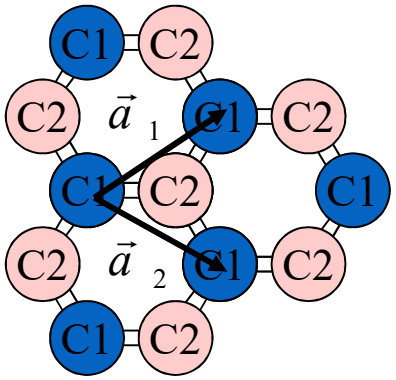
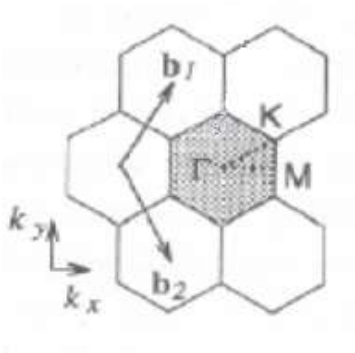
Graphene



$$\vec{a}_1 = \frac{\sqrt{3}}{2} a\hat{x} + \frac{1}{2} a\hat{y}$$

$$\vec{a}_2 = \frac{\sqrt{3}}{2} a\hat{x} - \frac{1}{2} a\hat{y}$$



Two atoms per unit cell

Graphene has an unusual dispersion relation in the vicinity of the Fermi energy.

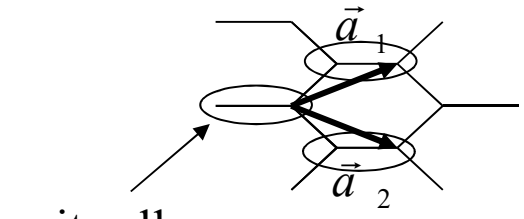
$$\psi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{h,j,l} e^{i\left(h\vec{k}\cdot\vec{a}_1 + j\vec{k}\cdot\vec{a}_2 + l\vec{k}\cdot\vec{a}_3\right)} \sum_{a} \sum_{ao} c_{ao,a} \phi_{ao}^{Z_a}(\vec{r} - \vec{r}_a)$$

Tight binding graphene

$$\begin{vmatrix} \varepsilon - E & -t\sum_m e^{i\vec{k}\cdot\vec{\rho}_m} \\ -t\sum_m e^{-i\vec{k}\cdot\vec{\rho}_m} & \varepsilon - E \end{vmatrix} = 0$$

$$\sum_m e^{i\vec{k}\cdot\vec{\rho}_m} = \left(1 + \exp\left(i\left(\frac{\sqrt{3}k_x a}{2} + \frac{k_y a}{2}\right)\right) + \exp\left(i\left(\frac{\sqrt{3}k_x a}{2} - \frac{k_y a}{2}\right)\right)\right)$$

$\vec{k}\cdot\vec{a}_1$ $\qquad$ $\vec{k}\cdot\vec{a}_2$



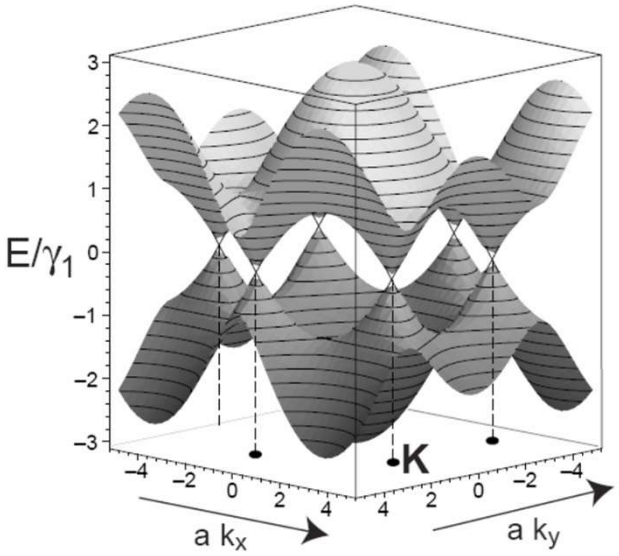
$$\vec{a}_1 = \frac{\sqrt{3}}{2}a\hat{x} + \frac{1}{2}a\hat{y}$$

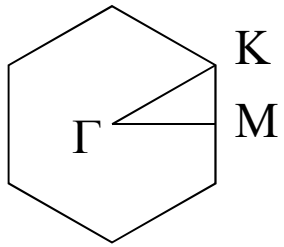
$$\vec{a}_2 = \frac{\sqrt{3}}{2}a\hat{x} - \frac{1}{2}a\hat{y}$$

There will be two eigen energies for every *k*.

Tight binding, graphene

$$E = \varepsilon \pm t\sqrt{1 + 4\cos\left(\frac{\sqrt{3}k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right) + 4\cos^2\left(\frac{k_y a}{2}\right)}$$



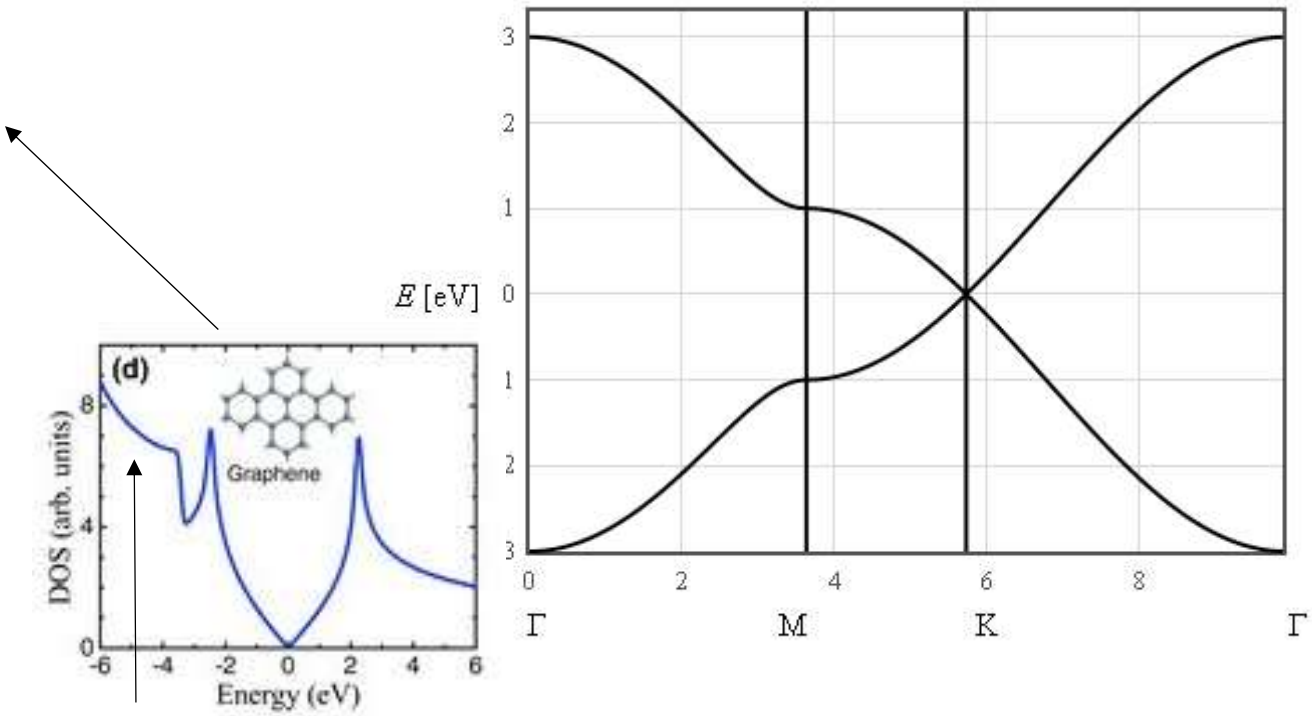


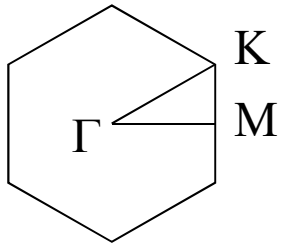
www.physics.umd.edu/courses/Phys732/hdrew/spring07/Schoenenberger%20tutorial%20on%20CNT%20bands.pdf

http://onlinelibrary.wiley.com/doi/10.1002/adfm.201101241/full

Tight binding dispersion relation for graphene

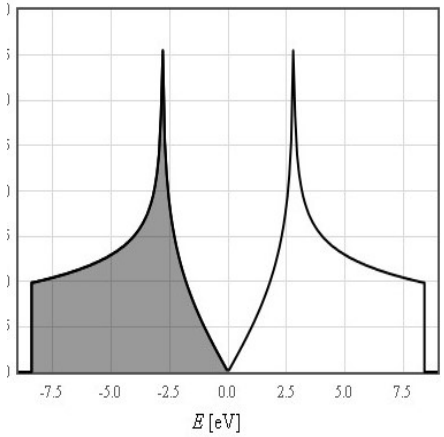
$$E = \varepsilon \pm t\sqrt{1+4\cos\left(\frac{\sqrt{3}k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right)+4\cos^2\left(\frac{k_y a}{2}\right)}$$



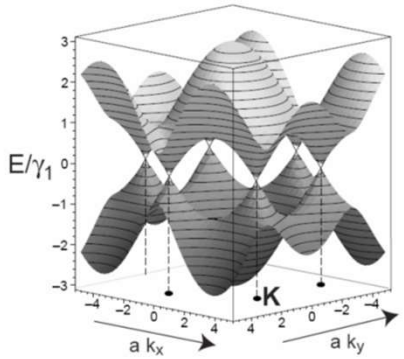


ε = 0 [eV]
t = 2.8 [eV]
Replot E(k)

Another band is included here.

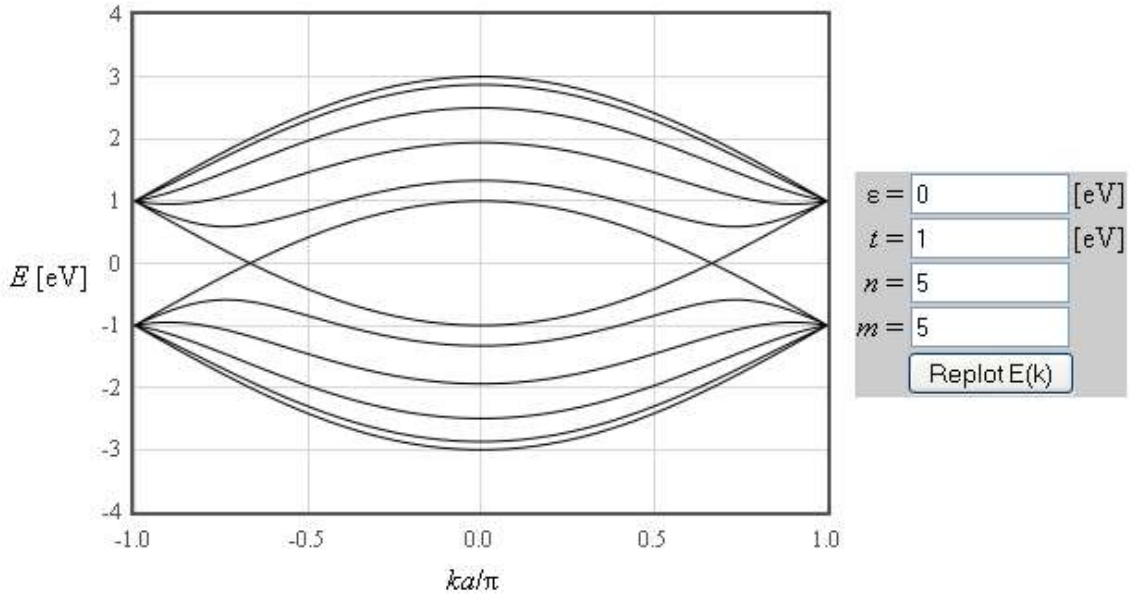


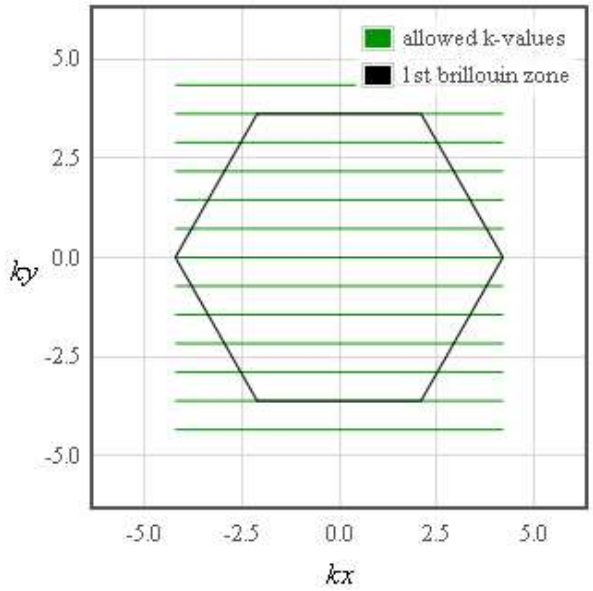
http://lamp.tu-graz.ac.at/~hadley/ss1/bands/tbtable/dispgraphene.html



Carbon nanotubes

$$E = \varepsilon \pm t\sqrt{1 + 4\cos\left(\frac{\sqrt{3}k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right) + 4\cos^2\left(\frac{k_y a}{2}\right)}$$





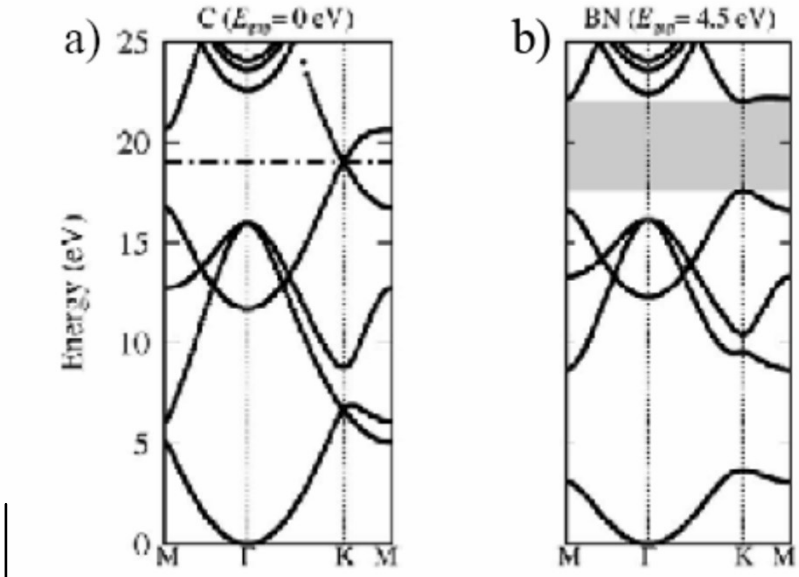
metallic (5,5) armchair tube

http://lamp.tu-graz.ac.at/~hadley/ss1/bands/tbtable/CNTs.html

Other nanotubes

Tungsten disulfide
Boron nitride
Silicon
Titanium dioxide
Molybdenum disulfide

$$\begin{vmatrix} \langle \psi_a | H | \psi_a \rangle - E & \langle \psi_a | H | \psi_b \rangle \sum_m e^{i\vec{k}\cdot\vec{\rho}_m} \\ \langle \psi_b | H | \psi_a \rangle \sum_m e^{-i\vec{k}\cdot\vec{\rho}_m} & \langle \psi_b | H | \psi_b \rangle - E \end{vmatrix} = 0$$



graphene

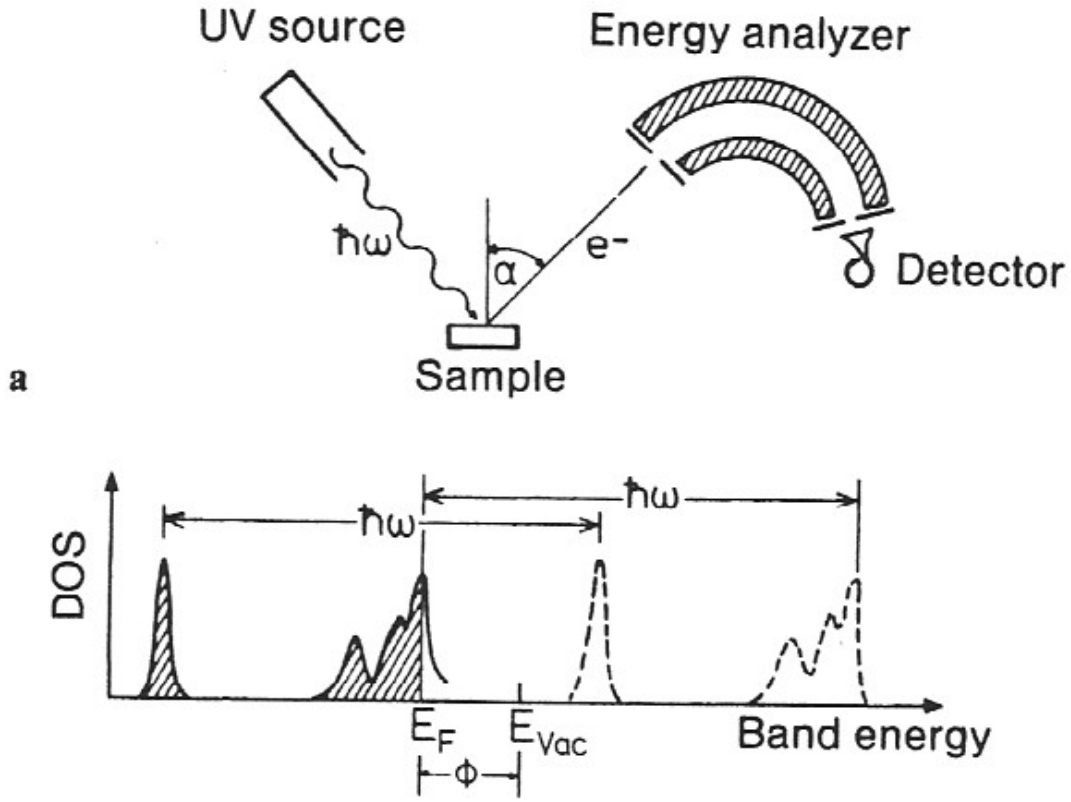
Boron nitride

Photoemission spectroscopy

UPS - Ultraviolet photoemission spectroscopy

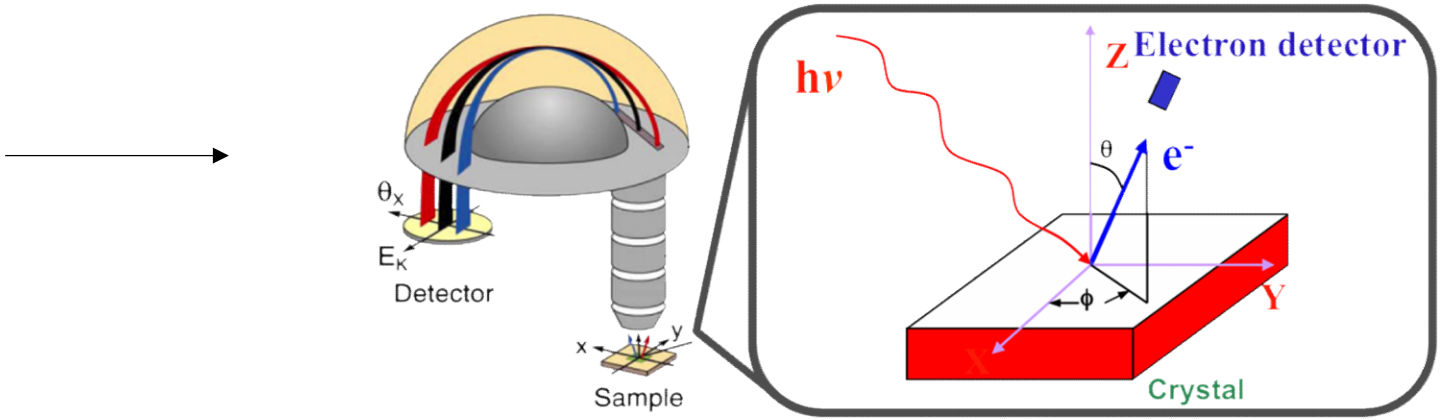
XPS - X-ray photoemission spectroscopy

Measure the density of states with photoemission spectroscopy

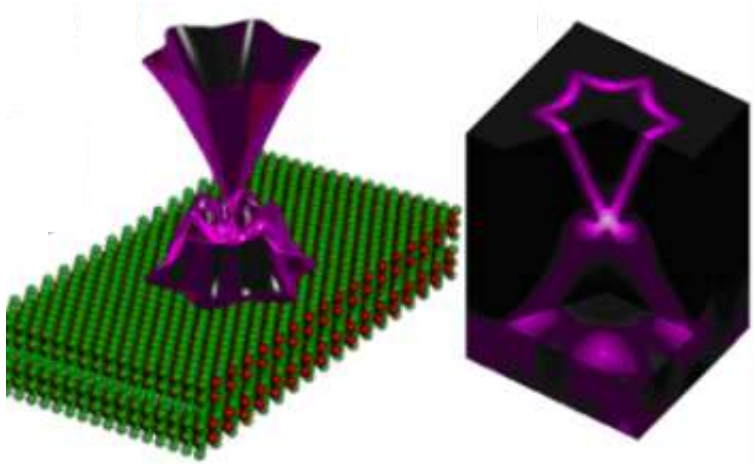


From: Ibach & Lueth

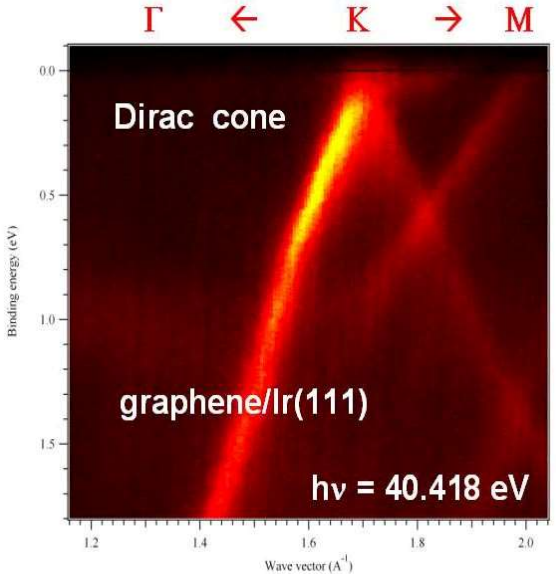
Angle resolved photoemission spectroscopy (ARPES)



Bi_2Te_3



Topological insulator

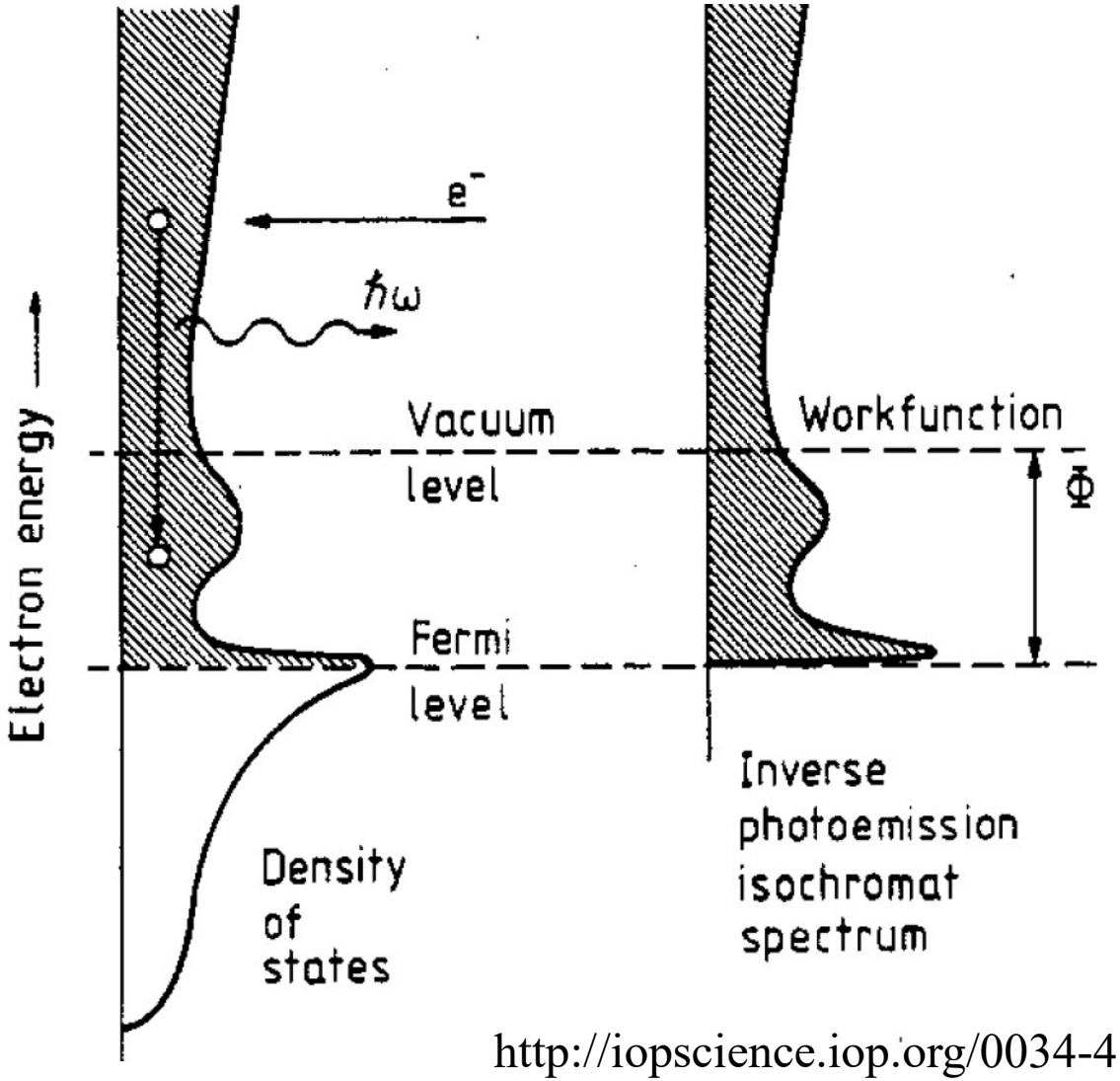


Measure the dispersion relation with angle resolved photoemission

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

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

Inverse photoemission spectroscopy (IPES)



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

k-resolved Inverse Photoemission Spectroscopy (KRIPES)

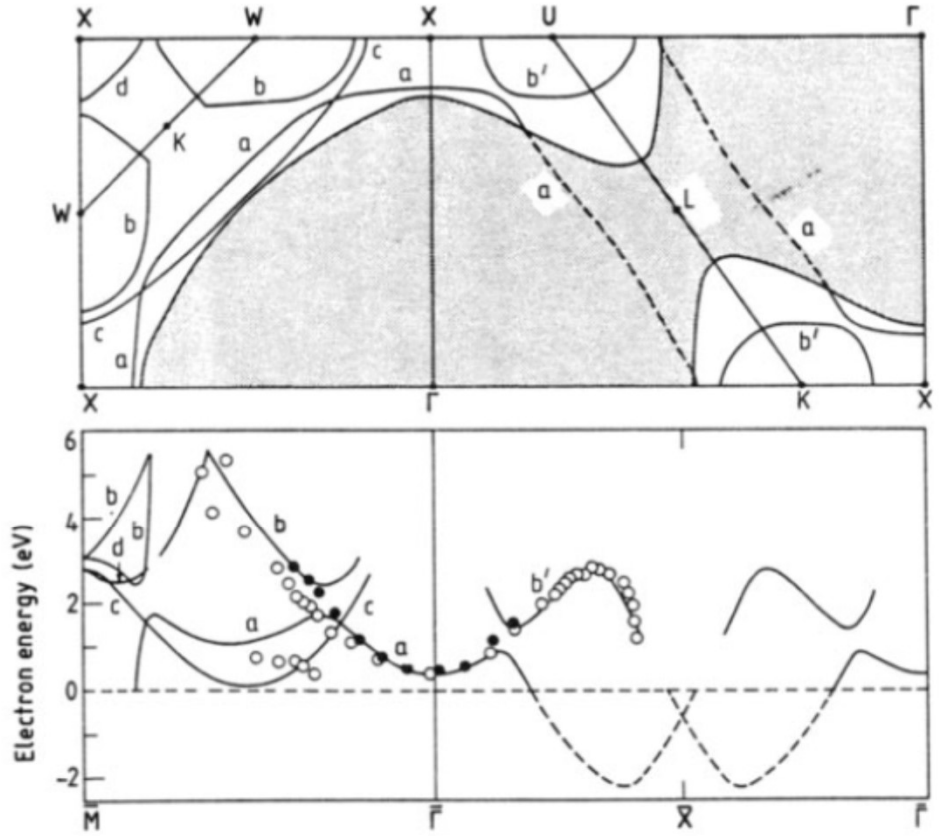
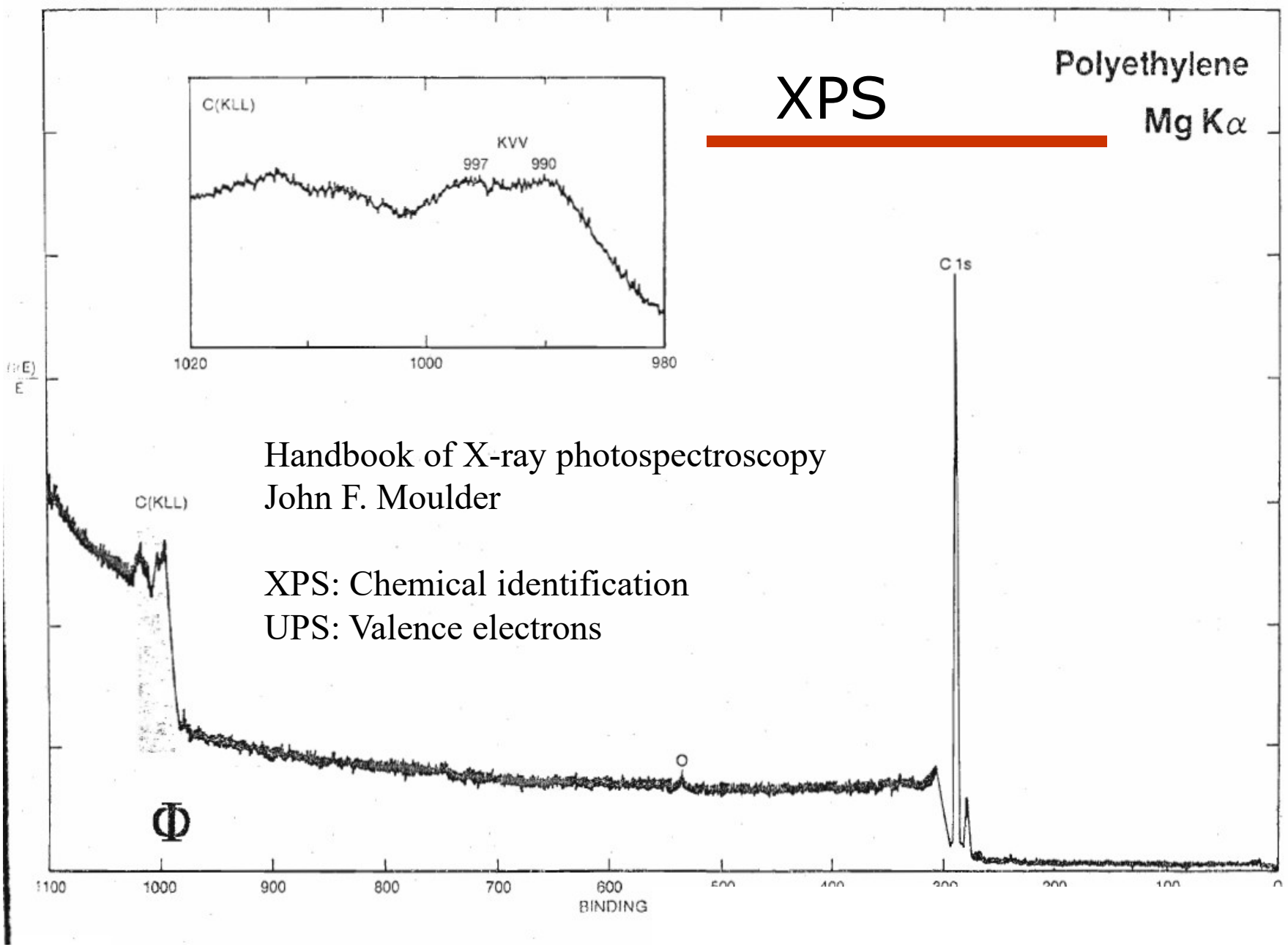


Figure 9. Band calculations and data for bulk direct transitions in the two principal azimuths $\bar{\Gamma}\bar{M}$ and $\bar{\Gamma}\bar{X}$ and Cu(001). Upper panel shows the Fermi surface and isochromat curves at $\hbar\omega = 9.7$ eV for transitions into band 6. Lower panel shows the corresponding $E_f(k_\parallel)$ 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



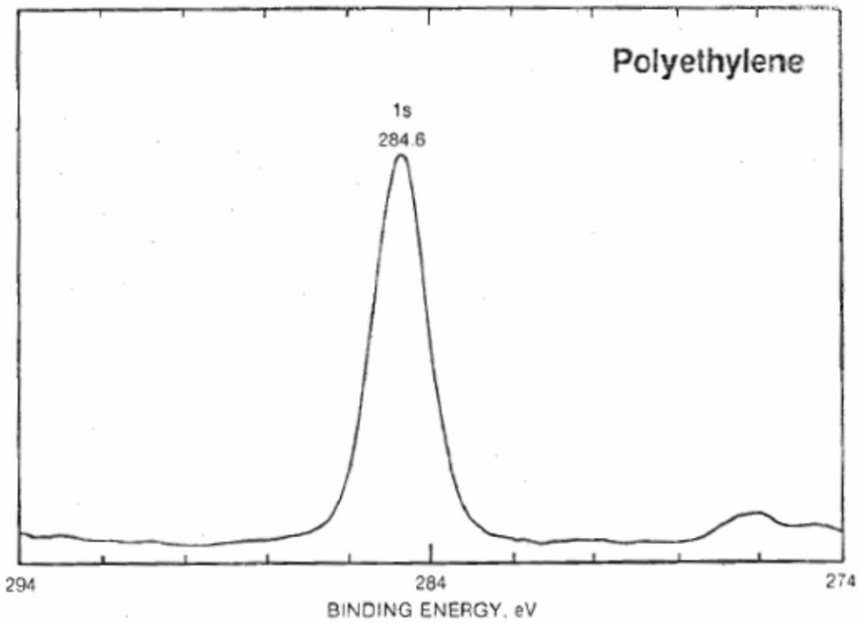
Handbook of X-ray photospectroscopy
John F. Moulder

XPS: Chemical identification
UPS: Valence electrons

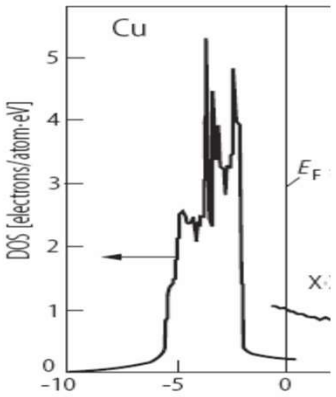
XPS

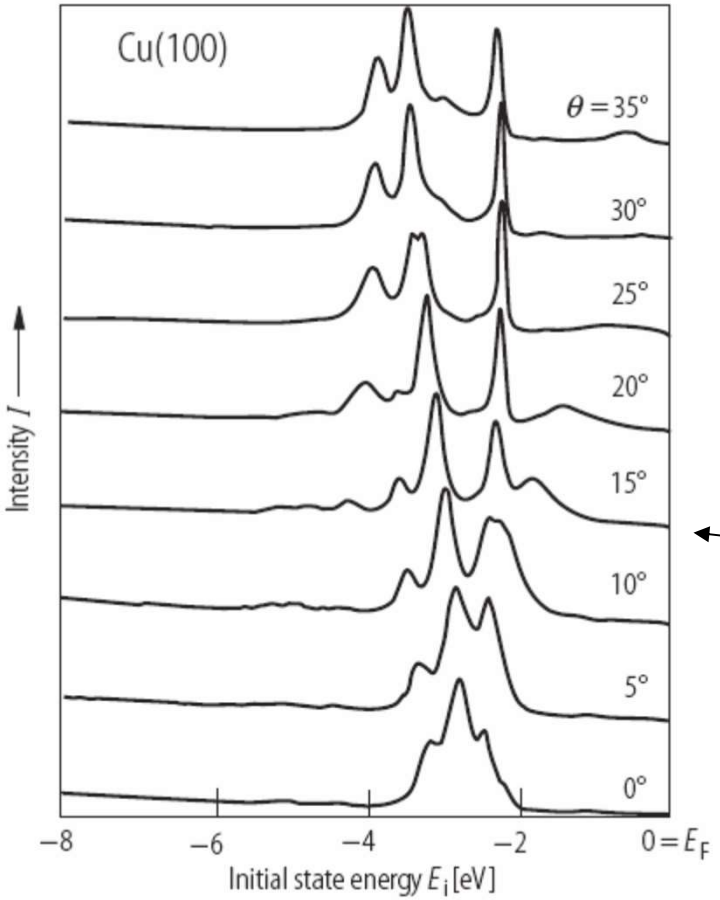
Carbon, C Atomic Number 6

COMPOUND	1s BINDING ENERGY, eV (280 284 288 292 296)	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
$MeCH_2OOCMe$		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
$(CHFCH_2)_n$		CFK
$(CHFCHF)_n$		CFK
$(CHFCF_2)_n$		CFK
$(CF_2CH_2)_n$		CFK
$(CF_2CHF)_n$		CFK
$(CF_2)_n$		CFK
CF_3COONa		GHH
CCl_4		GHH
CF_3COMe		GHH
CF_3COOEt		GHH

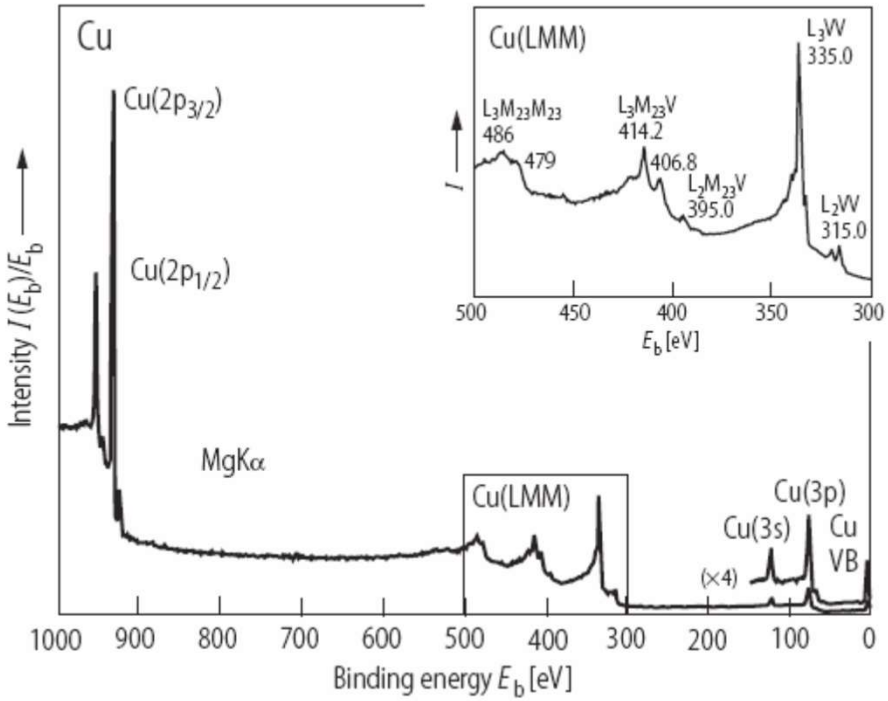


Cu





ARPES



XPS

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].

Thermodynamic properties

$$n = \int_{-\infty}^{\infty} D(E) f(E) dE$$ Implicitly defines μ.

$$u = \int_{-\infty}^{\infty} E D(E) f(E) dE$$

$$c_v = \left. \frac{\partial u}{\partial T} \right|_{N,V}$$

$$f = \mu n - k_B T \int_{-\infty}^{\infty} D(E) \ln\left(1 + \exp\left(\frac{\mu - E}{k_B T}\right)\right) dE$$

$$P = -\left. \frac{\partial F}{\partial V} \right|_{N,T}$$

$$s = -\left. \frac{\partial f}{\partial T} \right|_{N,V}$$

$$B = -V \frac{\partial P}{\partial V}$$

Thermodynamic properties

$$n = \int_{-\infty}^{\infty} D(E) f(E) dE$$

$$u = \int_{-\infty}^{\infty} E D(E) f(E) dE$$

Have a form that can be integrated by parts (Partielle Integration)

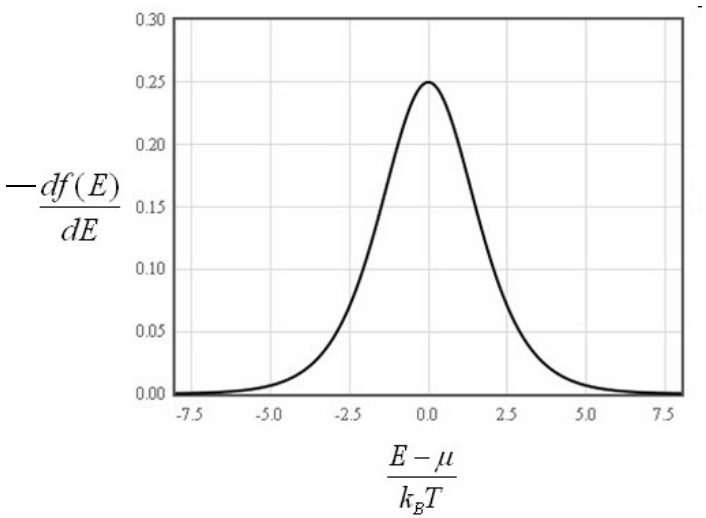
$$\int_{-\infty}^{\infty} H(E) f(E) dE = K(\infty) f(\infty) - K(-\infty) f(-\infty) - \int_{-\infty}^{\infty} K(E) \frac{df(E)}{dE} dE$$

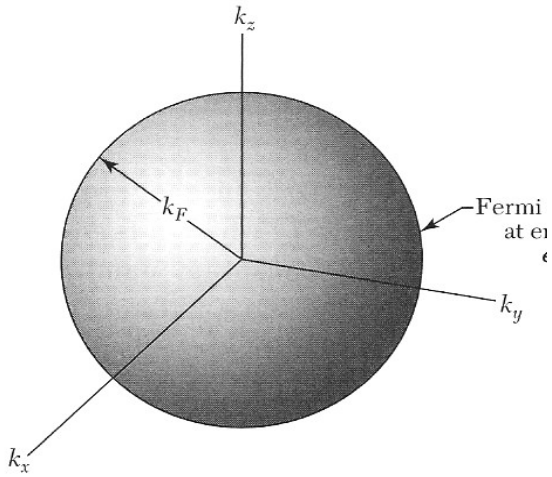
$$K(E) = \int_{-\infty}^{E} H(E') dE'$$

Thermodynamic properties

$$\int_{-\infty}^{\infty} H(E) f(E) dE = -\int_{-\infty}^{\infty} K(E) \frac{df(E)}{dE} dE$$

$$\frac{-df(E)}{dE} = \frac{\frac{1}{k_B T} \exp\left(\frac{E-\mu}{k_B T}\right)}{\left(1+\exp\left(\frac{E-\mu}{k_B T}\right)\right)^2}$$





Chemical potential

$$n = \int_{-\infty}^{\infty} D(E) f(E) dE = \int_{-\infty}^{\infty} \frac{D(E)}{\exp\left(\frac{E-\mu}{k_B T}\right)+1} dE$$

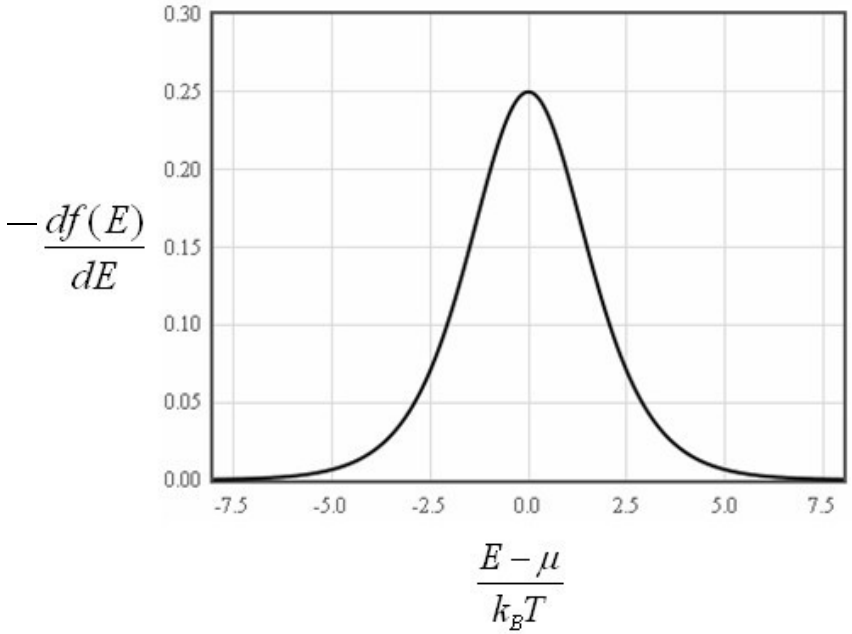
$$K(E) = \int_{-\infty}^{E} D(E') dE'$$

$$n = -\int_{-\infty}^{\infty} K(E) \frac{df(E)}{dE} dE = -\int_{-\infty}^{\infty} \frac{K(E) \exp\left(\frac{E-\mu}{k_B T}\right)}{k_B T \left(\exp\left(\frac{E-\mu}{k_B T}\right)+1\right)^2} dE$$

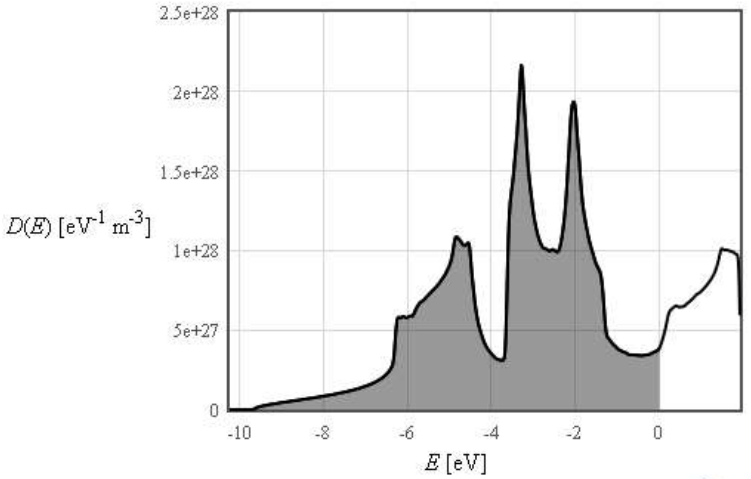
Chemical potential

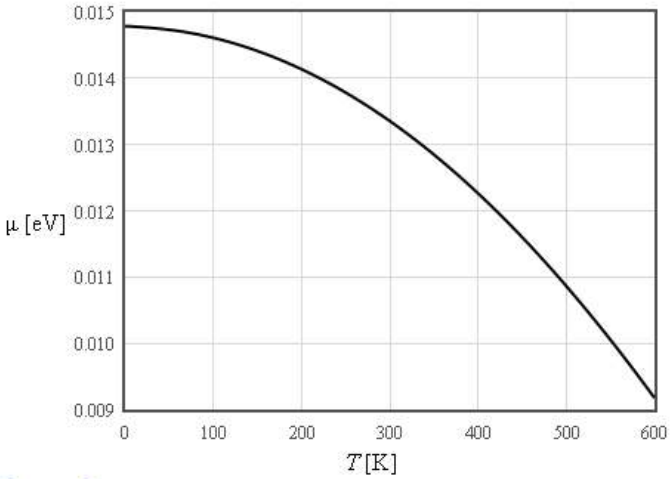
$$n = \int_{-\infty}^{\infty} D(E) f(E) dE \approx -\int_{\mu-10k_BT}^{\mu-10k_BT} \frac{K(E)\exp\left(\frac{E-\mu}{k_BT}\right)}{k_BT\left(\exp\left(\frac{E-\mu}{k_BT}\right)+1\right)^2} dE$$

$$K(E) = \int_{-\infty}^{E} D(E')dE'$$

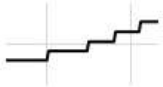


Chemical potential





Steps in the plot of μ vs. T are an artifact of the calculation that occurs when the chemical potential is nearly constant.



dimensionality: ○ 1 ○ 2 ◉ 3

number of electrons per primitive unit cell: 6 volume of a primitive unit cell: 1.0659e-28 m^3 electron density = 5.6290e+28 m^{-3}

T_{min}: 0 K T_{max}: 600 K DoS → μ

Density of states: E [eV], $D(E)$ [eV^{-1} m^{-3}]

```
-10.23143       0
-10.21782       0
-10.20421       0
-10.19061       0
-10.177 0
-10.1634        0
-10.14979       0
-10.13618       0
-10.12258       0
-10.10897       0
-10.09537       0
```

Chemical potential: T [K], μ(T) [eV]

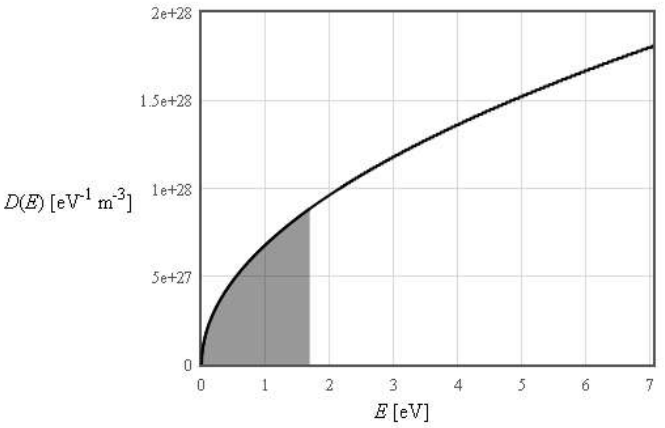
```
0       0.014783123488097162
2       0.014783123488097162
4       0.014783123488097162
6       0.014783123488097162
8       0.014780672725024467
10      0.01477912139065327
12      0.01477737382901395
14      0.014775311805457247
16      0.014773623691964513
18      0.014771823353458053
20      0.014769646557014536
```

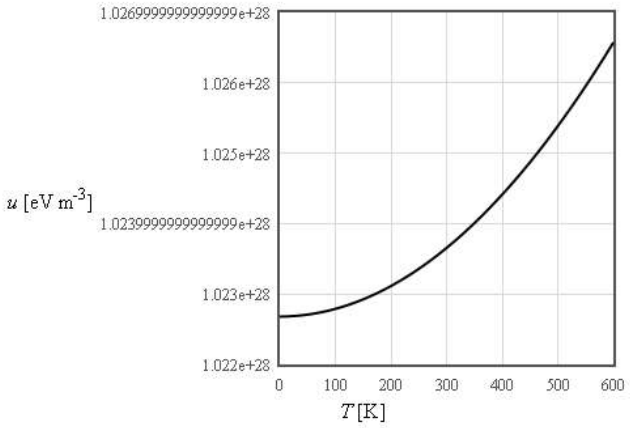
Free electron model: 1D 2D 3D

Tight binding: 2d square 2d hexagonal graphene simple cubic

Al fcc Au fcc Cu fcc Na bcc Pt fcc W bcc

Internal energy density





dimensionality: ○ 1 ○ 2 ◉ 3

number of electrons per primitive unit cell: 1 volume of a primitive unit cell: 1E-28 m^3 electron density = 1.0000e+28 m^{-3}

T_{min}: 0 K T_{max}: 600 K DoS → u

Density of states: E [eV], $D(E)$ [eV^{-1} m^{-3}]

0	0
0.007055332	5.72E+26
0.014110664	8.09E+26
0.021165996	9.91E+26
0.028221327	1.14E+27
0.035276659	1.28E+27
0.042331991	1.40E+27
0.049387323	1.51E+27
0.056442655	1.62E+27
0.063497987	1.72E+27
0.070553319	1.81E+27

Internal energy density: T [K], $u(T)$ [eV m^{-3}]

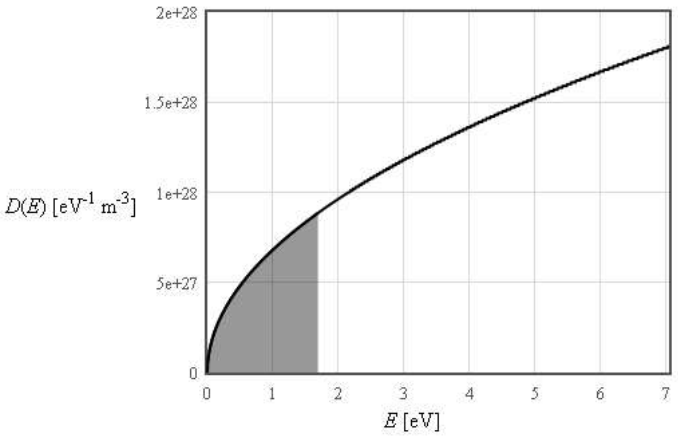
0	1.02267879040933e+28
2	1.02267882214103 6e+28
4	1.02267920224427 63e+28
6	1.02267957981379 36e+28
8	1.02268018850975 65e+28
10	1.02268084236626 43e+28
12	1.02268150615804 76e+28
14	1.02268227398876 9e+28
16	1.02268307055715 04e+28
18	1.02268388083540 95e+28
20	1.02268471468962 16e+28

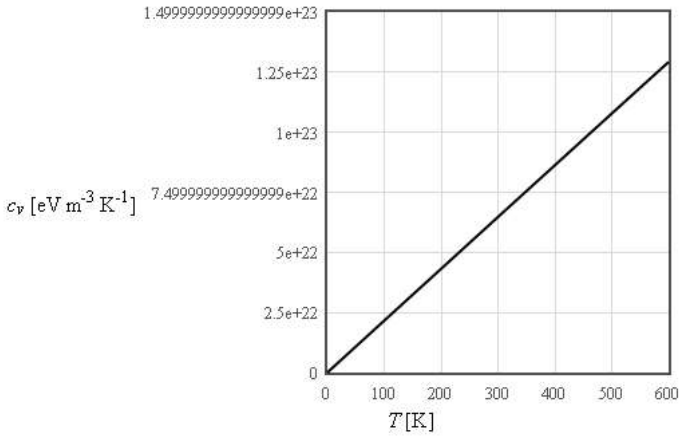
Free electron model: 1D 2D 3D

Tight binding: 2d square 2d hexagonal graphene simple cubic

Al fcc Au fcc Cu fcc Na bcc Pt fcc W bcc

Specific heat





dimensionality: ○ 1 ○ 2 ◉ 3

number of electrons per primitive unit cell: 1 volume of a primitive unit cell: 1E-28 m^3 electron density = 1.0000e+28 m^{-3}

T_{min}: 0 K T_{max}: 600 K DoS → cv

Density of states: E [eV], $D(E)$ [eV^{-1} m^{-3}]

0	0
0.007055332	5.72E+26
0.014110664	8.09E+26
0.021165996	9.91E+26
0.028221327	1.14E+27
0.035276659	1.28E+27
0.042331991	1.40E+27
0.049387323	1.51E+27
0.056442655	1.62E+27
0.063497987	1.72E+27
0.070553319	1.81E+27

Internal energy density: T [K], $u(T)$ [eV m^{-3}]

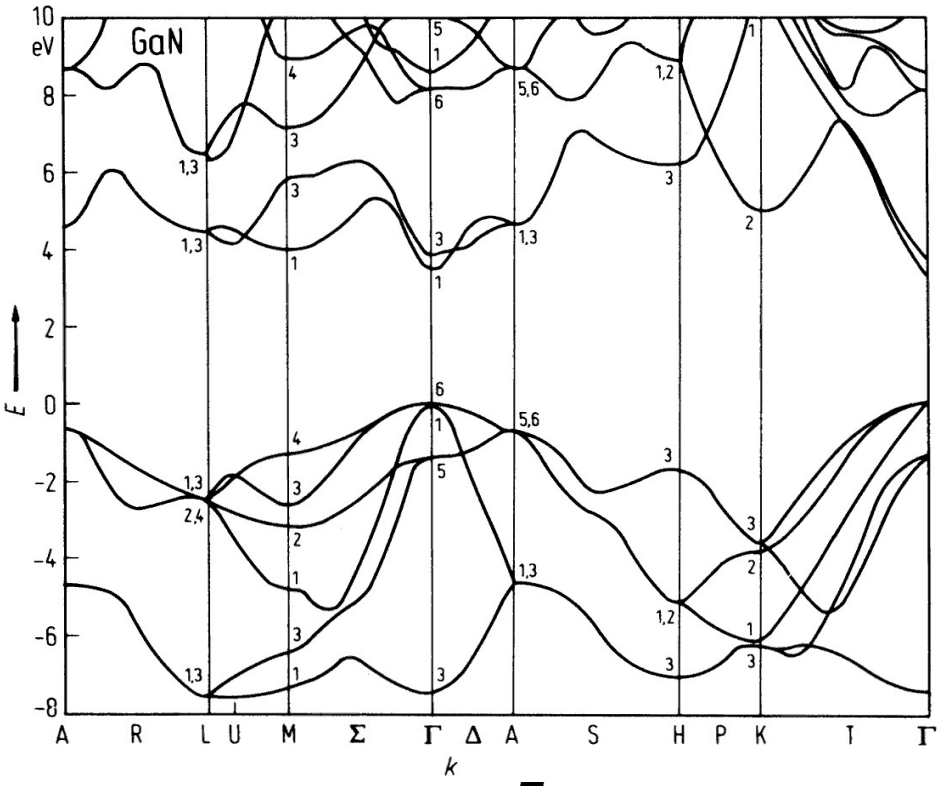
0	0
2	431433887775866100000
4	862897311767092800000
6	1.294401219141122e+21
8	1.7259446382160304e+21
10	2.157524280009776e+21
12	2.589133843197587e+21
14	3.0207659535567857e+21
16	3.452413471457561e+21
18	3.884070539353225e+21
20	4.315732794885769e+21

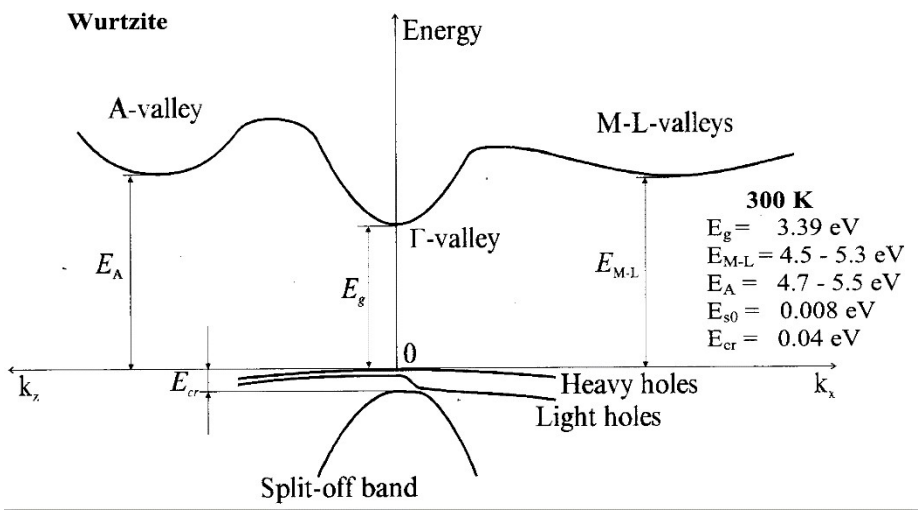
Free electron model: 1D 2D 3D

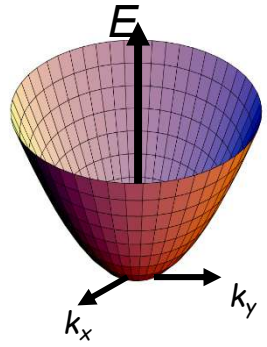
Tight binding: 2d square 2d hexagonal graphene simple cubic

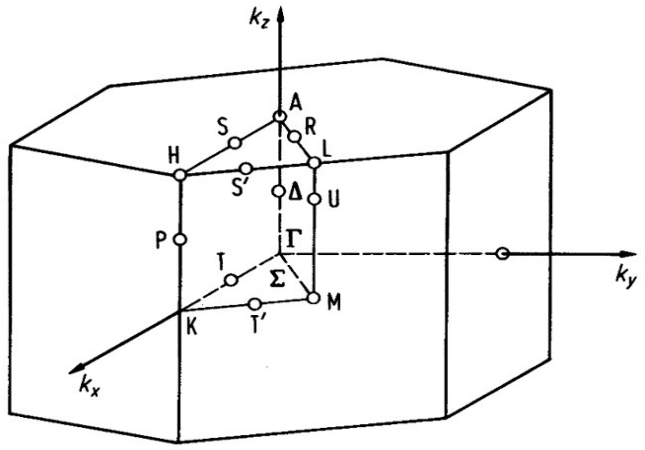
Al fcc Au fcc Cu fcc Na bcc Pt fcc W bcc

GaN









1st Brillioun zone of hcp