Exam

One A4 handwritten notes
One hour
Like the exams online

Plane wave method
Tight binding

Plane wave method

$$-\frac{\hbar^2}{2m}\nabla^2\psi_{\vec{k}} + U(\vec{r})\psi_{\vec{k}} = E\psi_{\vec{k}}.$$

The potential is periodic $$U(\vec{r}) = \sum_{\vec{G}} U_{\vec{G}} e^{i\vec{G}\cdot\vec{r}}$$

Bloch form $$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} \sum_{\vec{G}'} C_{\vec{G}'} e^{i\vec{G}'\cdot\vec{r}}$$

$$\sum_{\vec{G}} C_{\vec{G}} e^{i\vec{G}\cdot\vec{r}} = \sum_{\vec{G}'} C_{\vec{G}'} e^{i\vec{G}'\cdot\vec{r}} = \sum_{\vec{G}''} C_{\vec{G}''} e^{i\vec{G}''\cdot\vec{r}}$$

We can relabel the reciprocal lattice vectors since we sum over them.

Plane wave method

$$\sum_{\vec{G}'} \frac{\hbar^2(\vec{k}+\vec{G}')^2}{2m} C_{\vec{G}'} e^{i(\vec{k}+\vec{G}')\cdot\vec{r}} + \sum_{\vec{G}} \sum_{\vec{G}''} U_{\vec{G}} C_{\vec{G}''} e^{i(\vec{k}+\vec{G}+\vec{G}'')\cdot\vec{r}} = E \sum_{\vec{G}'} C_{\vec{G}'} e^{i(\vec{k}+\vec{G}')\cdot\vec{r}}$$

Only the terms with the same wavelength can be equal to each other.

$$\vec{G}' = \vec{G} + \vec{G}''$$

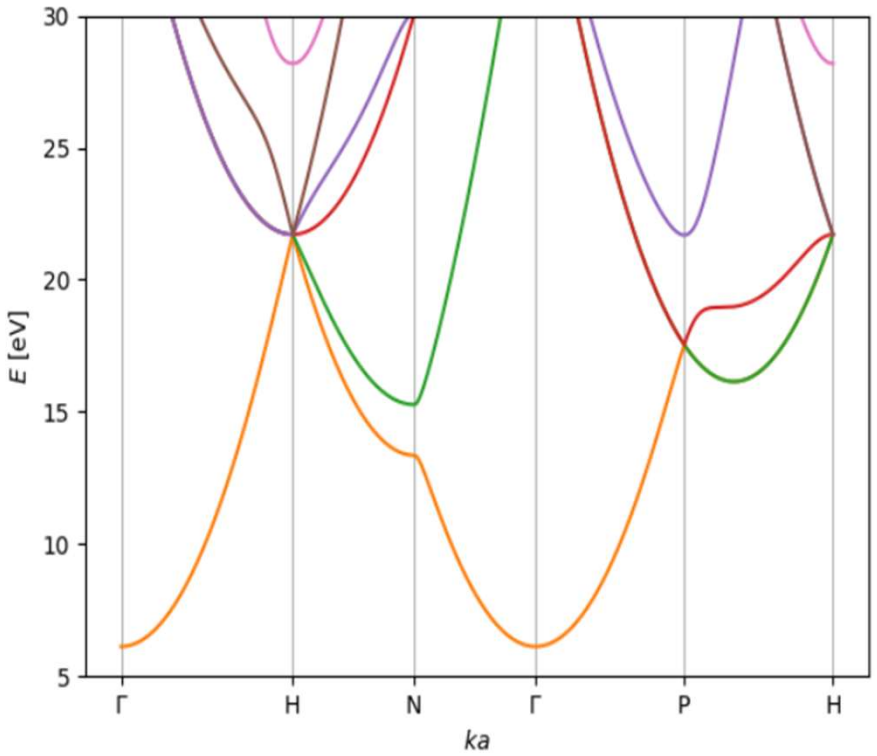
Central equations: $$\frac{\hbar^2(\vec{k}+\vec{G}')^2}{2m} C_{\vec{G}'} + \sum_{\vec{G}} U_{\vec{G}} C_{\vec{G}'-\vec{G}} = E C_{\vec{G}'}$$

There is one equation for each $\vec{G}'$ vector.

+ - Body Centered Cubic with a Comb Potential

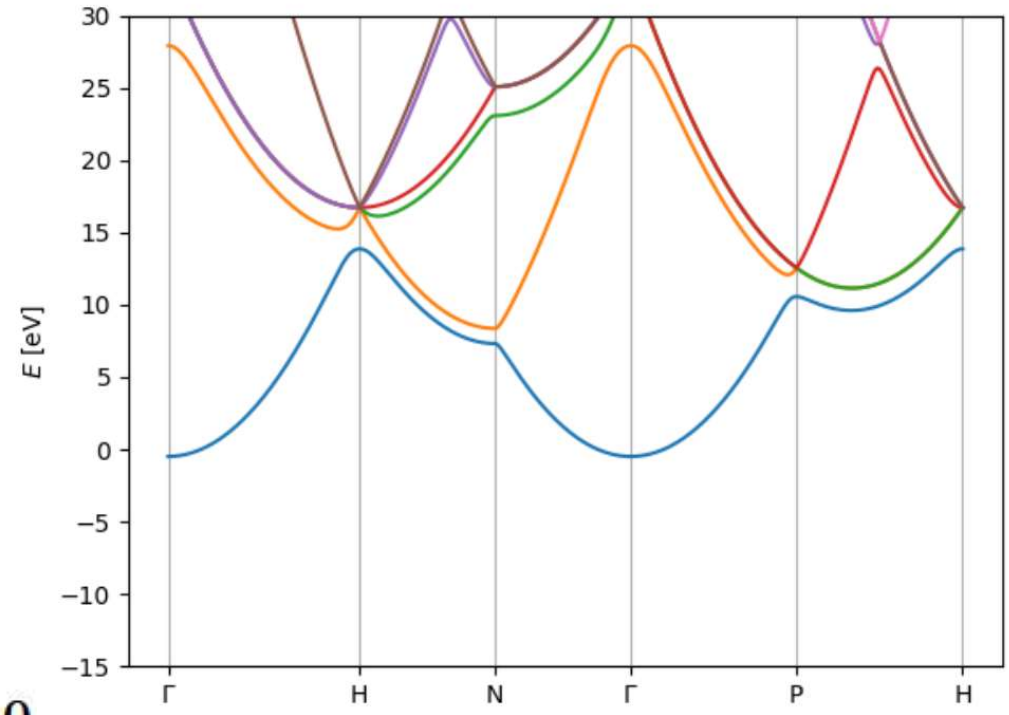
If all of the components of a Fourier series are real and have the same amplitude, there is constructive interference at the Bravais lattice points and this produces a comb function with one large amplitude peak per Bravais lattice point. Below is python code to calculate the band structure of a bcc comb potential. One hundred twenty five reciprocal lattice points are included in the calculation where h, k, and l are in the range $-2, -2, 0, 1, 2$.

Every band is drawn in a different color and there must be an energy for that band for every k. If a color is not visible for some range of k that band must be degenerate in energy with another band.



Nearly free electron model

$$\begin{bmatrix} \frac{\hbar^2\vec{k}^2}{2m} - E & U \\ U & \frac{\hbar^2(\vec{k}-\vec{G})^2}{2m} - E \end{bmatrix} \begin{bmatrix} C_0 \\ C_{-\vec{G}} \end{bmatrix} = 0$$

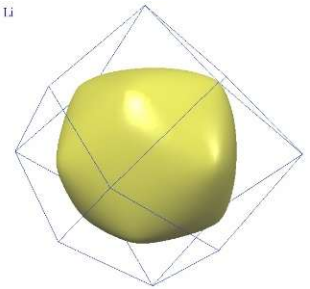


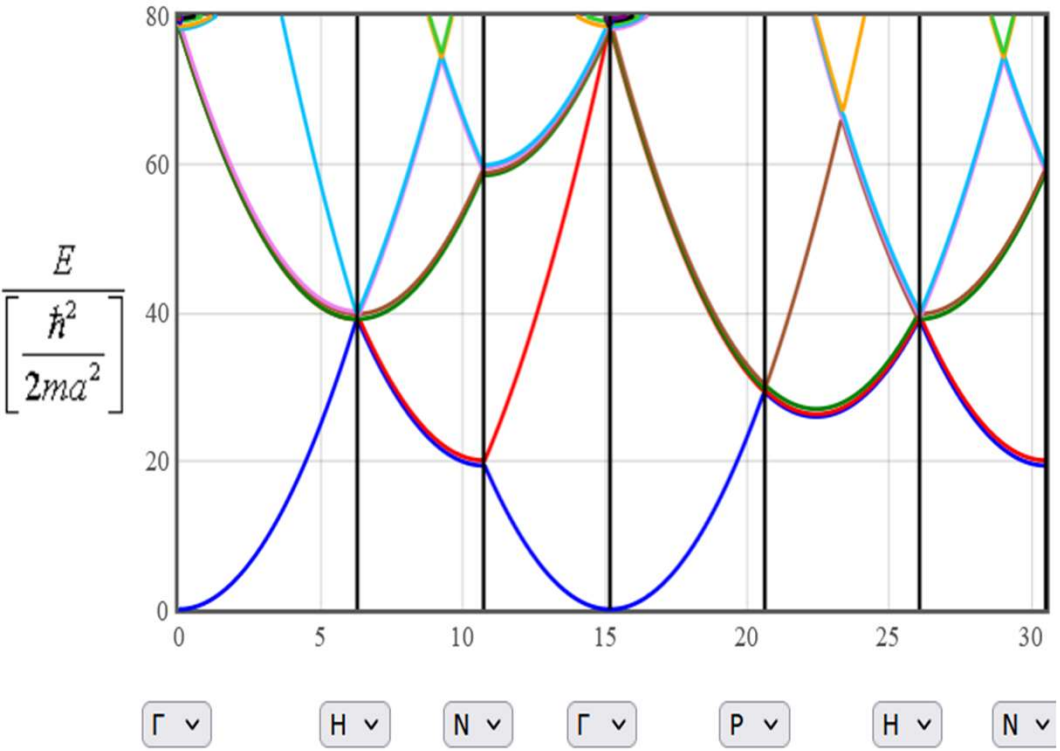
At the Brillouin zone boundary, $k = \frac{G}{2}$

$$\begin{bmatrix} \frac{\hbar^2(G/2)^2}{2m} - E & U \\ U & \frac{\hbar^2(G/2)^2}{2m} - E \end{bmatrix} \begin{bmatrix} C_0 \\ C_{-\vec{G}} \end{bmatrix} = 0$$

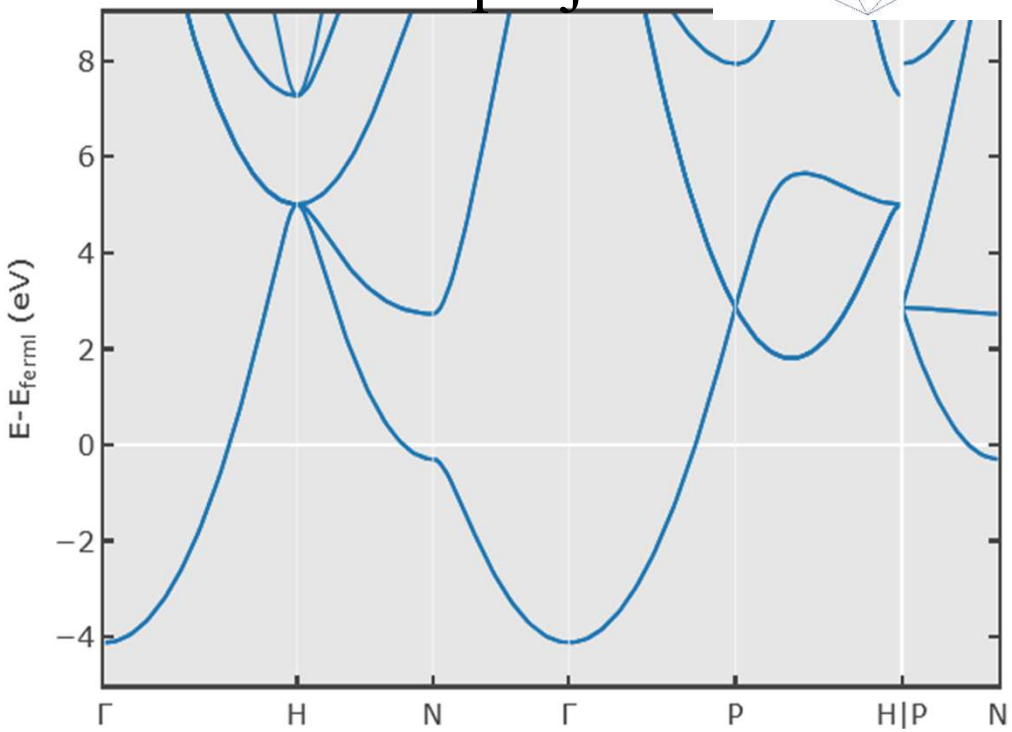
$$E = \frac{\hbar^2\left(\frac{G}{2}\right)^2}{2m} \pm U$$

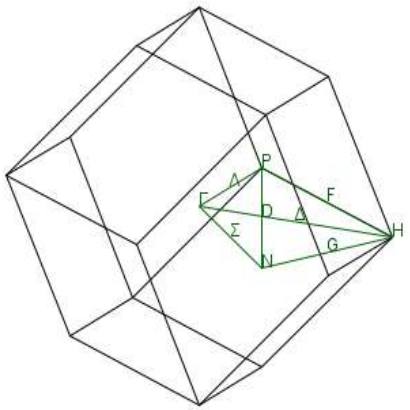
Lithium bcc

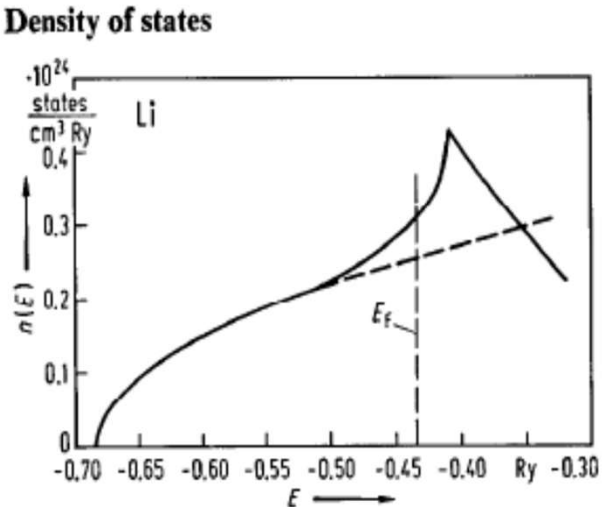


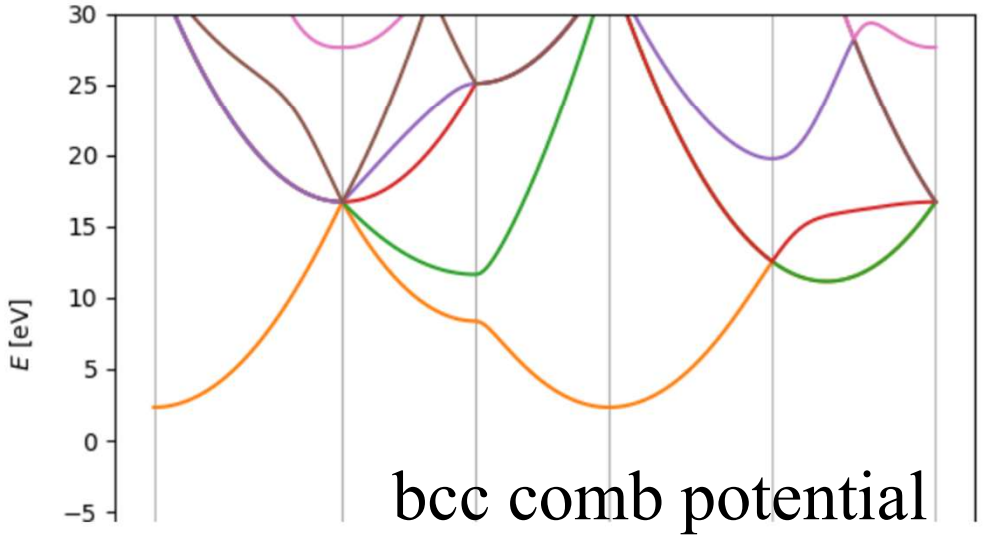


Materials project



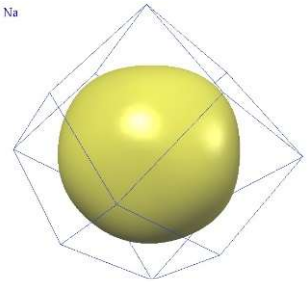


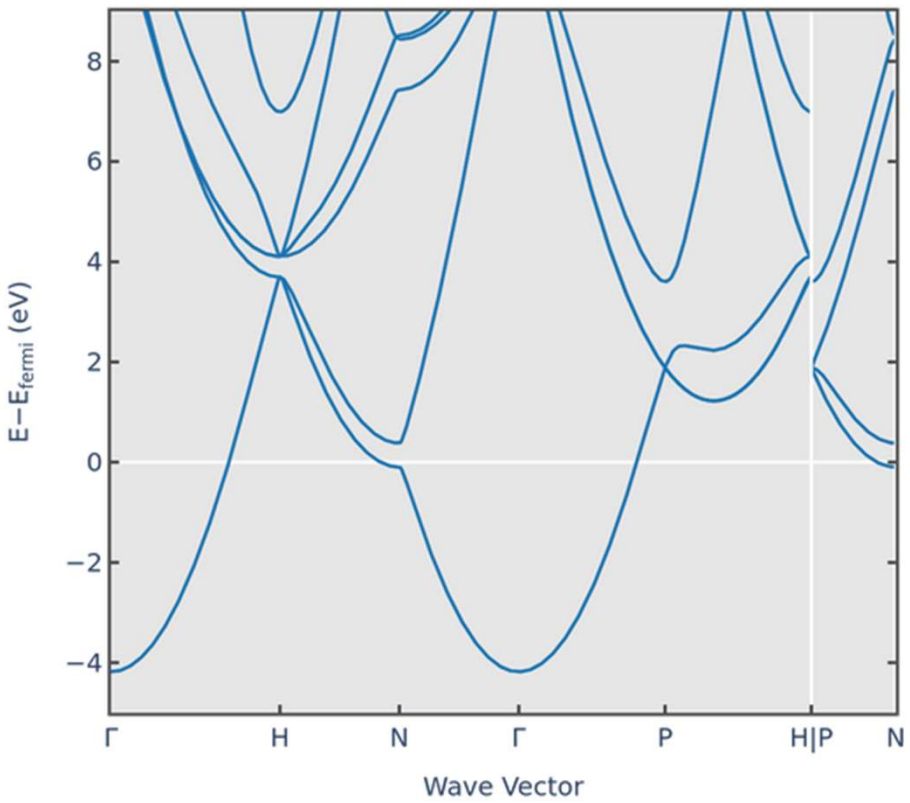


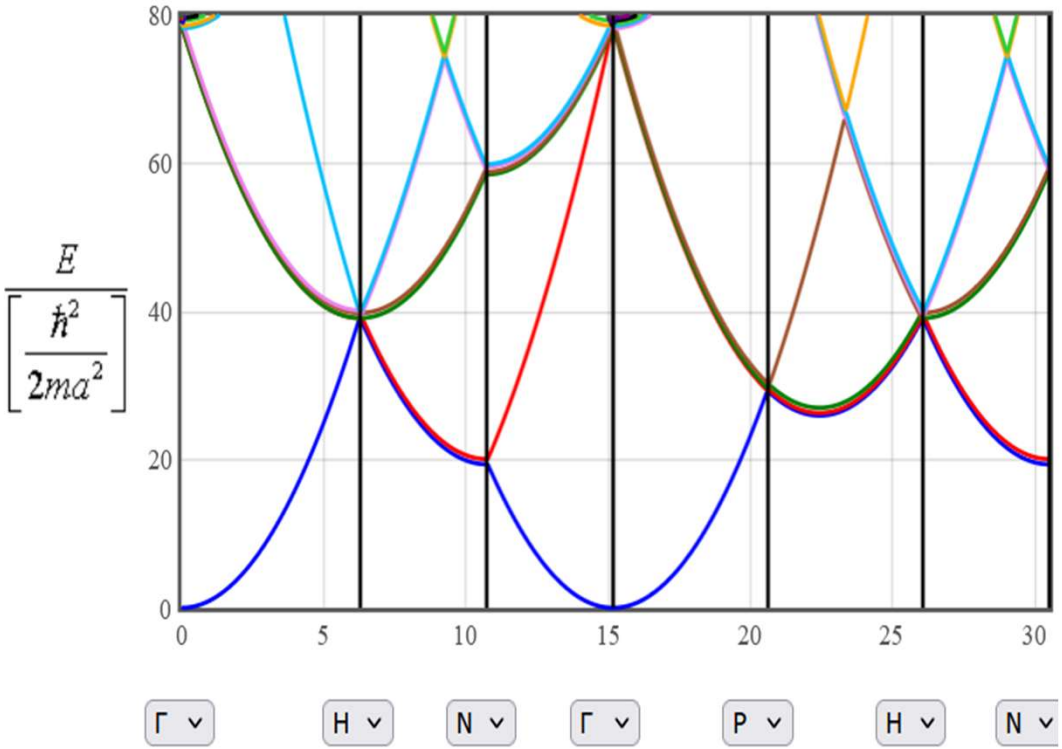


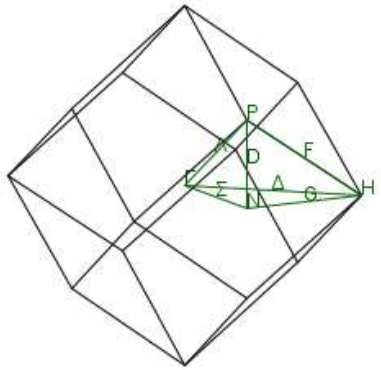
bcc comb potential

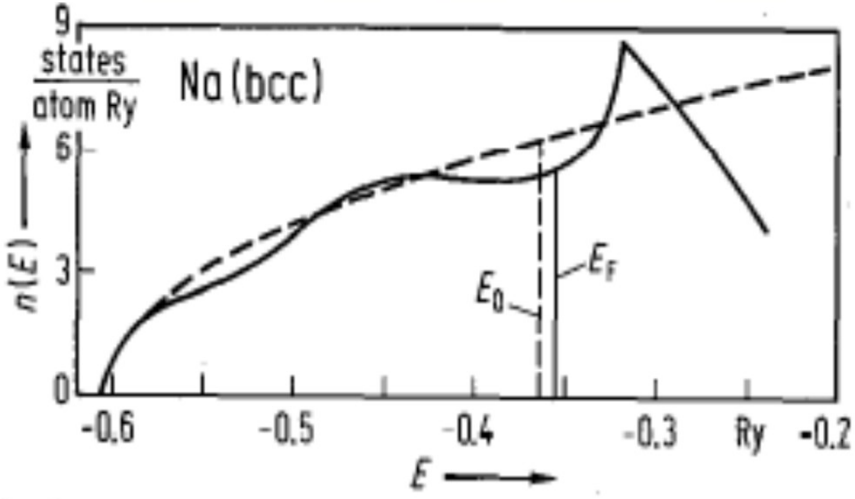
Sodium


Na


E−E_fermi (eV)
8
6
4
2
0
−2
−4
Γ
H
N
Γ
P
H|P
N
Wave Vector


E / [ħ²/2ma²]
80
60
40
20
0
0
5
10
15
20
25
30
Γ
H
N
Γ
P
H
N


P
N
D
F
Γ
Σ
Δ
G
H


9
states / atom Ry
Na (bcc)
6
3
0
n(E)
E_0
E_F
-0.6
-0.5
-0.4
-0.3
Ry
-0.2
E

Tight binding

Guess a wave function of the form

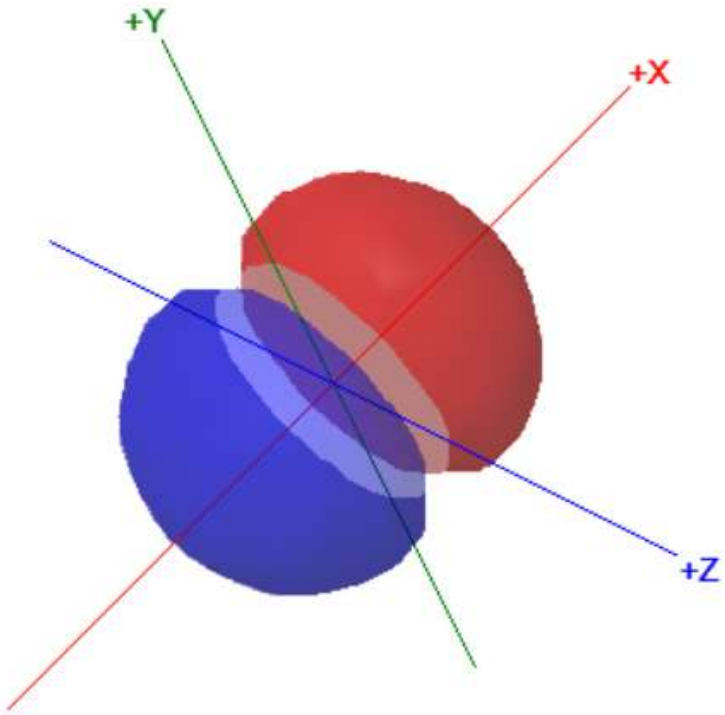
$$\psi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{h,j,l} e^{i\left(h\vec{k}\cdot\vec{a}_1 + j\vec{k}\cdot\vec{a}_2 + l\vec{k}\cdot\vec{a}_3\right)} \psi_{\text{unit cell}}\left(\vec{r} - h\vec{a}_1 - j\vec{a}_2 - l\vec{a}_3\right).$$

$$\psi_{\text{unit cell}}(\vec{r}) = \sum_a \sum_{ao} c_{ao,a} \phi_{ao}^{Z_a}\left(\vec{r} - \vec{r}_a\right)$$

Insert in the Schroedinger equation, calculate the energy, find the parameters that minimize the energy.

Atomic orbitals

$2p_x$



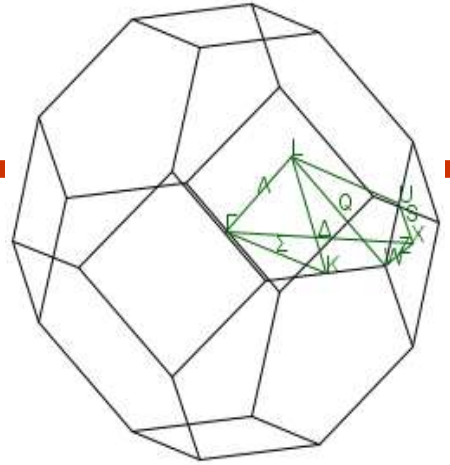
1s						2px	2py	2pz
2s						3px	3py	3pz
3s						4px	4py	4pz
4s	3d xy	3d yz	3d xz	3d z^2	3d x^2-y^2	5px	5py	5pz
5s	4d xy	4d yz	4d xz	4d z^2	4d x^2-y^2	6px	6py	6pz
	5d xy	5d yz	5d xz	5d z^2	5d x^2-y^2			

d bands
transition metals

4f	4f	4f	4f	4f	4f	4f
5f	5f	5f	5f	5f	5f	5f

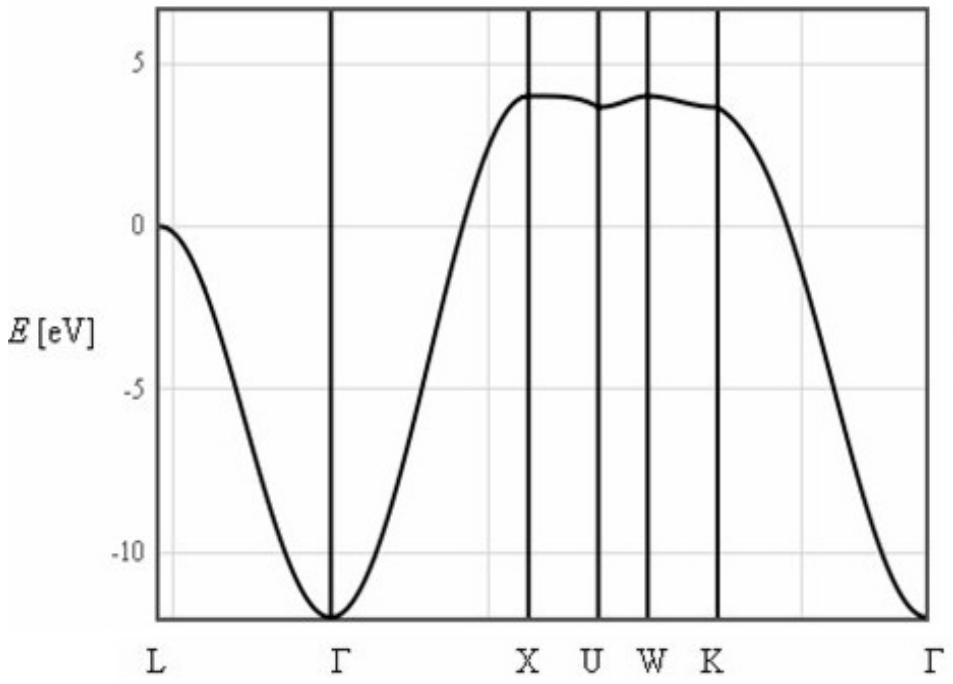
f bands
rare earths

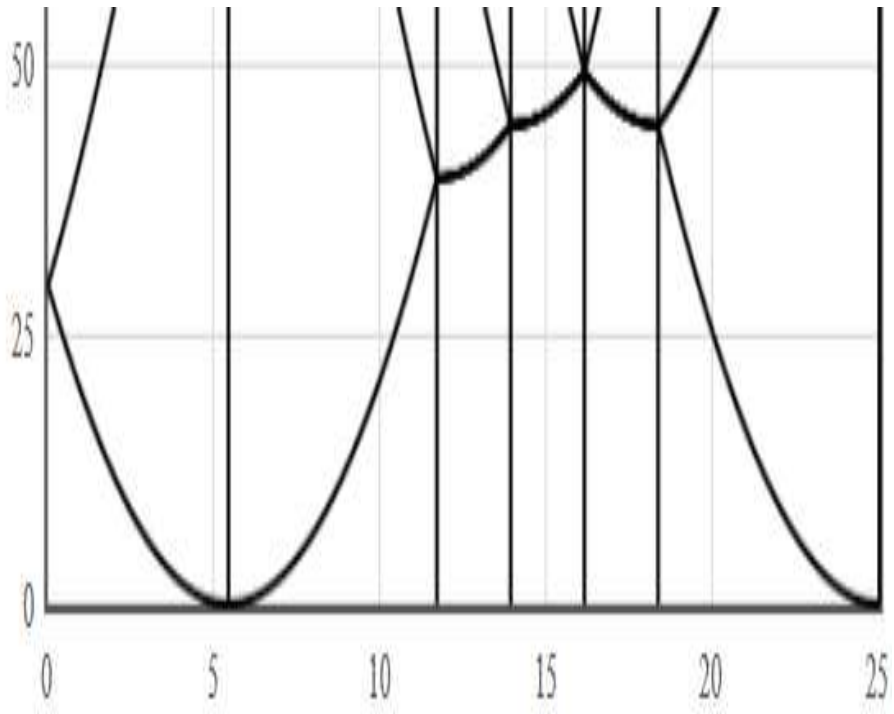
Tight binding, fcc



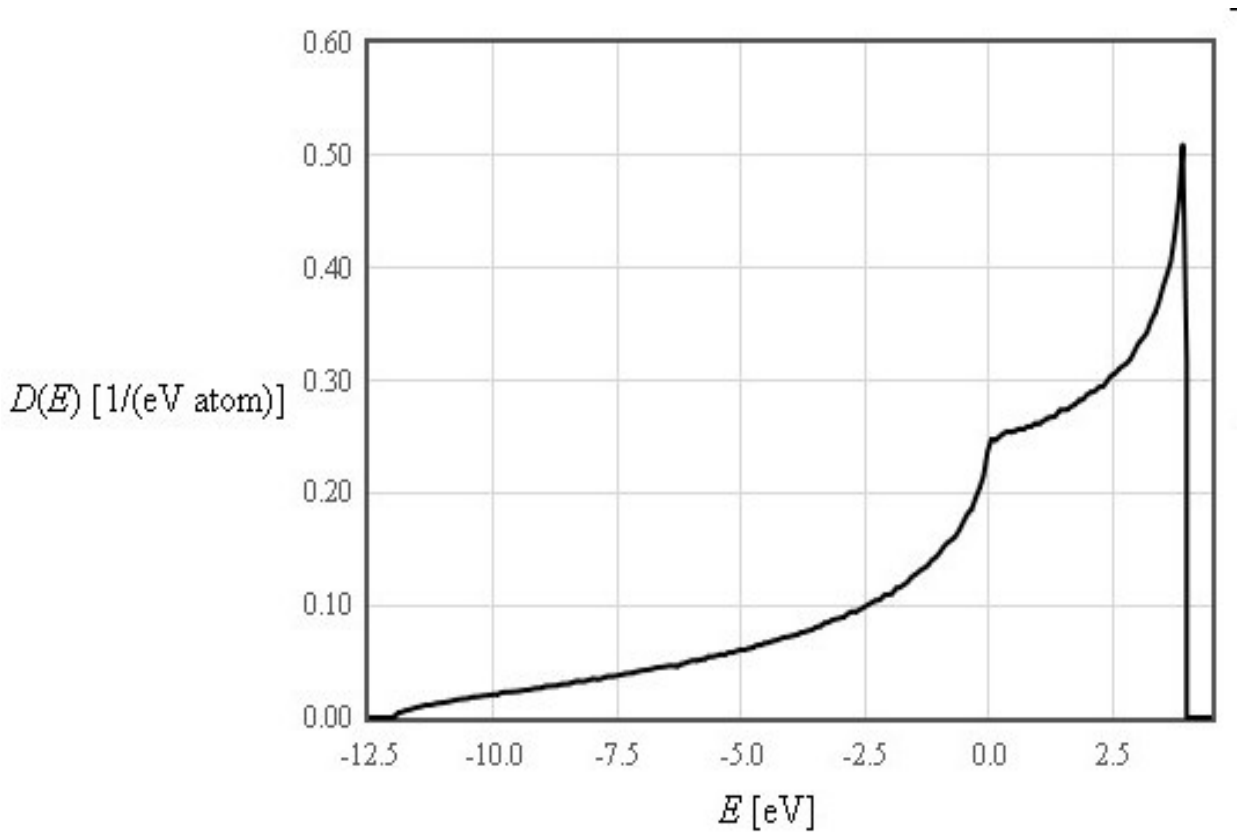
$$E = \varepsilon - t\sum_{lmn} e^{i\vec{k}\cdot\vec{\rho}_{lmn}}$$

$$E = \varepsilon - 4t\left(\cos\left(\frac{k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right) + \cos\left(\frac{k_x a}{2}\right)\cos\left(\frac{k_z a}{2}\right) + \cos\left(\frac{k_y a}{2}\right)\cos\left(\frac{k_z a}{2}\right)\right)$$





Density of states (fcc)

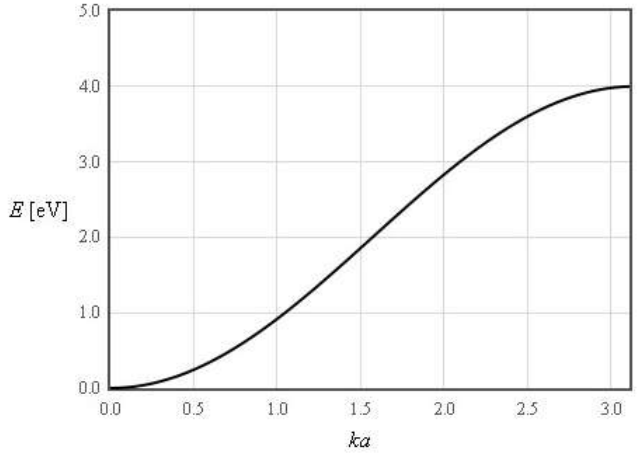
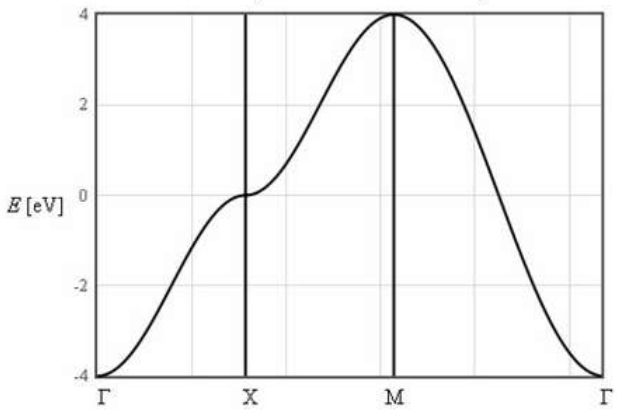
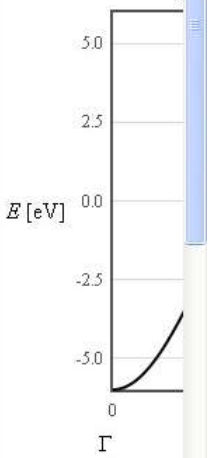
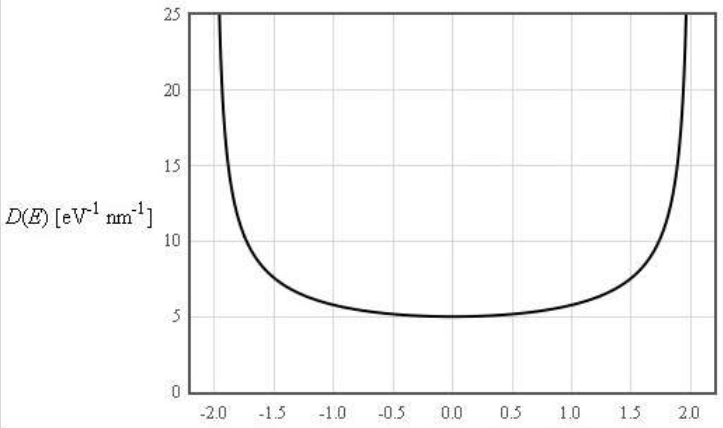
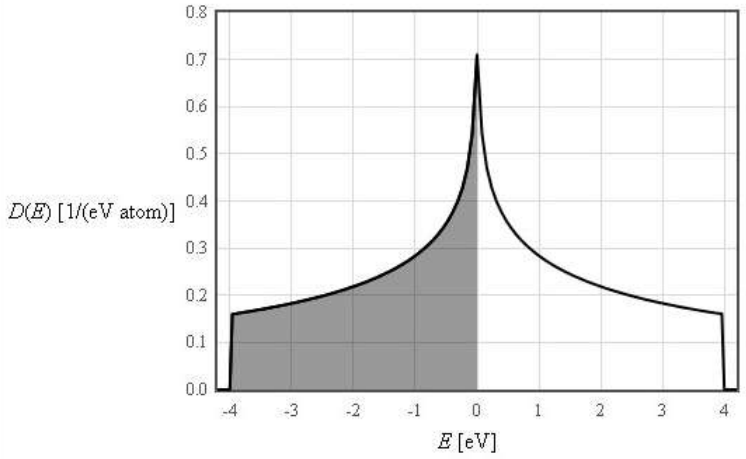
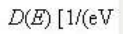


Calculate the energy for every allowed k in the Brillouin zone

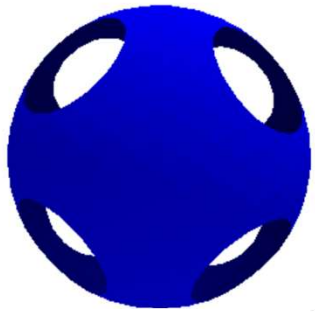
$$E = \varepsilon - 4t\left(\cos\left(\frac{k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right) + \cos\left(\frac{k_x a}{2}\right)\cos\left(\frac{k_z a}{2}\right) + \cos\left(\frac{k_y a}{2}\right)\cos\left(\frac{k_z a}{2}\right)\right)$$

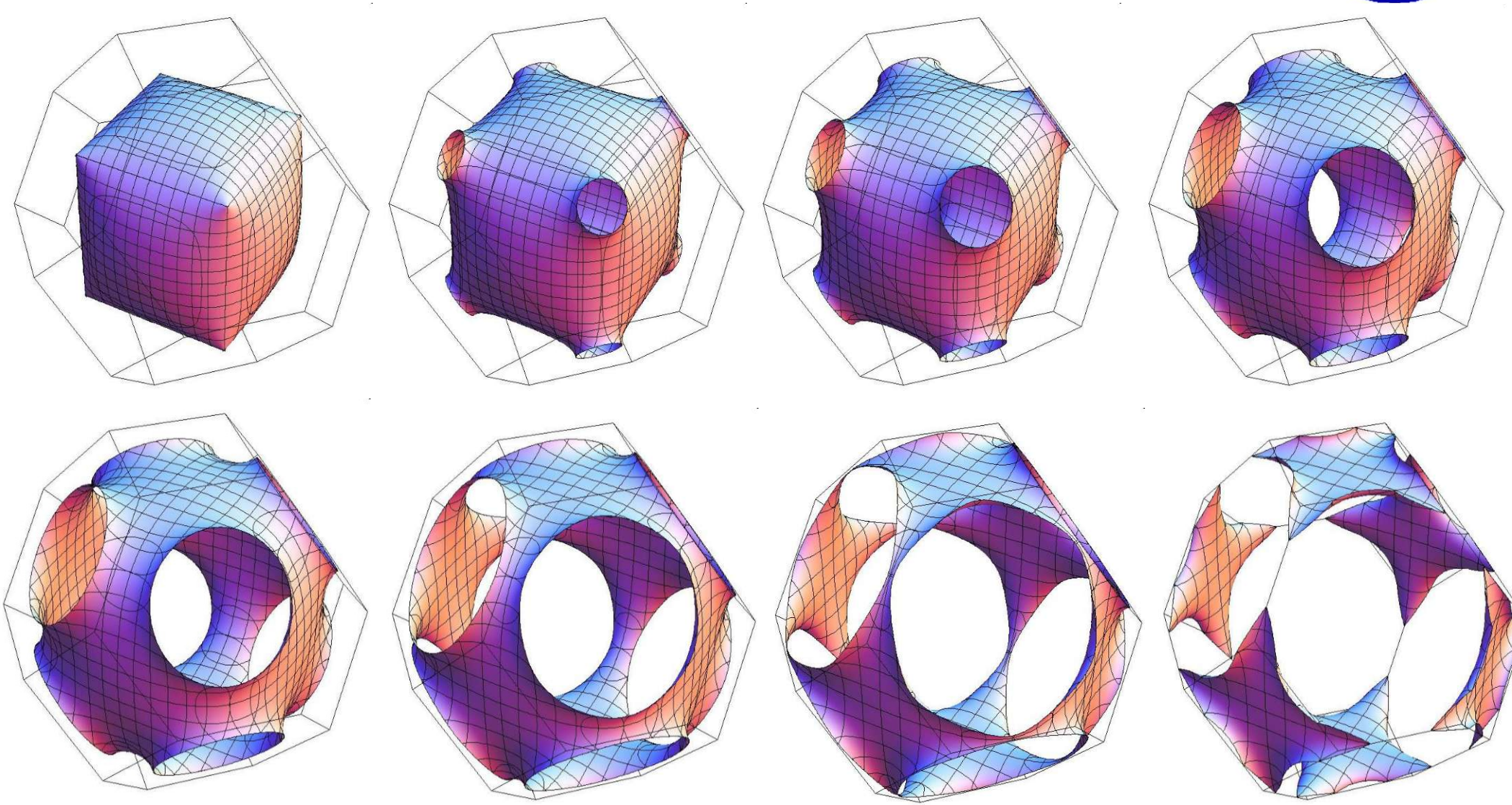
http://lamp.tu-graz.ac.at/~hadley/ss1/bands/tbtable/tbtable.html

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

	Linear Chain	2-D square lattice	
relation	$E = \varepsilon - 2t\cos(k_x a)$  Calculate E(k)	$E = \varepsilon - 2t\left(\cos(k_x a) + \cos(k_y a)\right)$  Calculate E(k)	$E = \varepsilon - 2t$ 
of states	$D(k) = \frac{2}{\pi}$	$D(k) = \frac{k}{\pi}$ m^{-1}	
of states	$D(E) = \frac{1}{at\sqrt{1-\left(\frac{\varepsilon - E}{2t}\right)^2}}$ J^{-1}m^{-1} 		

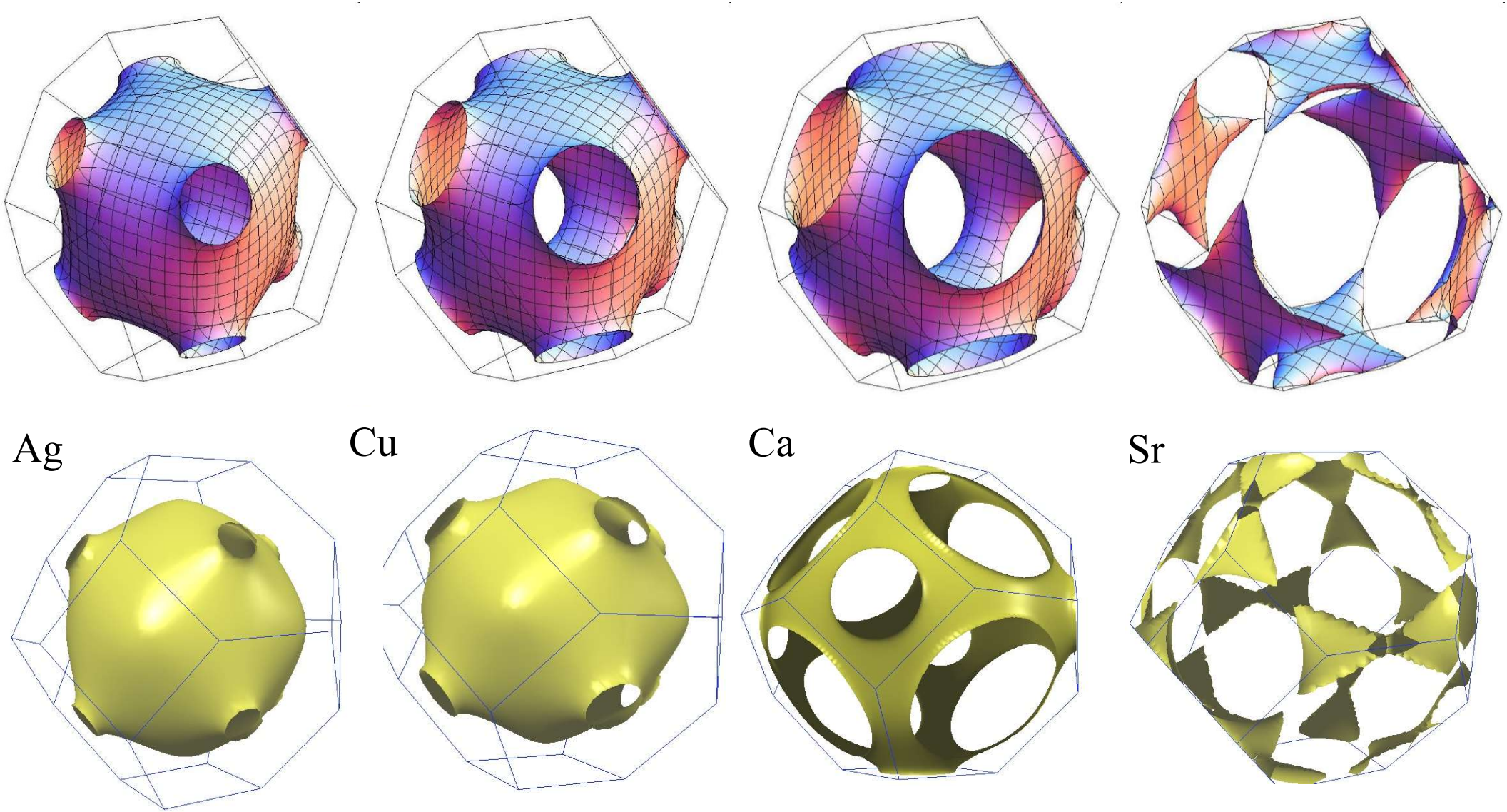
Tight binding, fcc





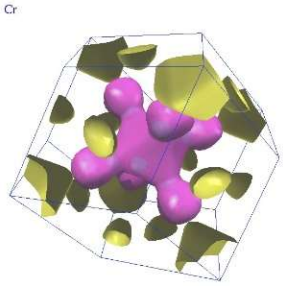
Christian Gruber, 2008

Tight binding, fcc

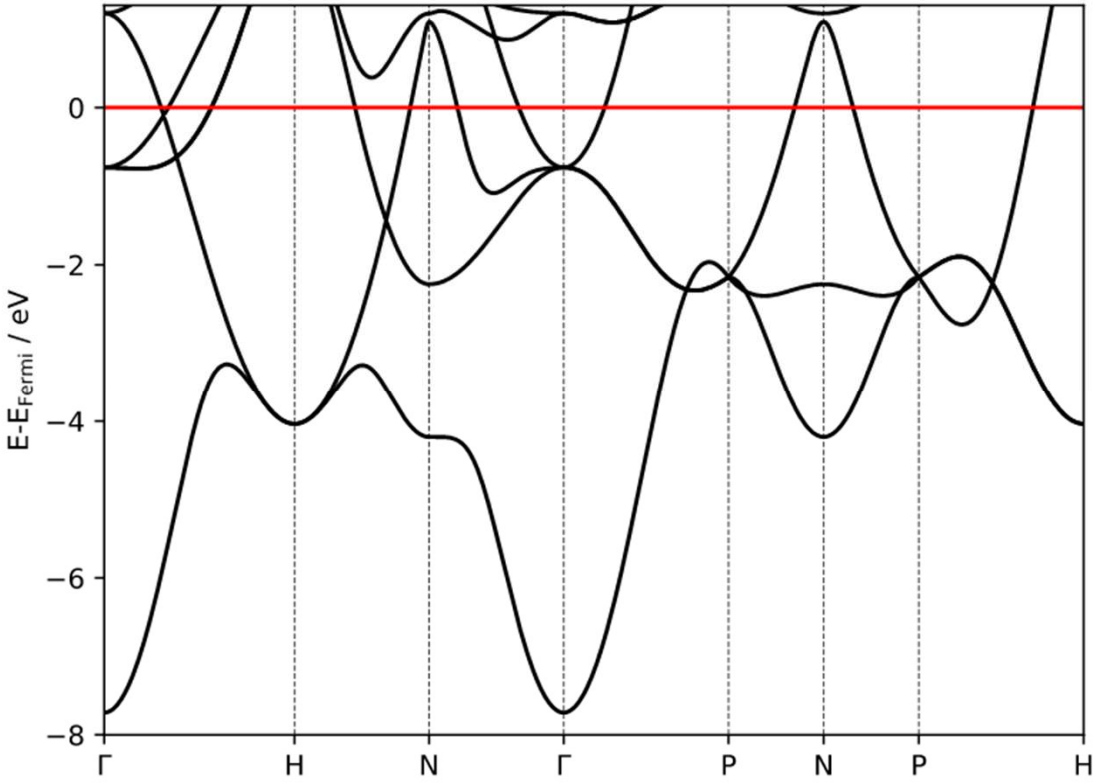


http://www.phys.ufl.edu/fermisurface/

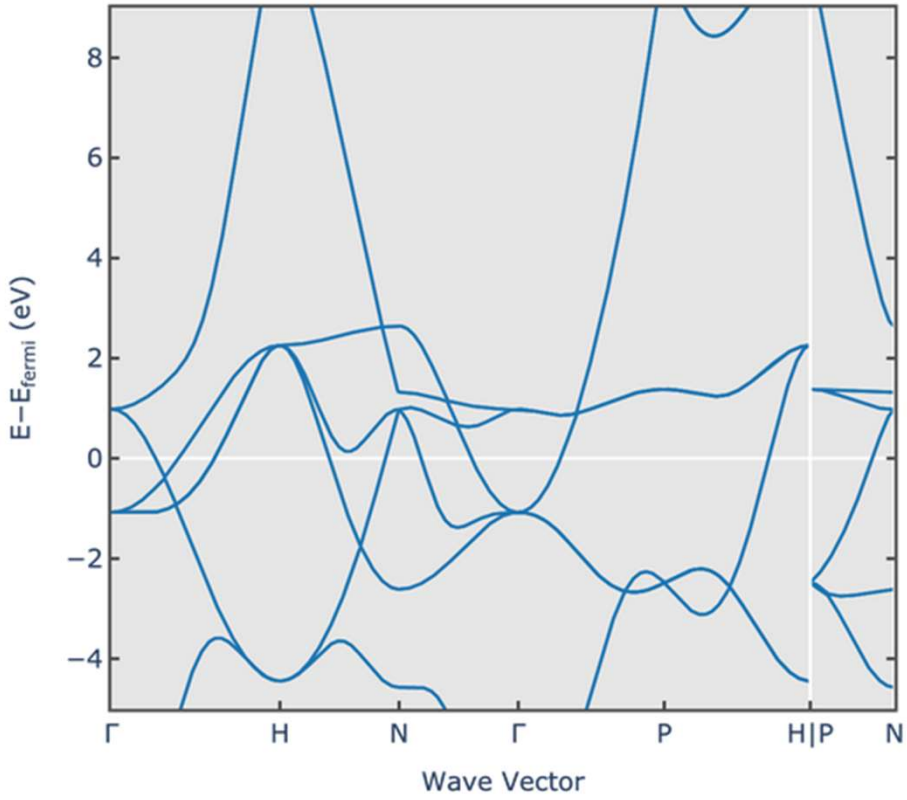
Bandstructure of bcc chromium (Cr)



Quantum Espresso

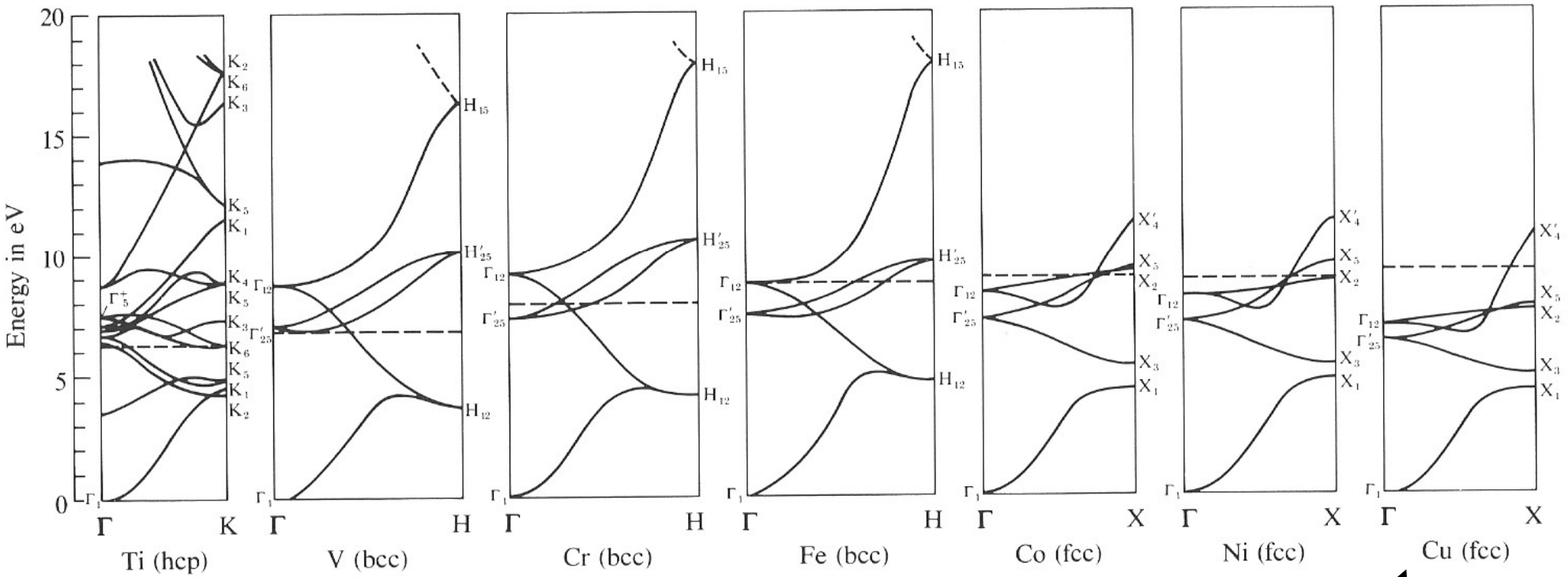


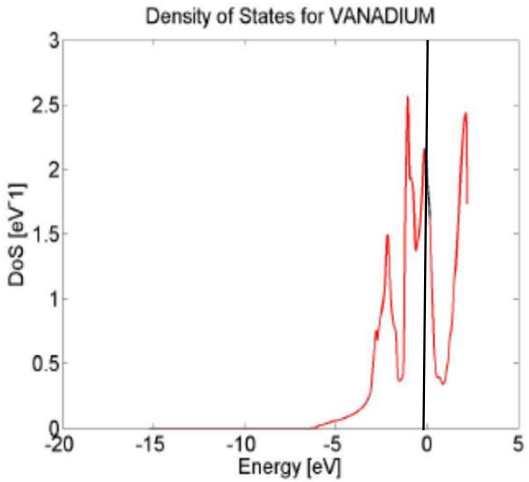
Materials Project

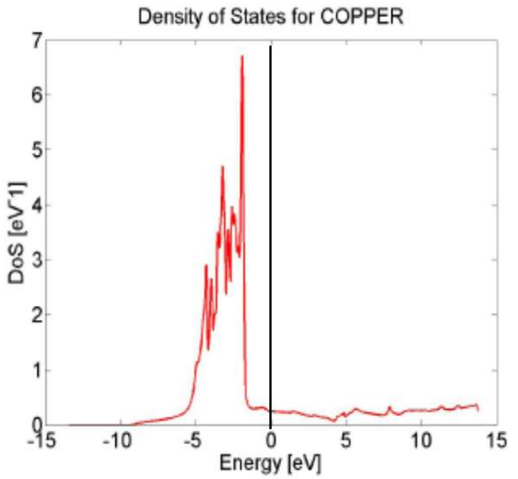


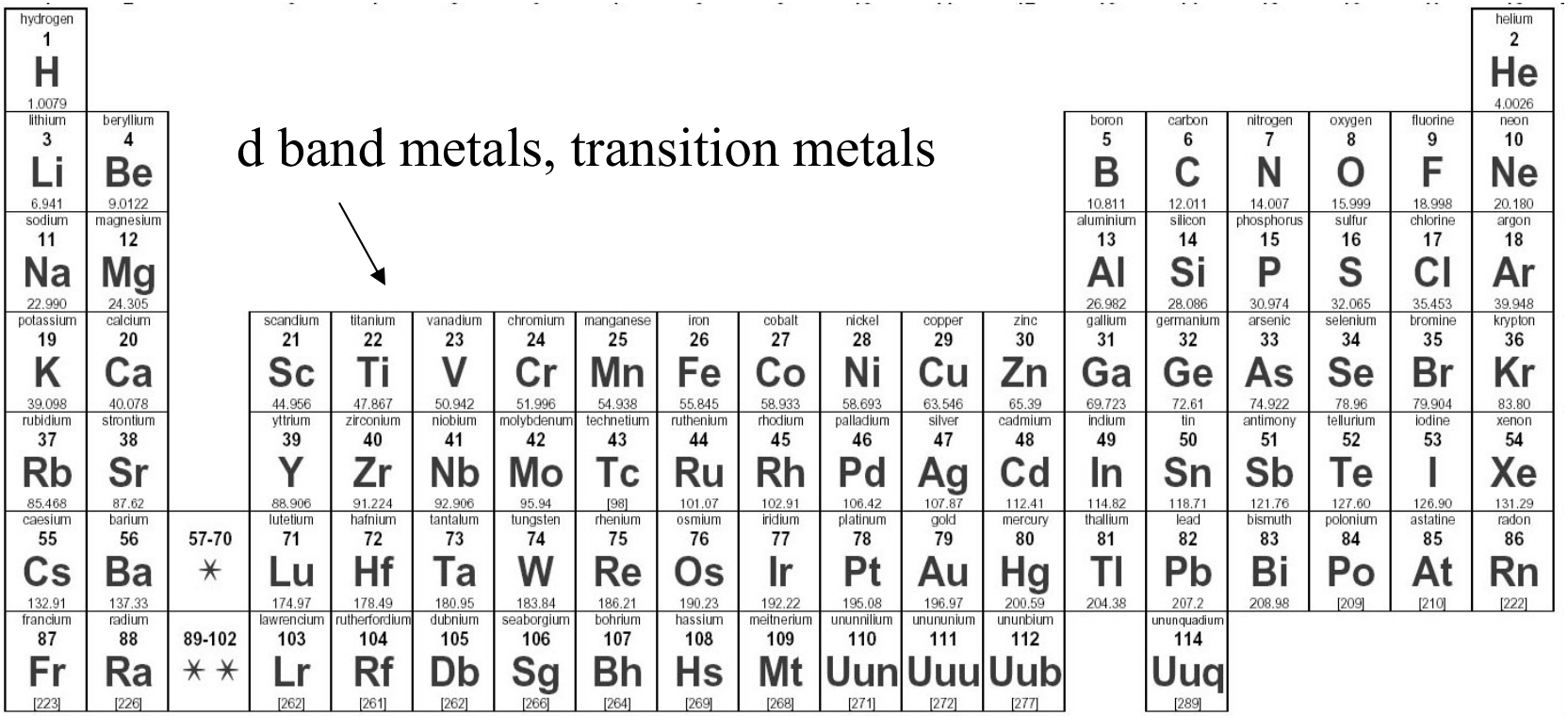
http://lampx.tugraz.at/~hadley/ss1/bands/bandstructures/Cr/Cr_Bandstructure.html

Transition metals

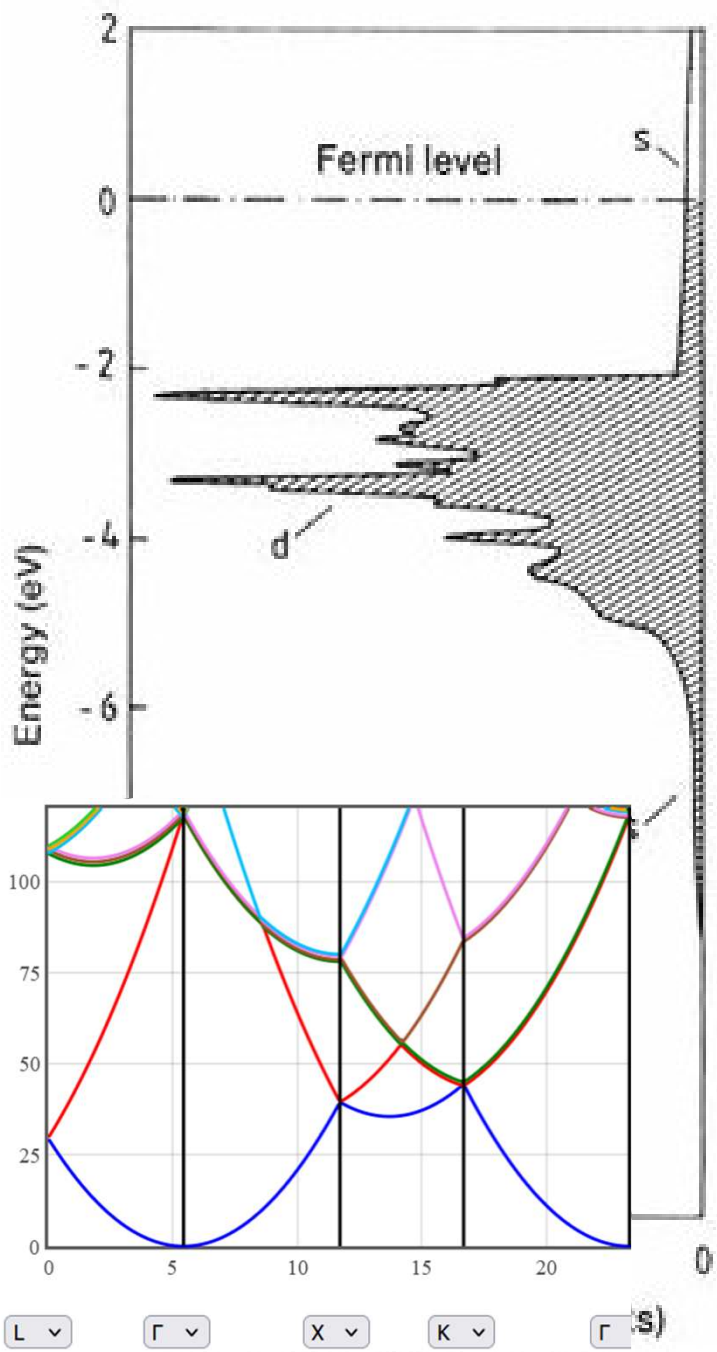


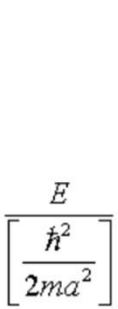


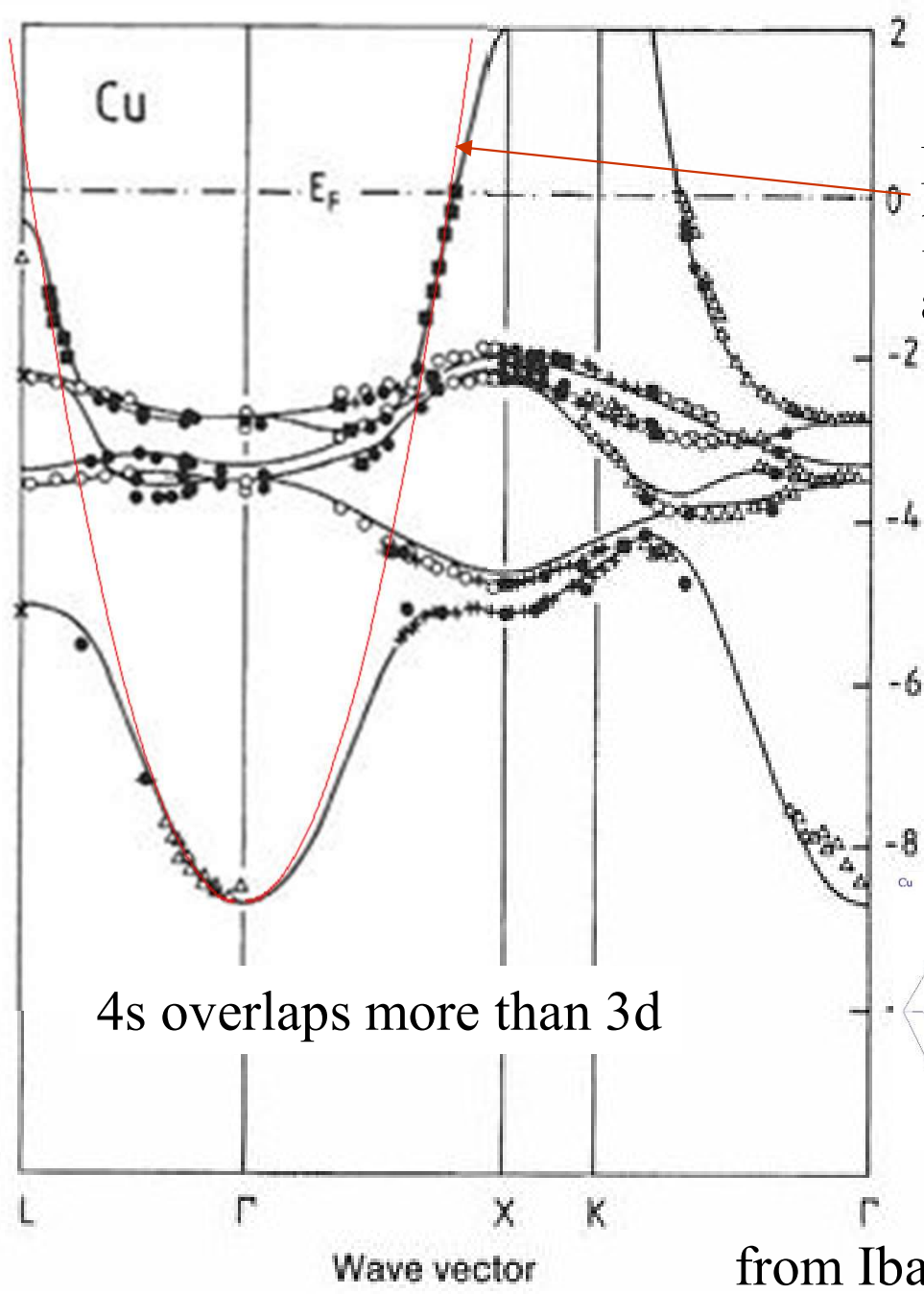



d band metals, transition metals
hydrogen 1 H 1.0079
helium 2 He 4.0026
lithium 3 Li 6.941
beryllium 4 Be 9.0122
boron 5 B 10.811
carbon 6 C 12.011
nitrogen 7 N 14.007
oxygen 8 O 15.999
fluorine 9 F 18.998
neon 10 Ne 20.180
sodium 11 Na 22.990
magnesium 12 Mg 24.305
aluminium 13 Al 26.982
silicon 14 Si 28.086
phosphorus 15 P 30.974
sulfur 16 S 32.065
chlorine 17 Cl 35.453
argon 18 Ar 39.948
potassium 19 K 39.098
calcium 20 Ca 40.078
scandium 21 Sc 44.956
titanium 22 Ti 47.867
vanadium 23 V 50.942
chromium 24 Cr 51.996
manganese 25 Mn 54.938
iron 26 Fe 55.845
cobalt 27 Co 58.933
nickel 28 Ni 58.693
copper 29 Cu 63.546
zinc 30 Zn 65.39
gallium 31 Ga 69.723
germanium 32 Ge 72.61
arsenic 33 As 74.922
selenium 34 Se 78.96
bromine 35 Br 79.904
krypton 36 Kr 83.80
rubidium 37 Rb 85.468
strontium 38 Sr 87.62
yttrium 39 Y 88.906
zirconium 40 Zr 91.224
niobium 41 Nb 92.906
molybdenum 42 Mo 95.94
technetium 43 Tc [98]
ruthenium 44 Ru 101.07
rhodium 45 Rh 102.91
palladium 46 Pd 106.42
silver 47 Ag 107.87
cadmium 48 Cd 112.41
indium 49 In 114.82
tin 50 Sn 118.71
antimony 51 Sb 121.76
tellurium 52 Te 127.60
iodine 53 I 126.90
xenon 54 Xe 131.29
caesium 55 Cs 132.91
barium 56 Ba 137.33
57-70 *
lutetium 71 Lu 174.97
hafnium 72 Hf 178.49
tantalum 73 Ta 180.95
tungsten 74 W 183.84
rhenium 75 Re 186.21
osmium 76 Os 190.23
iridium 77 Ir 192.22
platinum 78 Pt 195.08
gold 79 Au 196.97
mercury 80 Hg 200.59
thallium 81 Tl 204.38
lead 82 Pb 207.2
bismuth 83 Bi 208.98
polonium 84 Po [209]
astatine 85 At [210]
radon 86 Rn [222]
francium 87 Fr [223]
radium 88 Ra [226]
89-102 * *
lawrencium 103 Lr [262]
rutherfordium 104 Rf [261]
dubnium 105 Db [262]
seaborgium 106 Sg [266]
bohrium 107 Bh [264]
hassium 108 Hs [269]
meitnerium 109 Mt [268]
ununnilium 110 Uun [271]
unununium 111 Uuu [272]
ununbium 112 Uub [277]
ununquadium 114 Uuq [289]
*Lanthanide series
**Actinide series
lanthanum 57 La 138.91
cerium 58 Ce 140.12
praseodymium 59 Pr 140.91
neodymium 60 Nd 144.24
promethium 61 Pm [145]
samarium 62 Sm 150.36
europium 63 Eu 151.96
gadolinium 64 Gd 157.25
terbium 65 Tb 158.93
dysprosium 66 Dy 162.50
holmium 67 Ho 164.93
erbium 68 Er 167.26
thulium 69 Tm 168.93
ytterbium 70 Yb 173.04
actinium 89 Ac [227]
thorium 90 Th 232.04
protactinium 91 Pa 231.04
uranium 92 U 238.03
neptunium 93 Np [237]
plutonium 94 Pu [244]
americium 95 Am [243]
curium 96 Cm [247]
berkelium 97 Bk [247]
californium 98 Cf [251]
einsteinium 99 Es [252]
fermium 100 Fm [257]
mendelevium 101 Md [258]
nobelium 102 No [259]
f band metals, rare earths

Copper dispersion relation and density of states

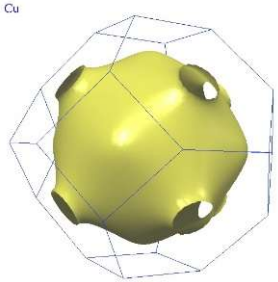






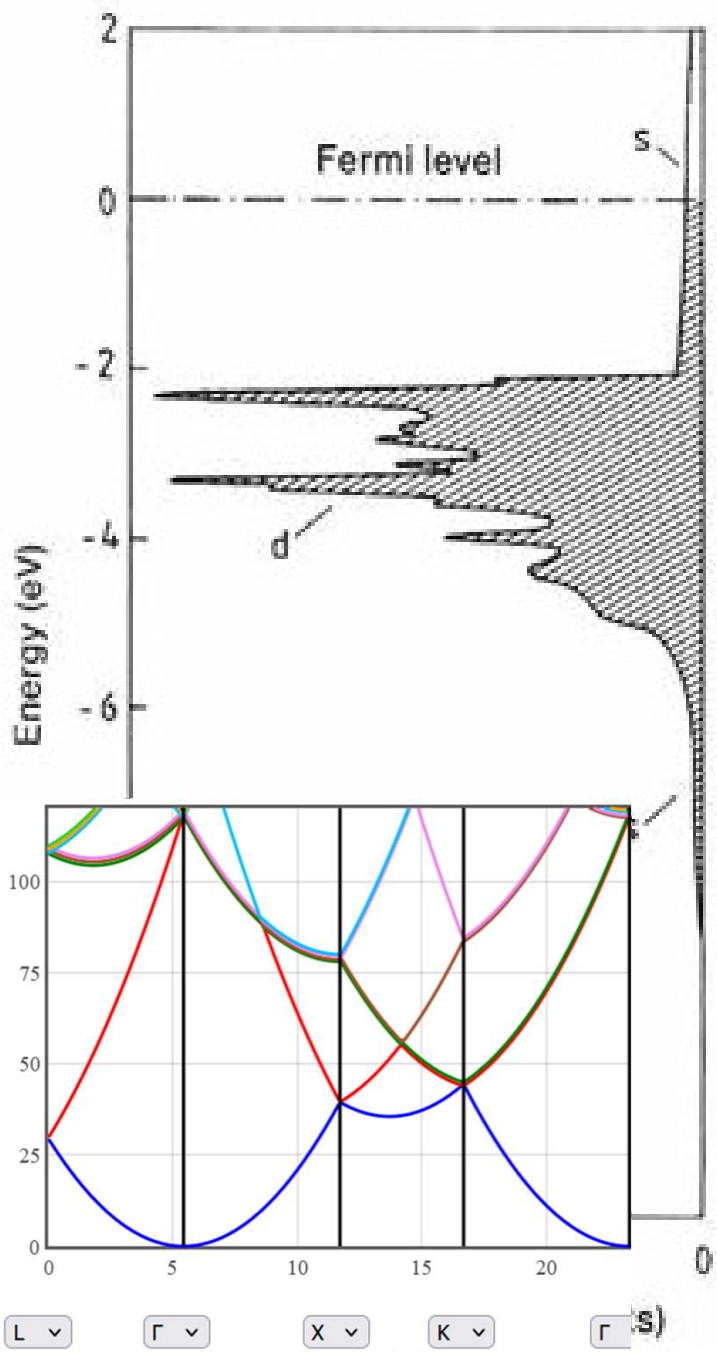
Empty lattice approx.

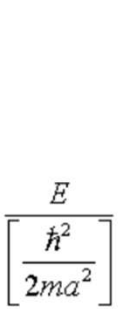
4s overlaps more than 3d

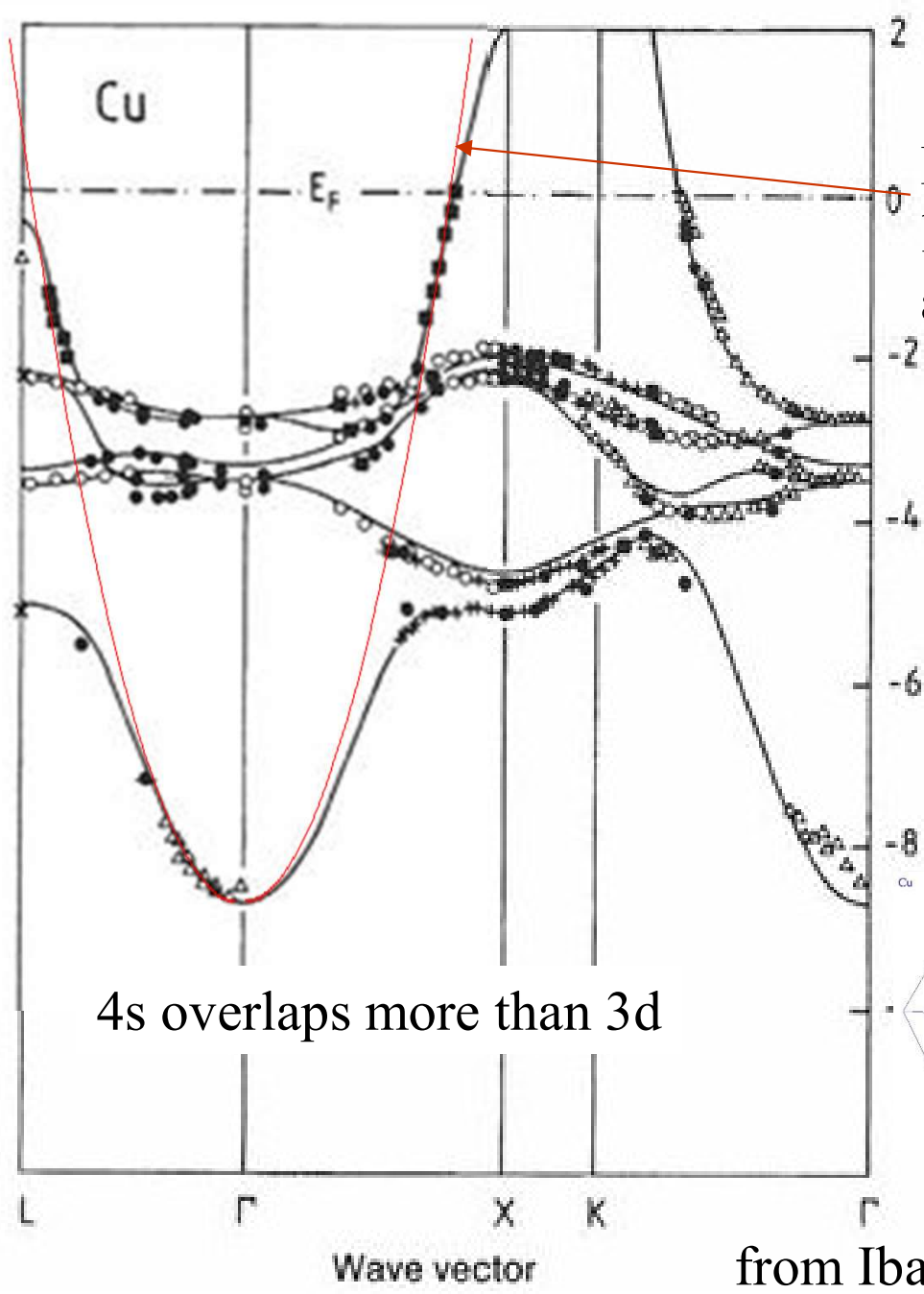


from Ibach & Lueth

Copper dispersion relation and density of states

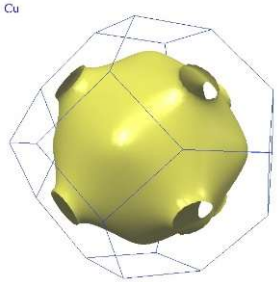






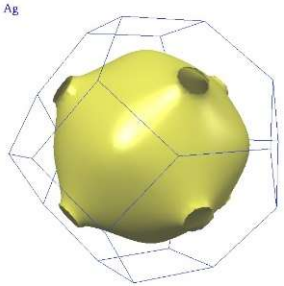
Empty lattice approx.

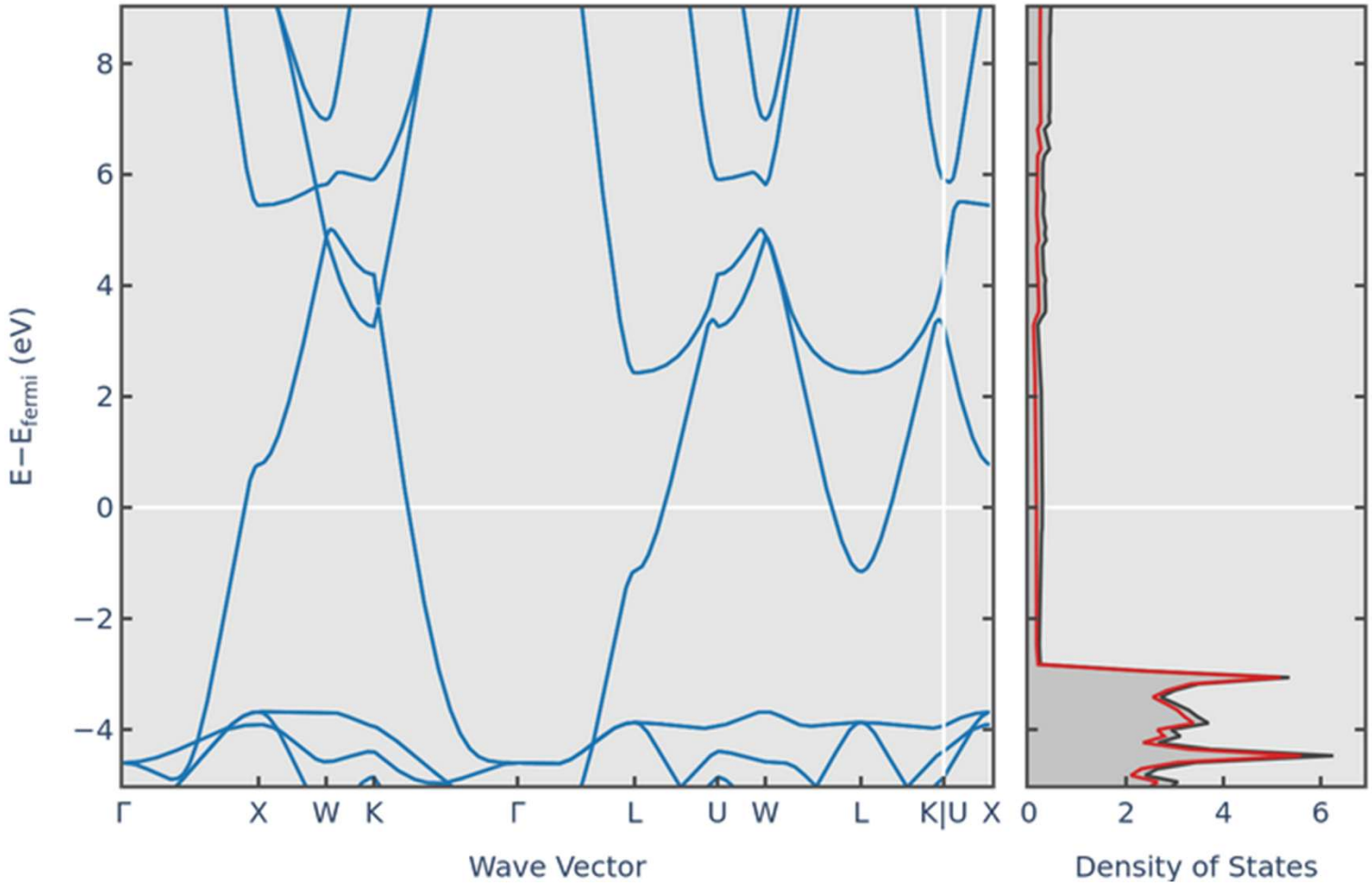
4s overlaps more than 3d



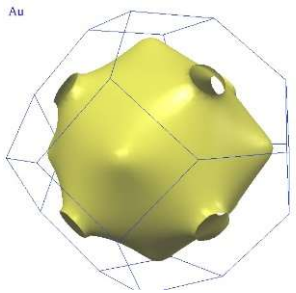
from Ibach & Lueth

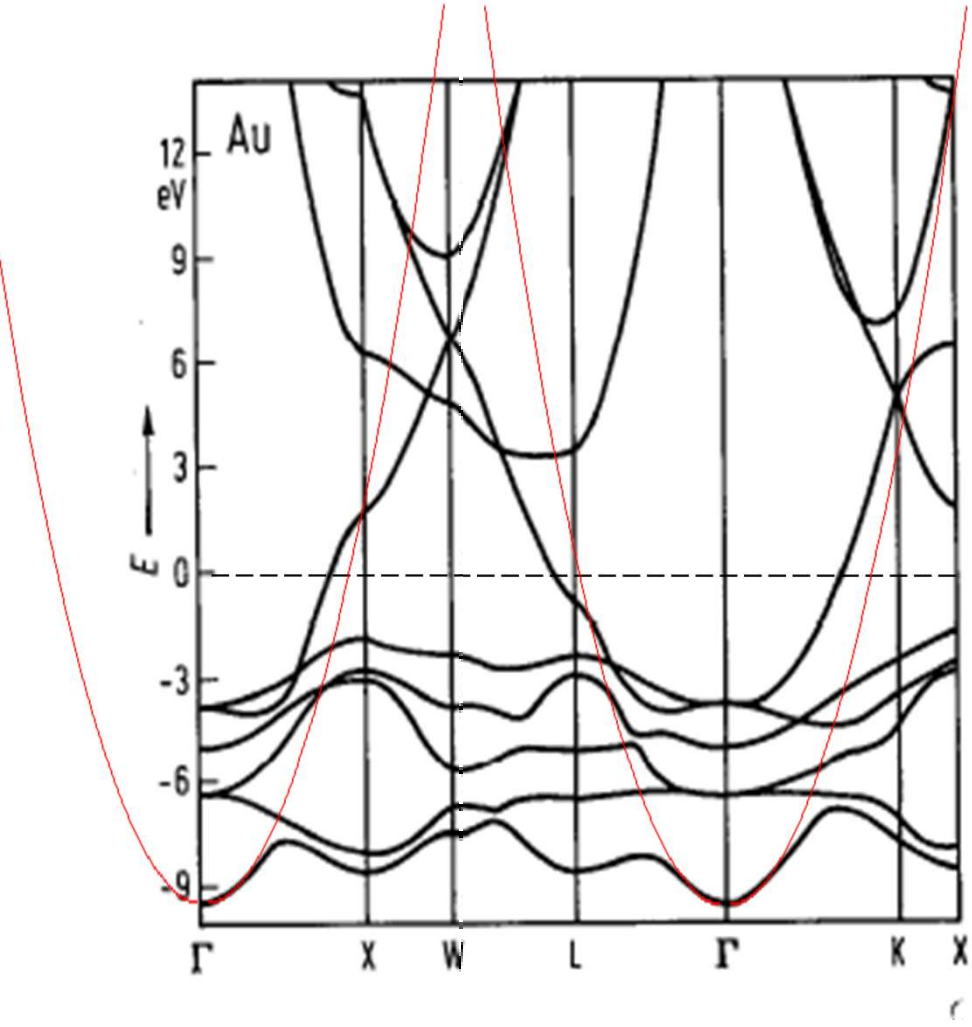
Silver


Ag


E−E_fermi (eV)
8
6
4
2
0
−2
−4
Γ
X
W
K
Γ
L
U
W
L
K|U
X
Wave Vector
0
2
4
6
Density of States

Gold





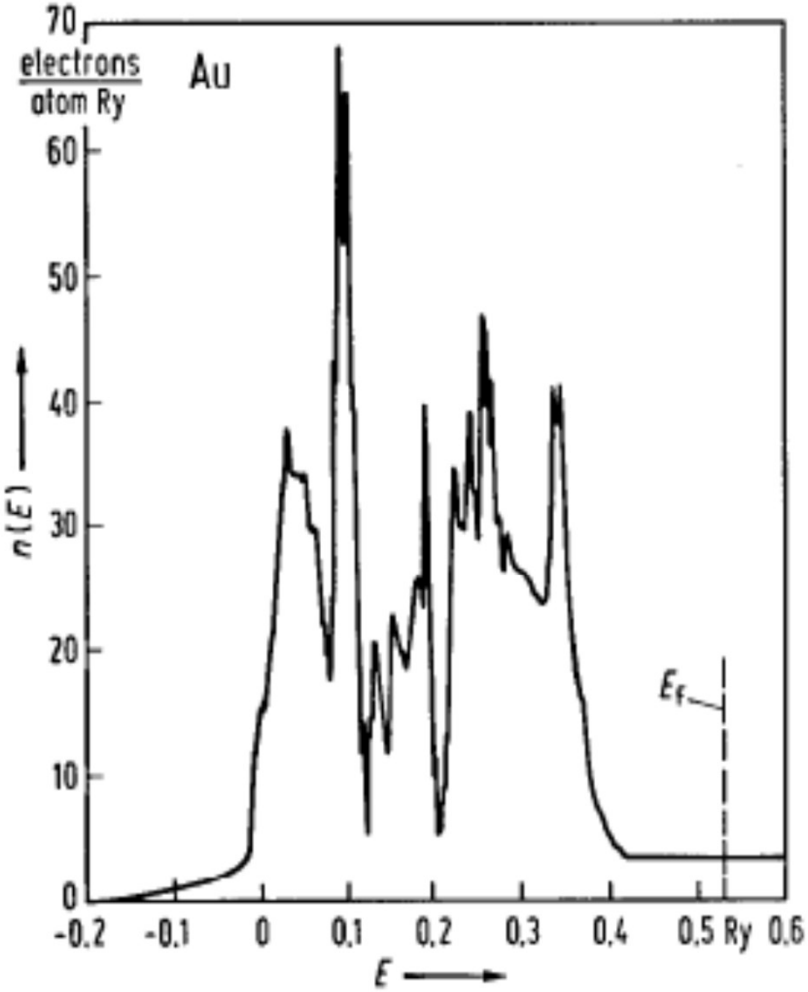
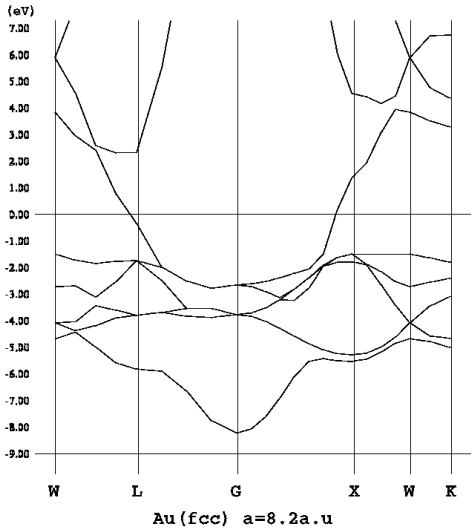
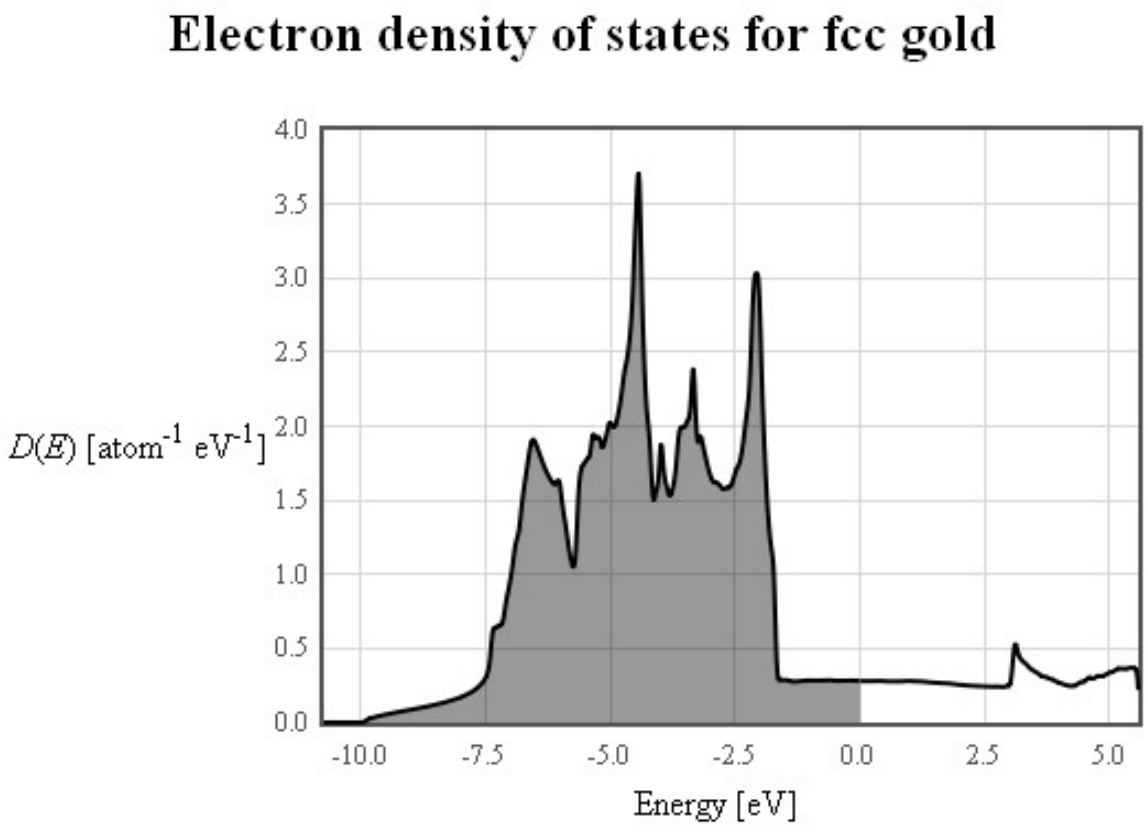


Fig. 9. Au. Density of states calculated from the energy bands in Fig. 4b. Au [71Chr2].

Thermodynamic properties of metals

From the band structure measurements, we obtain the electron density of states.



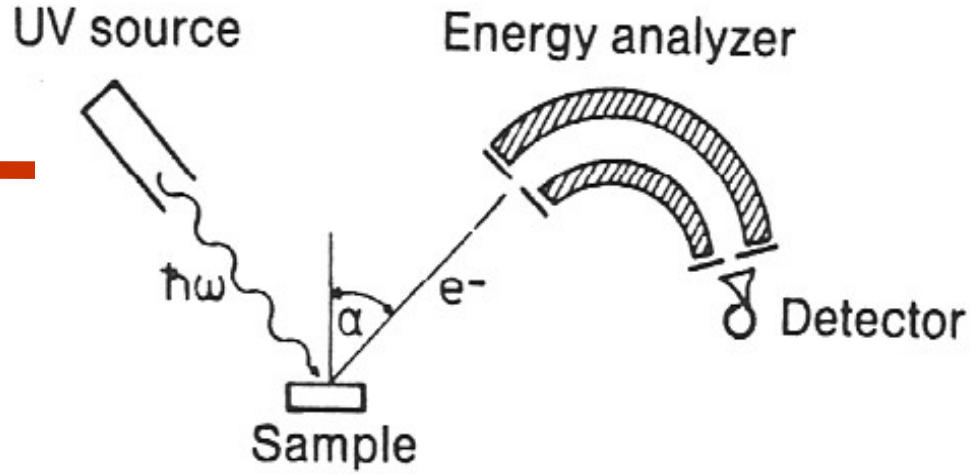


Thermodynamic properties can be calculated from the tabulated data for the density of states

E [eV]	$D(E)$ [atom^{-1} eV^{-1}]
-10.74913	0
-10.73552	0
-10.72192	0

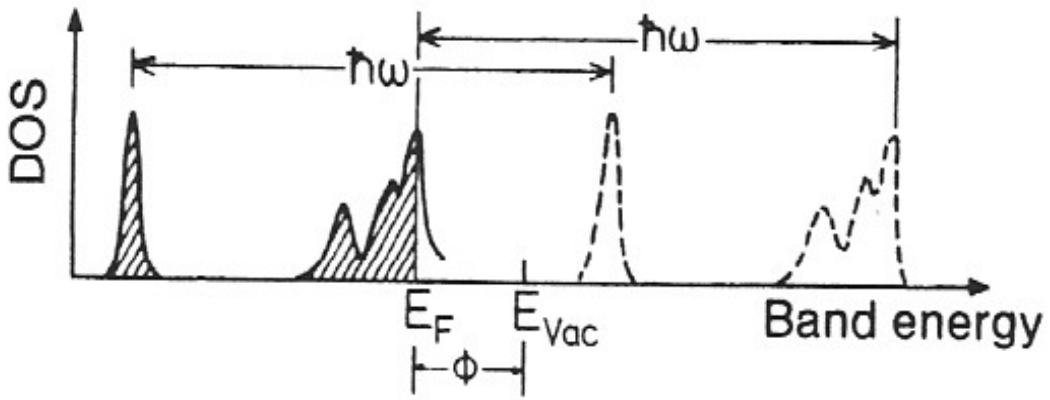
Photoemission spectroscopy

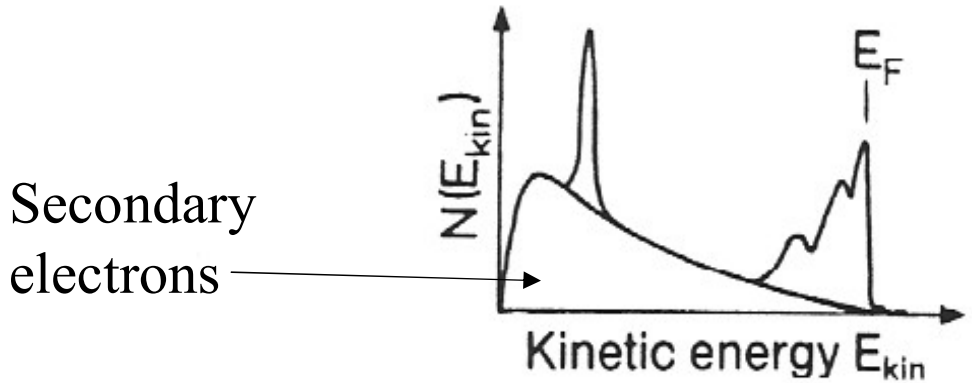
UPS - Ultraviolet photoemission spectroscopy



a

Measure the density of states with photoemission spectroscopy

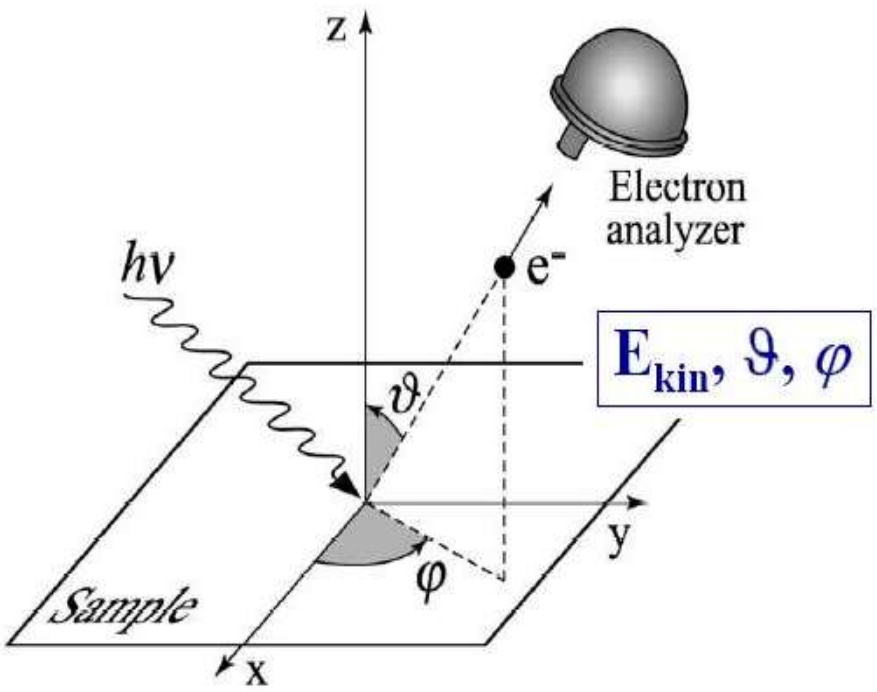


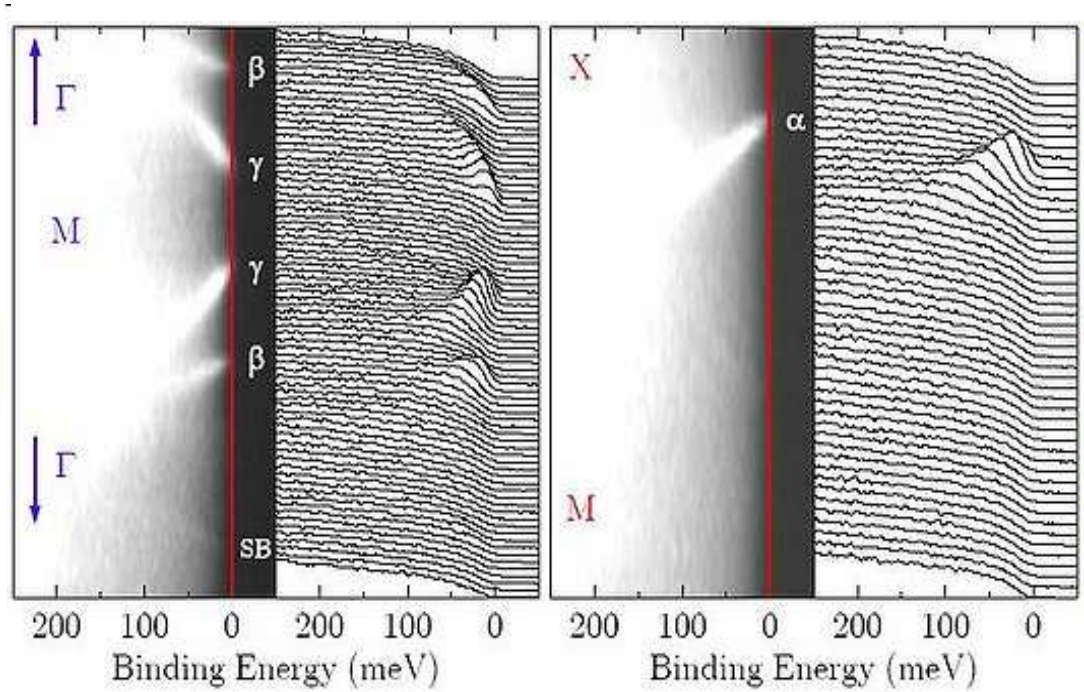


From: Ibach & Lueth

b

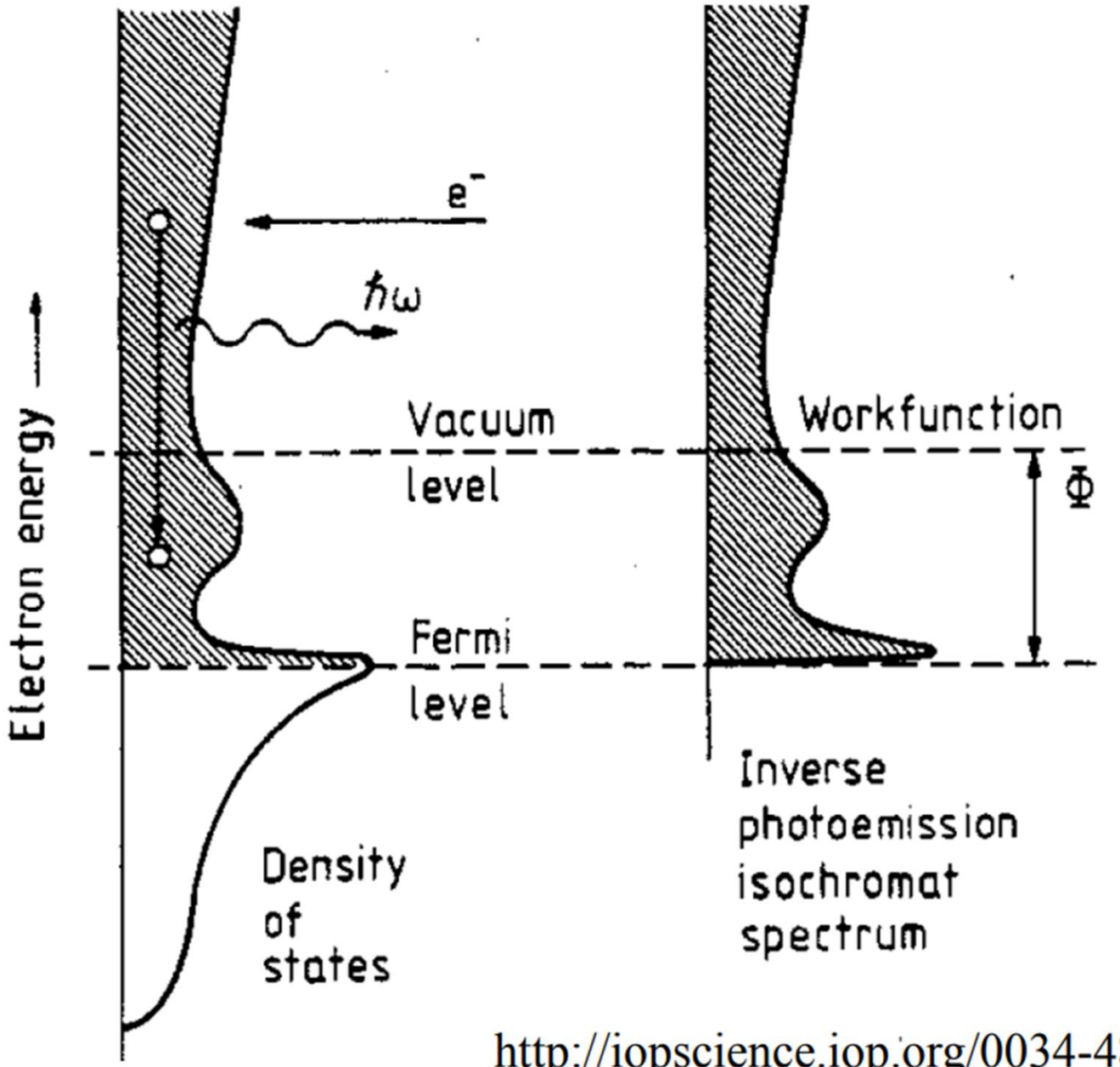
Angle resolved photoemission spectroscopy (ARPES)





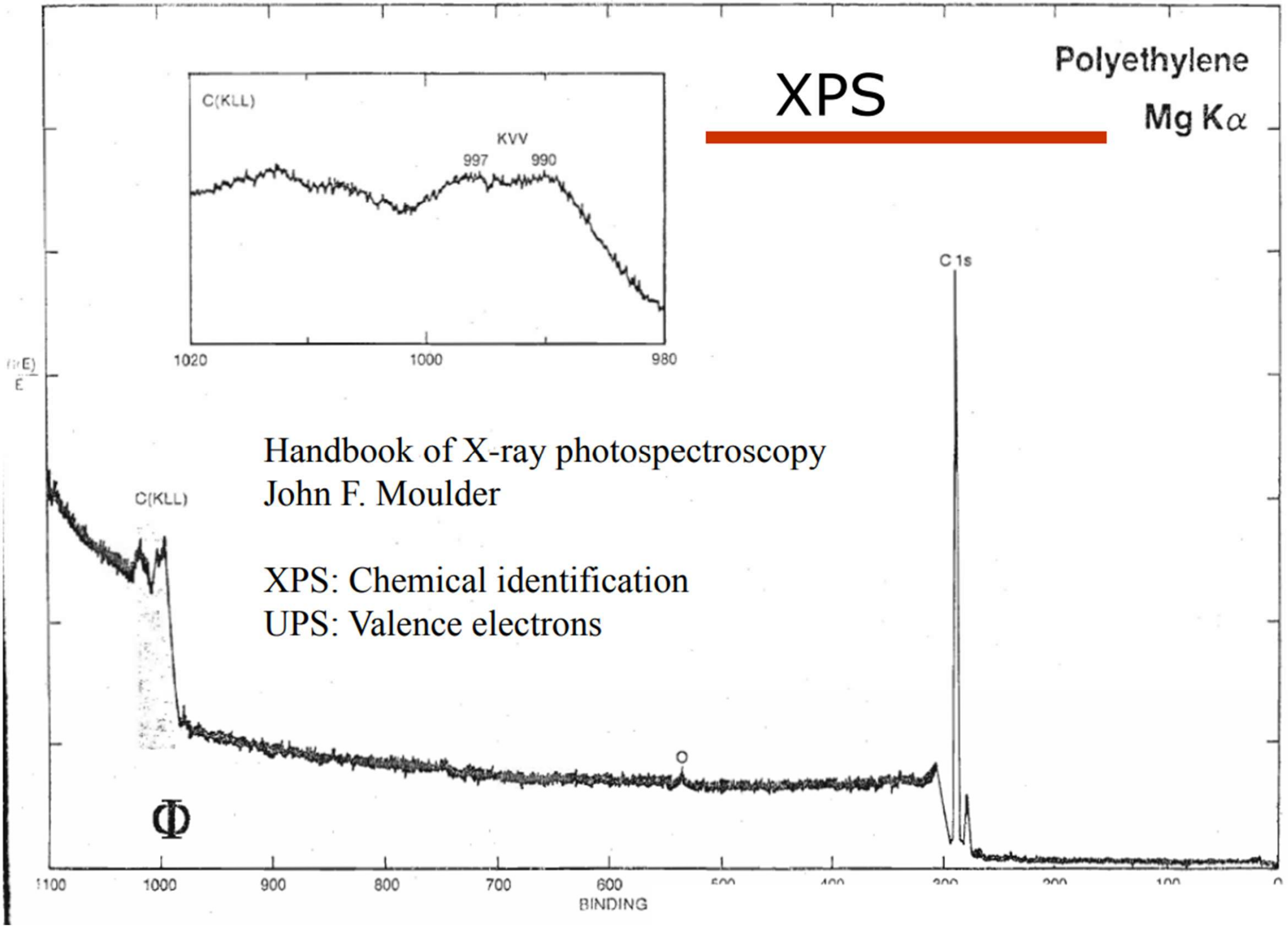
Measure the dispersion relation with angle resolved photoemission

Inverse photoemission spectroscopy (IPES)



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

XPS



Handbook of X-ray photospectroscopy
John F. Moulder

XPS: Chemical identification
UPS: Valence electrons

Optical absorption