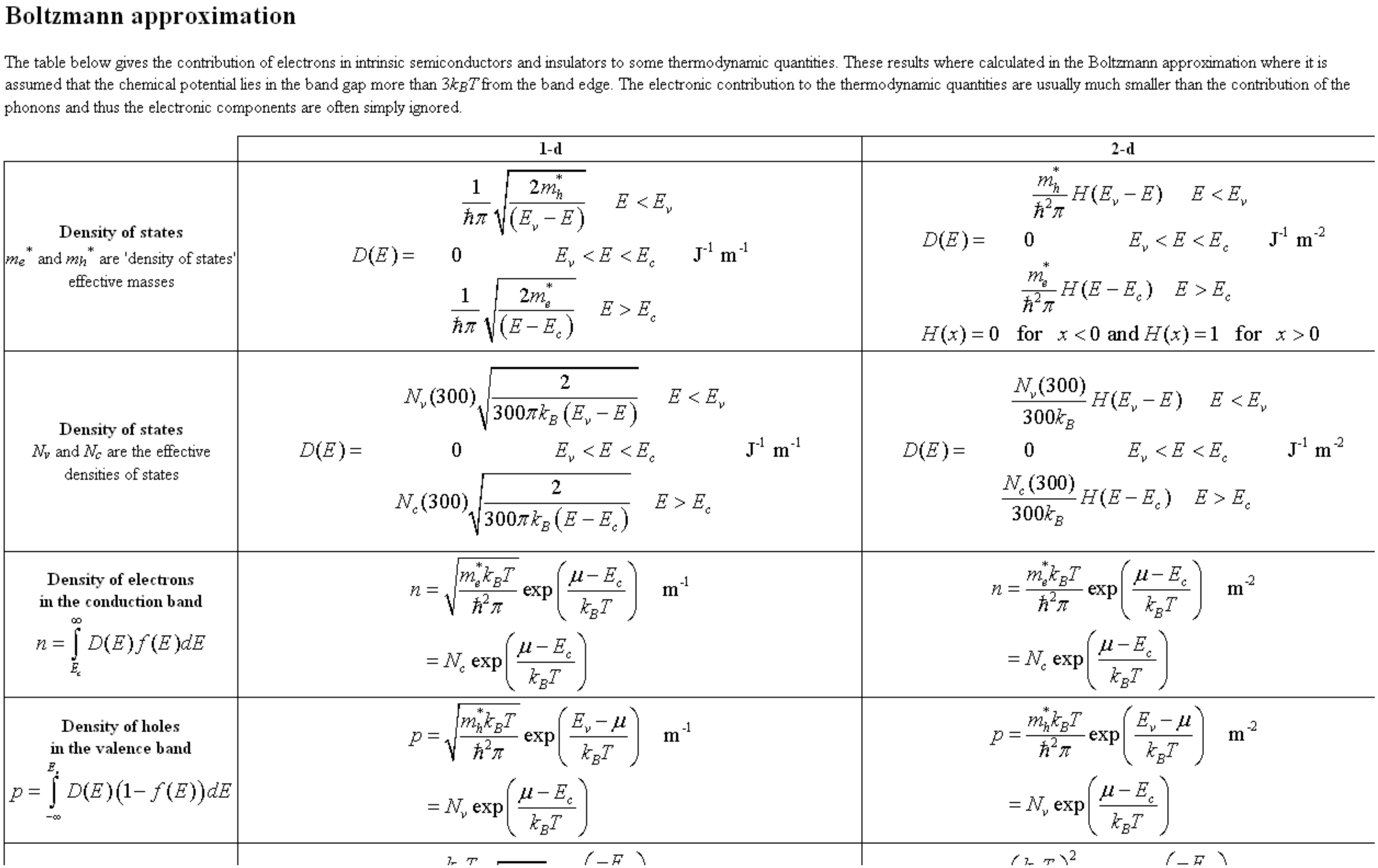


$$n = N_{c300}\left(\frac{T}{300}\right)^{3/2}\exp\left(\frac{\mu - E_c}{k_B T}\right)$$

$$p = N_{v300}\left(\frac{T}{300}\right)^{3/2}\exp\left(\frac{E_v - \mu}{k_B T}\right)$$

Properties	**Si**	**Ge**	**GaAs**
Bandgap E_g	1.12 eV	0.66 eV	1.424 eV
Effective density of states in conduction band (300 K) N_c	2.78×10^{25} m^{-3}	1.04×10^{25} m^{-3}	4.45×10^{23} m^{-3}
Effective density of states in valence band (300 K) N_v	9.84×10^{24} m^{-3}	6.0×10^{24} m^{-3}	7.72×10^{24} m^{-3}
Effective mass electrons m^*/m_0	$m_l^* = 0.98$ $m_t^* = 0.19$	$m_l^* = 1.64$ $m_t^* = 0.082$	$m^* = 0.067$
Effective mass holes m^*/m_0	$m_{lh}^* = 0.16$ $m_{hh}^* = 0.49$	$m_{lh}^* = 0.044$ $m_{hh}^* = 0.28$	$m_{lh}^* = 0.082$ $m_{hh}^* = 0.45$
Crystal structure	diamond	diamond	zincblende
Density	2.328 g/cm^3	5.3267 g/cm^3	5.32 g/cm^3
Atoms/m^3	5.0×10^{28}	4.42×10^{28}	4.42×10^{28}

The thermodynamic properties of insulators depend on band edges



Boltzmann approximation

The table below gives the contribution of electrons in intrinsic semiconductors and insulators to some thermodynamic quantities. These results where calculated in the Boltzmann approximation where it is assumed that the chemical potential lies in the band gap more than $3k_BT$ from the band edge. The electronic contribution to the thermodynamic quantities are usually much smaller than the contribution of the phonons and thus the electronic components are often simply ignored.

	1-d	**2-d**
Density of states m_e^* and m_h^* are 'density of states' effective masses	$D(E) = \begin{cases} \frac{1}{\hbar\pi}\sqrt{\frac{2m_h^*}{(E_v - E)}} & E < E_v \\ 0 & E_v < E < E_c \\ \frac{1}{\hbar\pi}\sqrt{\frac{2m_e^*}{(E - E_c)}} & E > E_c \end{cases}$ J^{-1} m^{-1}	$D(E) = \begin{cases} \frac{m_h^*}{\hbar^2\pi}H(E_v - E) & E < E_v \\ 0 & E_v < E < E_c \\ \frac{m_e^*}{\hbar^2\pi}H(E - E_c) & E > E_c \end{cases}$ J^{-1} m^{-2} $H(x) = 0$ for $x < 0$ and $H(x) = 1$ for $x > 0$
Density of states N_v and N_c are the effective densities of states	$D(E) = \begin{cases} N_v(300)\sqrt{\frac{2}{300\pi k_B(E_v - E)}} & E < E_v \\ 0 & E_v < E < E_c \\ N_c(300)\sqrt{\frac{2}{300\pi k_B(E - E_c)}} & E > E_c \end{cases}$ J^{-1} m^{-1}	$D(E) = \begin{cases} \frac{N_v(300)}{300k_B}H(E_v - E) & E < E_v \\ 0 & E_v < E < E_c \\ \frac{N_c(300)}{300k_B}H(E - E_c) & E > E_c \end{cases}$ J^{-1} m^{-2}
Density of electrons in the conduction band $n = \int_{E_c}^{\infty} D(E)f(E)dE$	$n = \sqrt{\frac{m_e^* k_B T}{\hbar^2\pi}}\exp\left(\frac{\mu - E_c}{k_BT}\right)$ m^{-1} $= N_c \exp\left(\frac{\mu - E_c}{k_BT}\right)$	$n = \frac{m_e^* k_B T}{\hbar^2\pi}\exp\left(\frac{\mu - E_c}{k_BT}\right)$ m^{-2} $= N_c \exp\left(\frac{\mu - E_c}{k_BT}\right)$
Density of holes in the valence band $p = \int_{-\infty}^{E_v} D(E)(1 - f(E))dE$	$p = \sqrt{\frac{m_h^* k_B T}{\hbar^2\pi}}\exp\left(\frac{E_v - \mu}{k_BT}\right)$ m^{-1} $= N_v \exp\left(\frac{\mu - E_c}{k_BT}\right)$	$p = \frac{m_h^* k_B T}{\hbar^2\pi}\exp\left(\frac{E_v - \mu}{k_BT}\right)$ m^{-2} $= N_v \exp\left(\frac{\mu - E_c}{k_BT}\right)$

Intrinsic semiconductors

In the Boltzmann approximation, the density of states of a semiconductor is,

$$D(E) = \begin{cases} \frac{(2m_h^*)^{3/2}}{2\pi^2\hbar^3}\sqrt{E_v - E}, & \text{for } E < E_v \\ 0, & \text{for } E_v < E < E_c \\ \frac{(2m_e^*)^{3/2}}{2\pi^2\hbar^3}\sqrt{E - E_c}, & \text{for } E_c < E \end{cases}$$

Here m_e^* and m_h^* are the 'density of states effective masses' for electrons and holes. Usually in the literature, effective density of states at 300 K is given instead of the 'density of states effective masses'. The relationship between the two is,

$$m_h^* = \frac{\pi\hbar^2}{300k_B}\left(\sqrt{2}N_v(300)\right)^{2/3}$$

$$m_e^* = \frac{\pi\hbar^2}{300k_B}\left(\sqrt{2}N_c(300)\right)^{2/3}$$

The density of states can therefore also be written as,

$$D(E) = \begin{cases} \frac{2N_v(300)}{\sqrt{\pi}}\left(\frac{1}{300k_B}\right)^{3/2}\sqrt{E_v - E}, & \text{for } E < E_v \\ 0, & \text{for } E_v < E < E_c \\ \frac{2N_c(300)}{\sqrt{\pi}}\left(\frac{1}{300k_B}\right)^{3/2}\sqrt{E - E_c}, & \text{for } E_c < E \end{cases}$$

In an intrinsic semiconductor, the density of electrons equals the density of holes. The intrinsic carrier concentration, n_i, depends exponentially on the bandgap, E_g. For most semiconductors the bandgap is a function of temperature. The plots on this page use the temperature dependence specified in the form below.

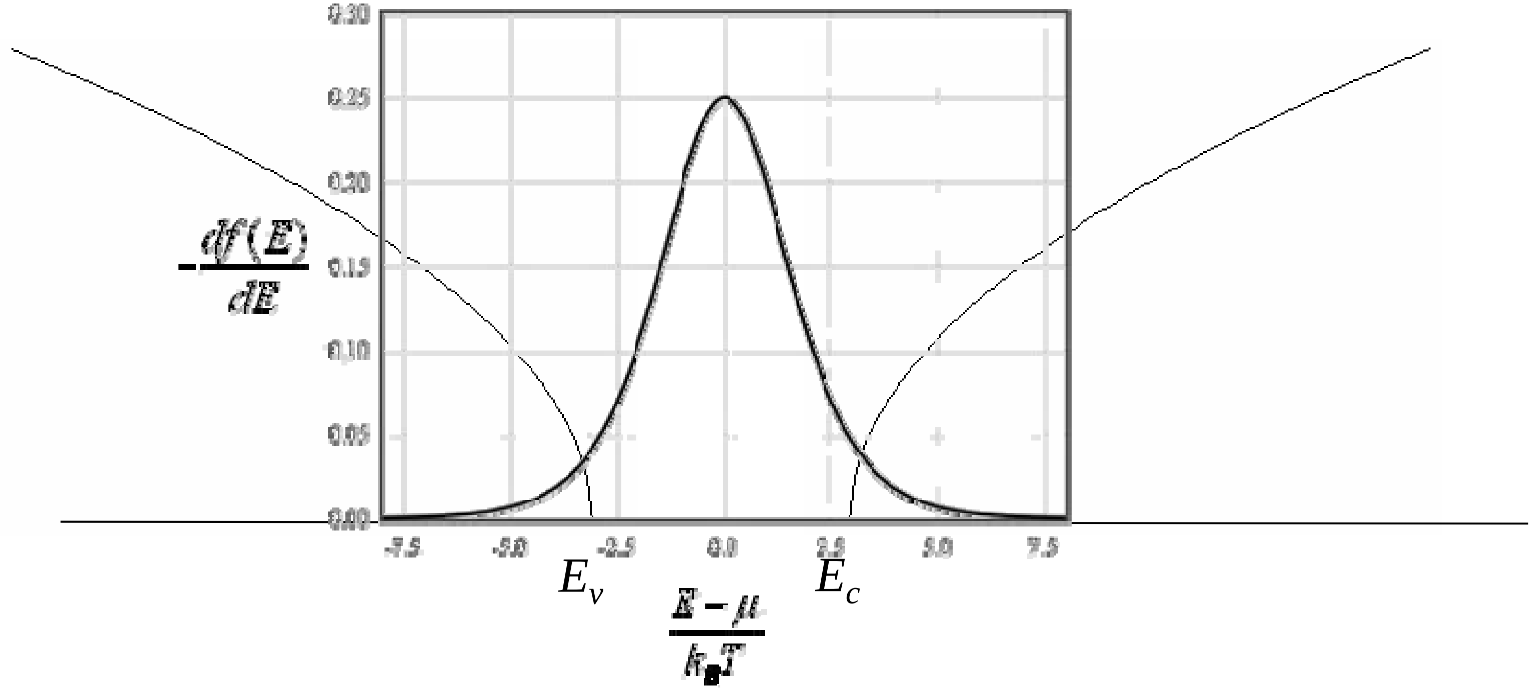
$$n = p = n_i = \sqrt{N_c\left(\frac{T}{300}\right)^{3/2}N_v\left(\frac{T}{300}\right)^{3/2}}\exp\left(\frac{-E_g}{2k_BT}\right).$$

By setting the concentration of electrons equal to the concentration of holes, it is possible to solve for the chemical potential.

$$n = N_c(300)\left(\frac{T}{300}\right)^{3/2}\exp\left(\frac{\mu - E_c}{k_BT}\right) = p = N_v(300)\left(\frac{T}{300}\right)^{3/2}\exp\left(\frac{E_v - \mu}{k_BT}\right).$$

$$\mu = \frac{E_v + E_c}{2} + k_BT\ln\left(\frac{N_v(300)}{N_c(300)}\right).$$

Narrow bandgap semiconductors



Use the programs for metals for small bandgap semiconductors.