

# Electron bands

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# Bloch Theorem

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$$\text{Bloch form} \quad \psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r})$$

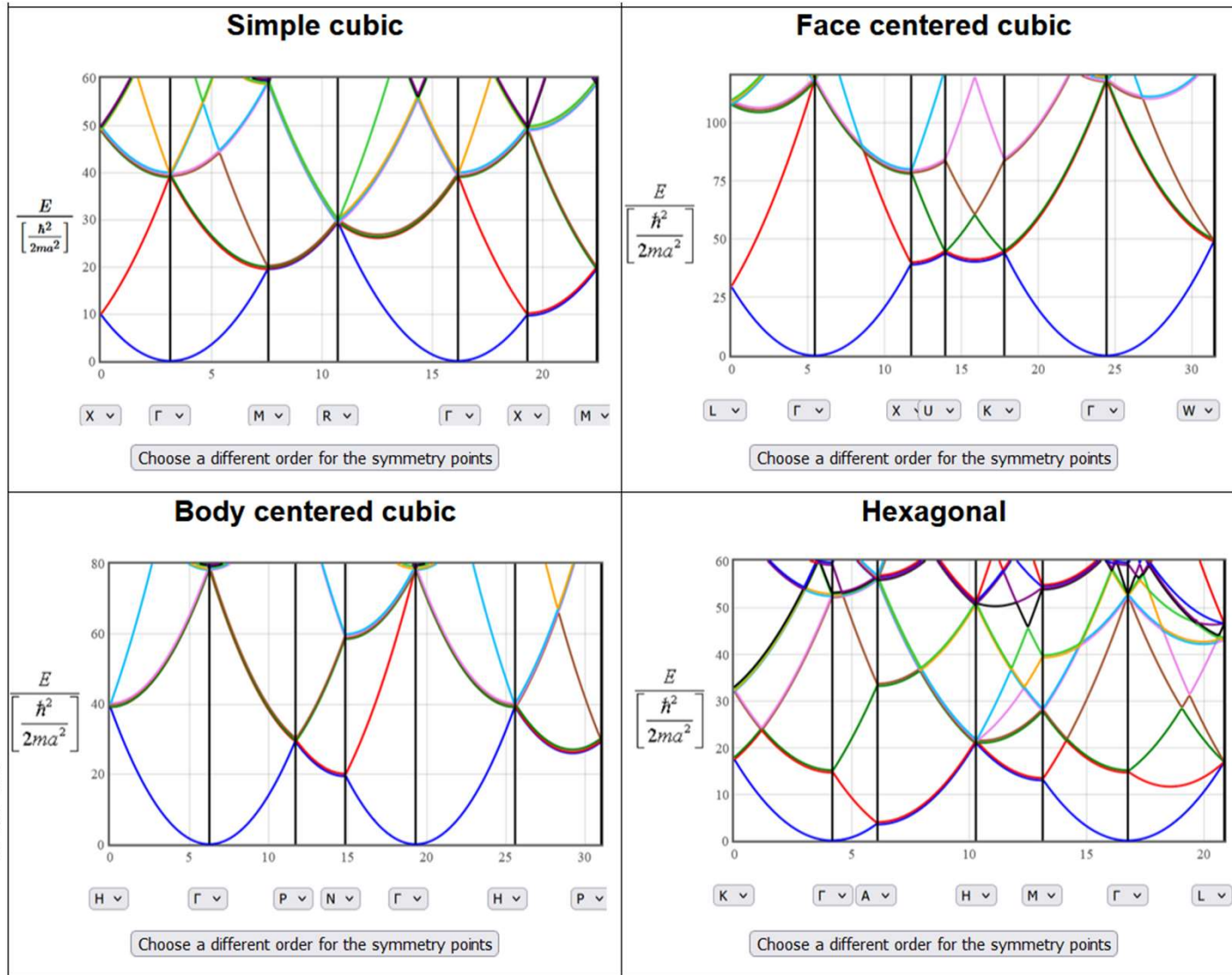
$u_{\vec{k}}(\vec{r})$  is a periodic function.

$\vec{k}$  is a wavevector in the first Brillouin zone.

Eigenfunction solutions of the Schrödinger equation have Bloch form.

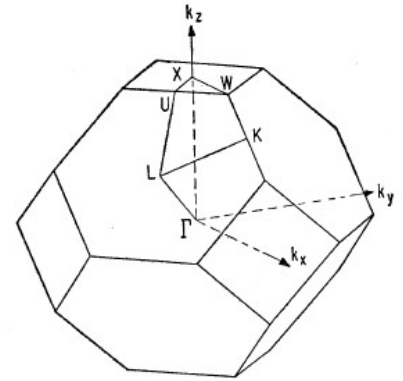
$$\mathbf{T}\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot(\vec{r}+\vec{T})} u_{\vec{k}}(\vec{r} + \vec{T}) = e^{i\vec{k}\cdot\vec{T}} e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{T}} \psi_{\vec{k}}(\vec{r})$$

# Empty lattice approximation

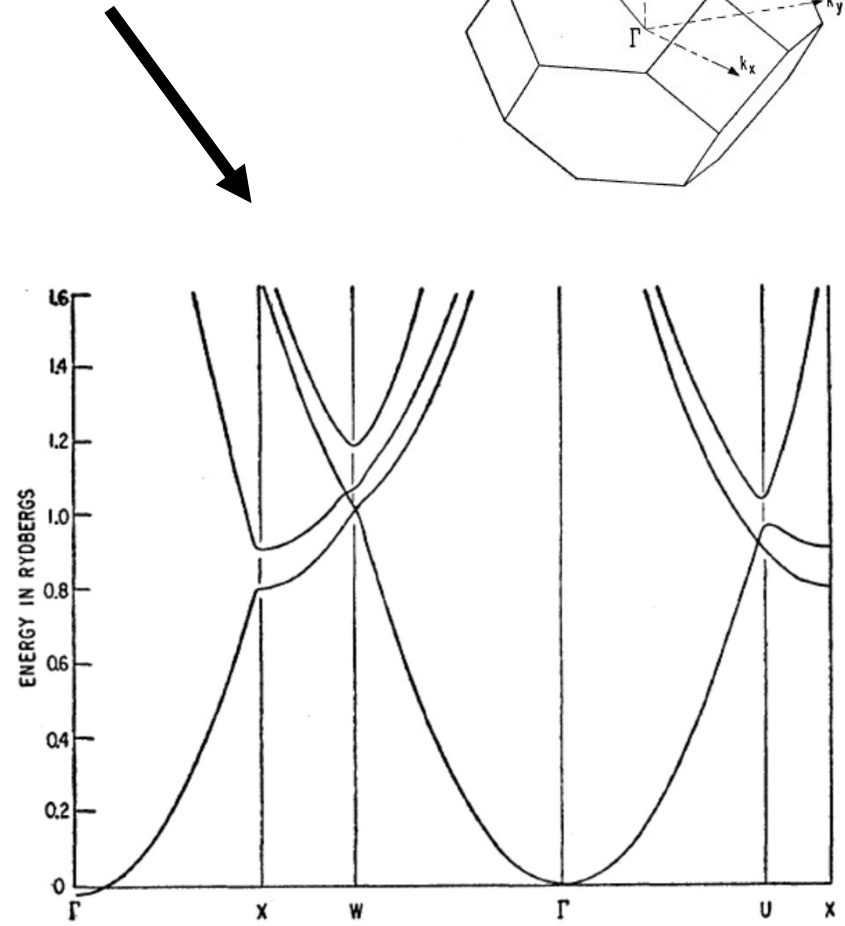
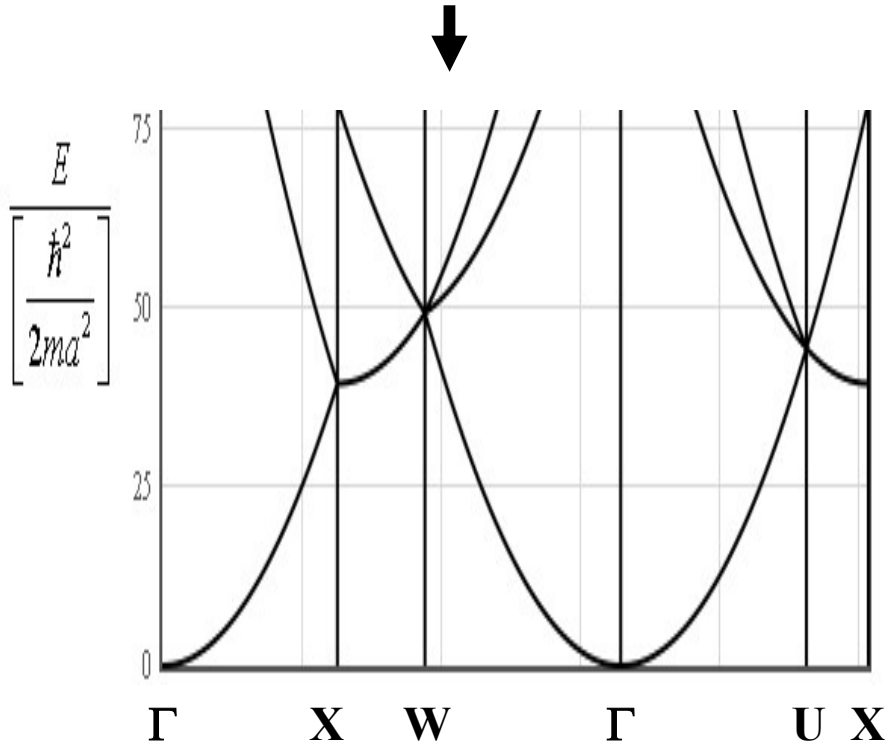


# Band Structure of Aluminum

WALTER A. HARRISON  
*General Electric Research Laboratory, Schenectady, New York*



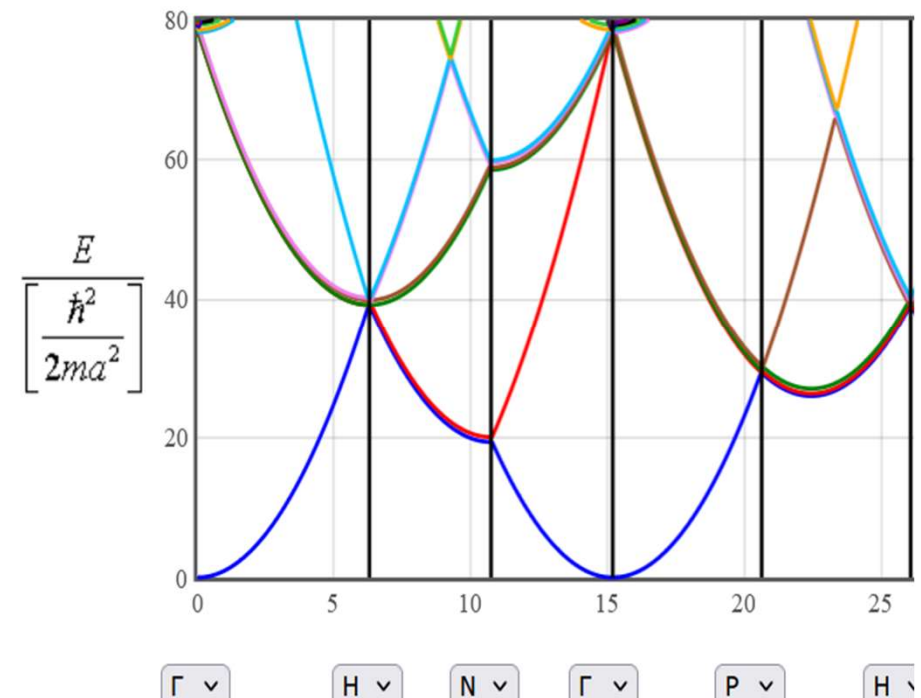
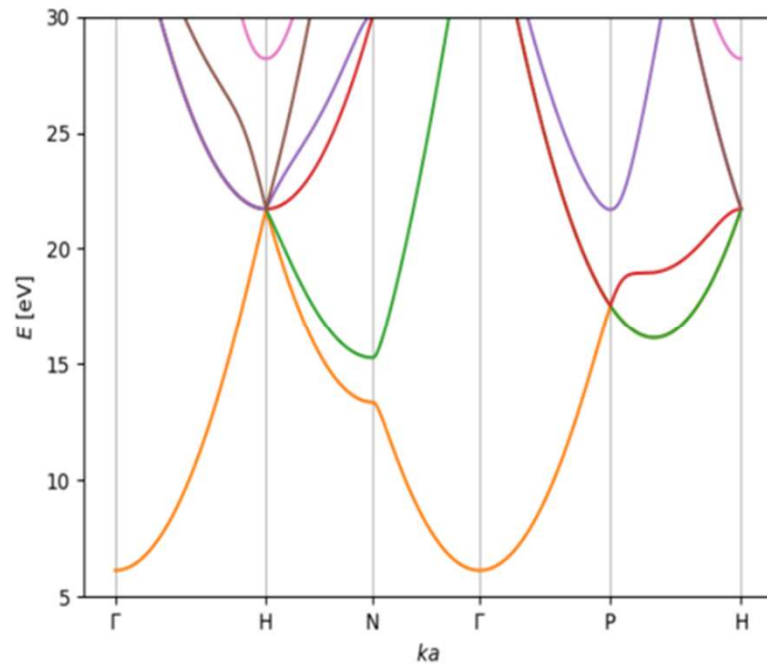
empty lattice approximation



## + - Body Centered Cubic with a Comb Potential

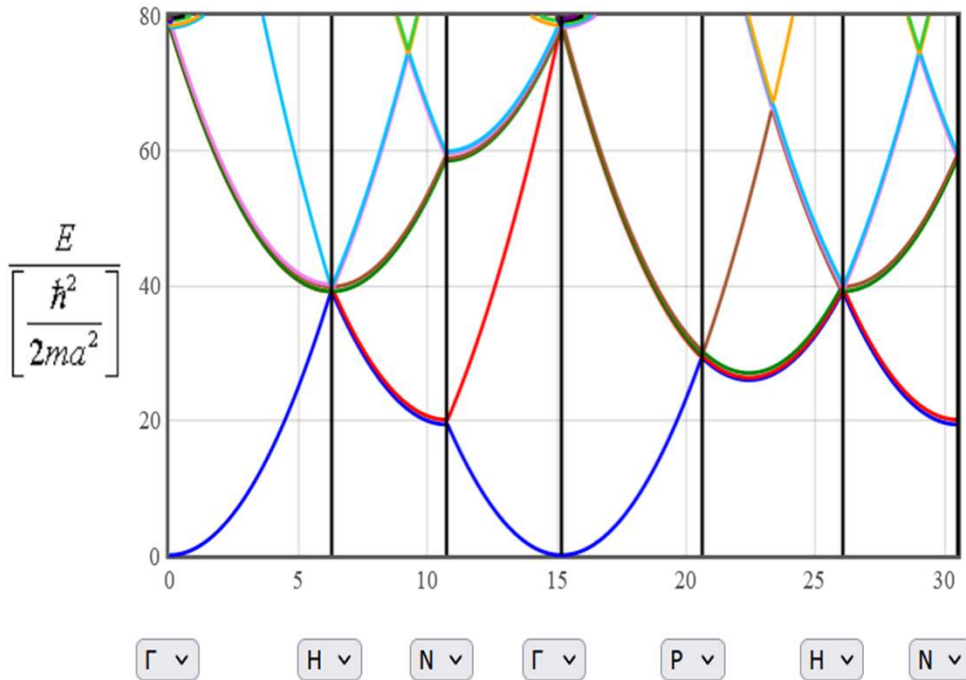
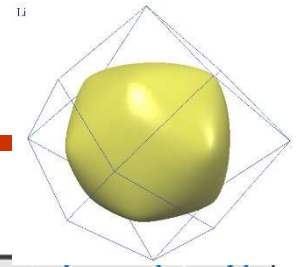
If all of the components of a Fourier series are real and have the same amplitude, there is constructive interference at the Bravais lattice points and this produces a comb function with one large amplitude peak per Bravais lattice point. Below is python code to calculate the band structure of a bcc 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.

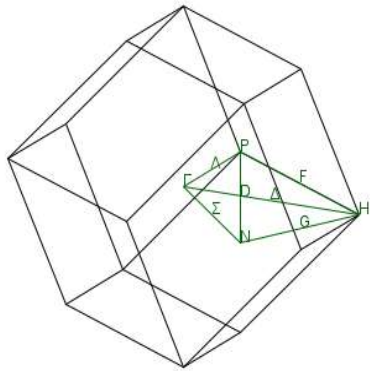
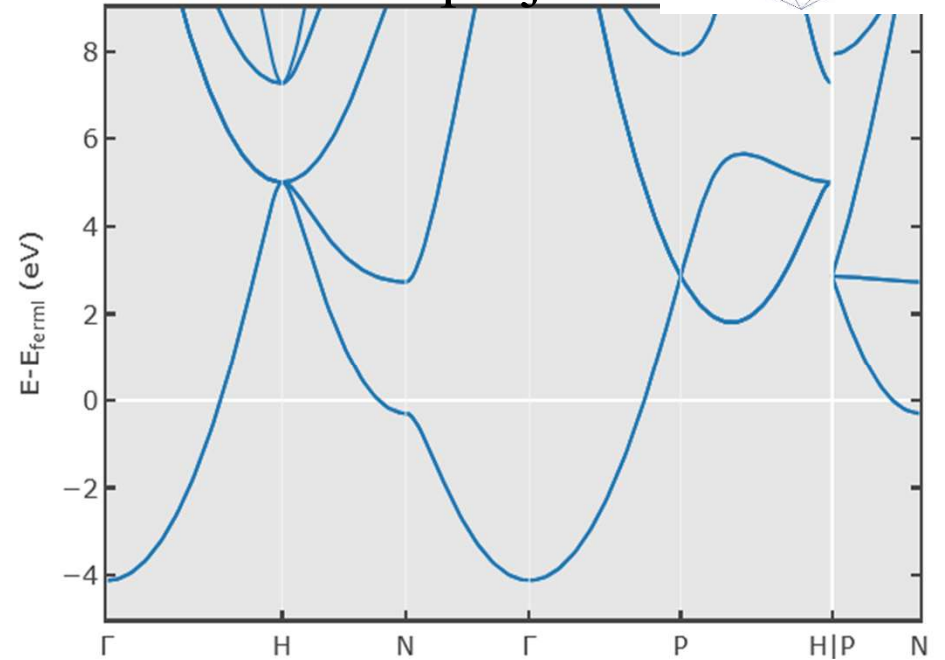




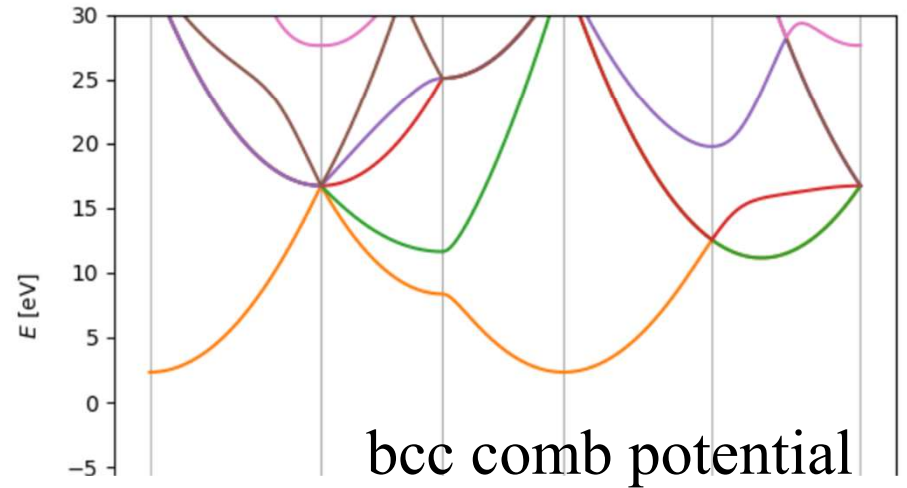
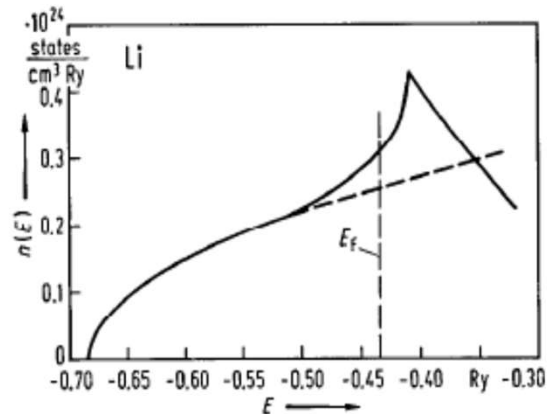
# Lithium bcc



## Materials project

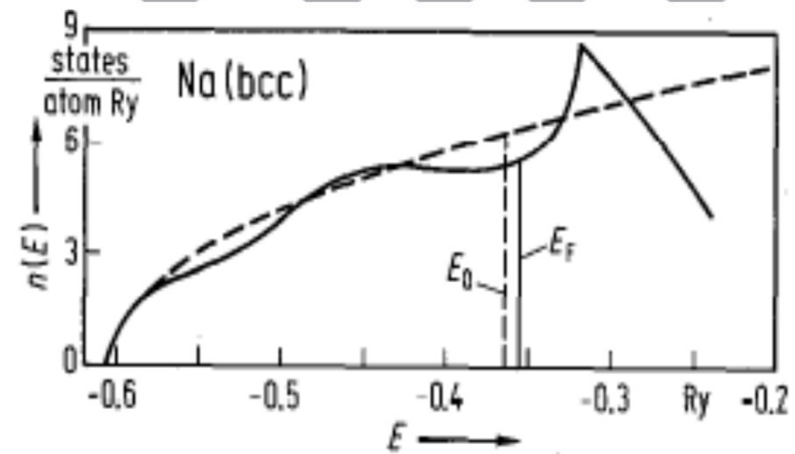
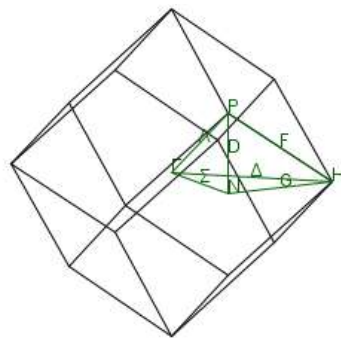
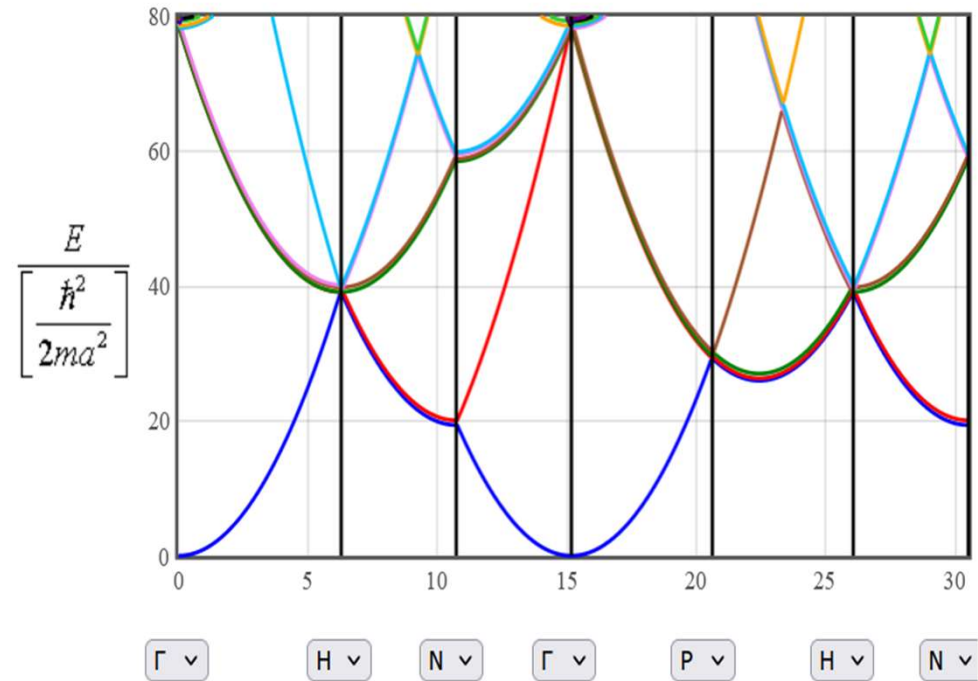
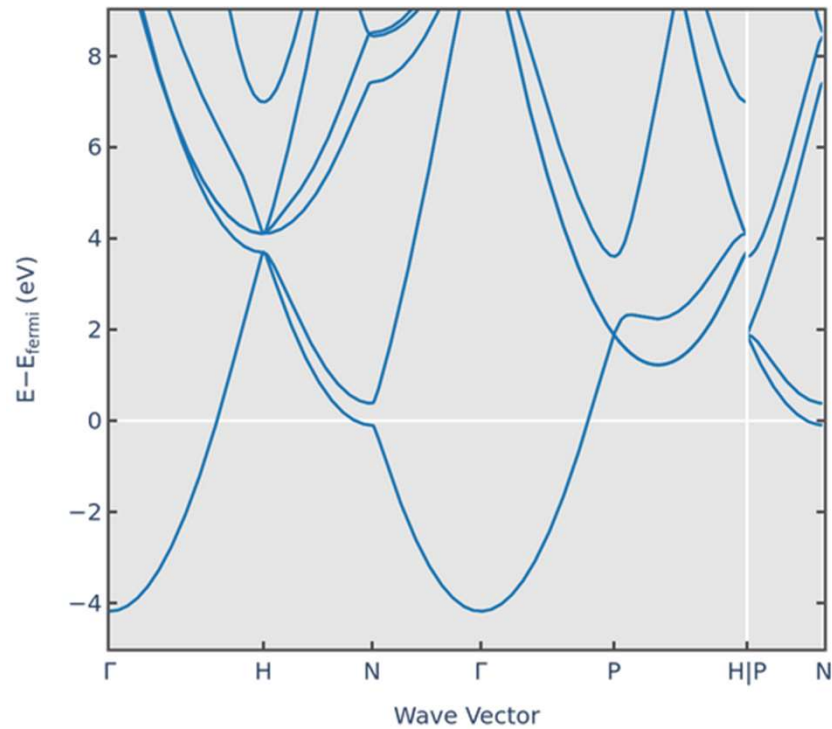
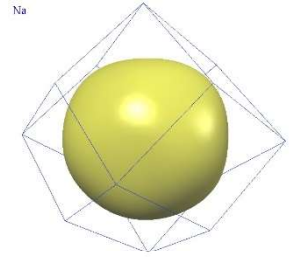


## Density of states



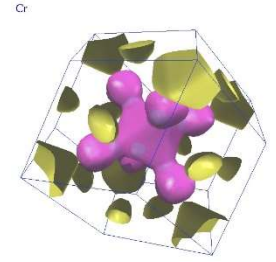
bcc comb potential

# Sodium

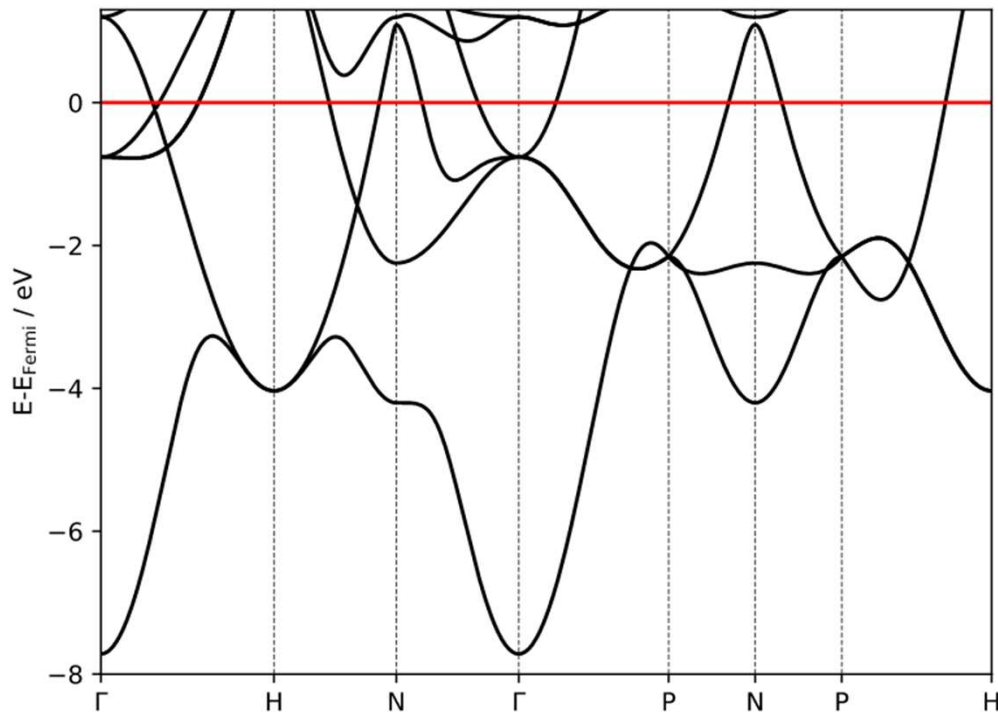




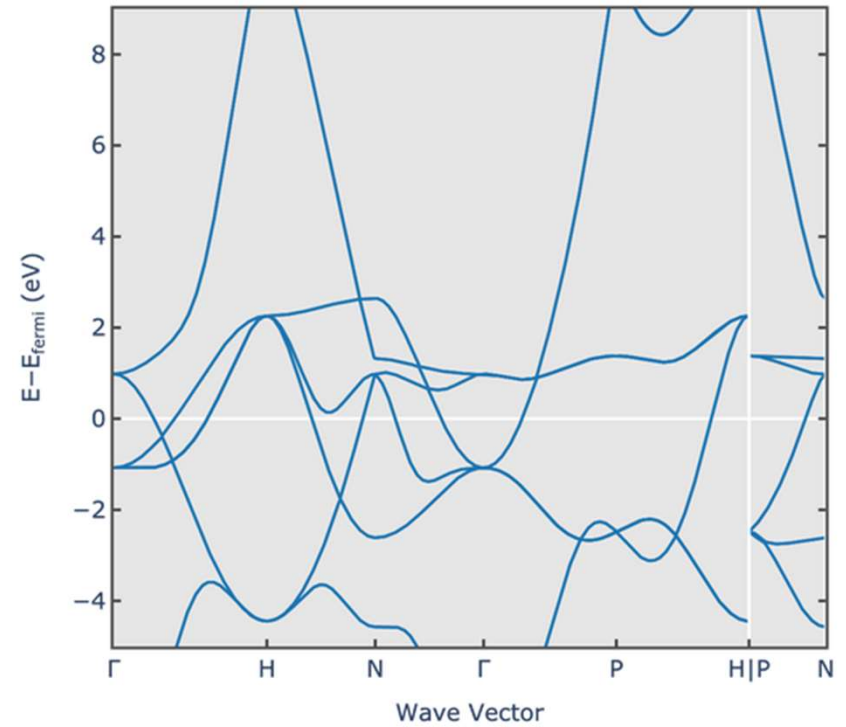
# Bandstructure of bcc chromium (Cr)



Quantum Espresso

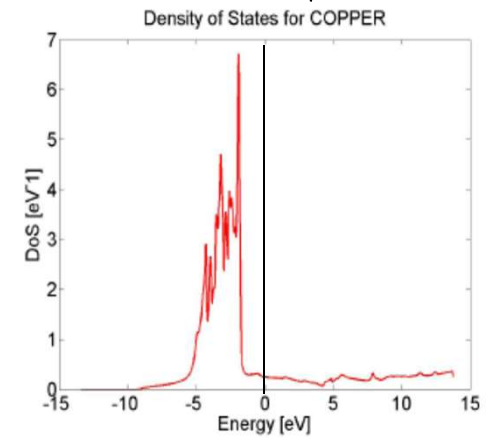
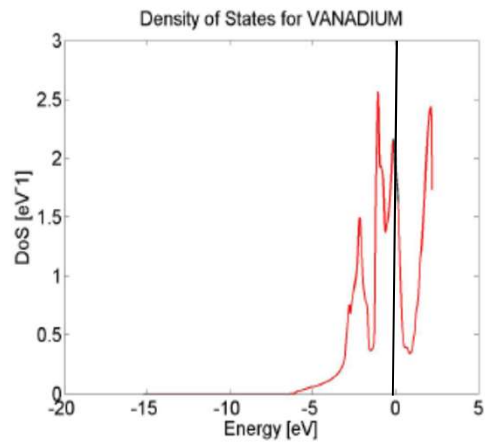
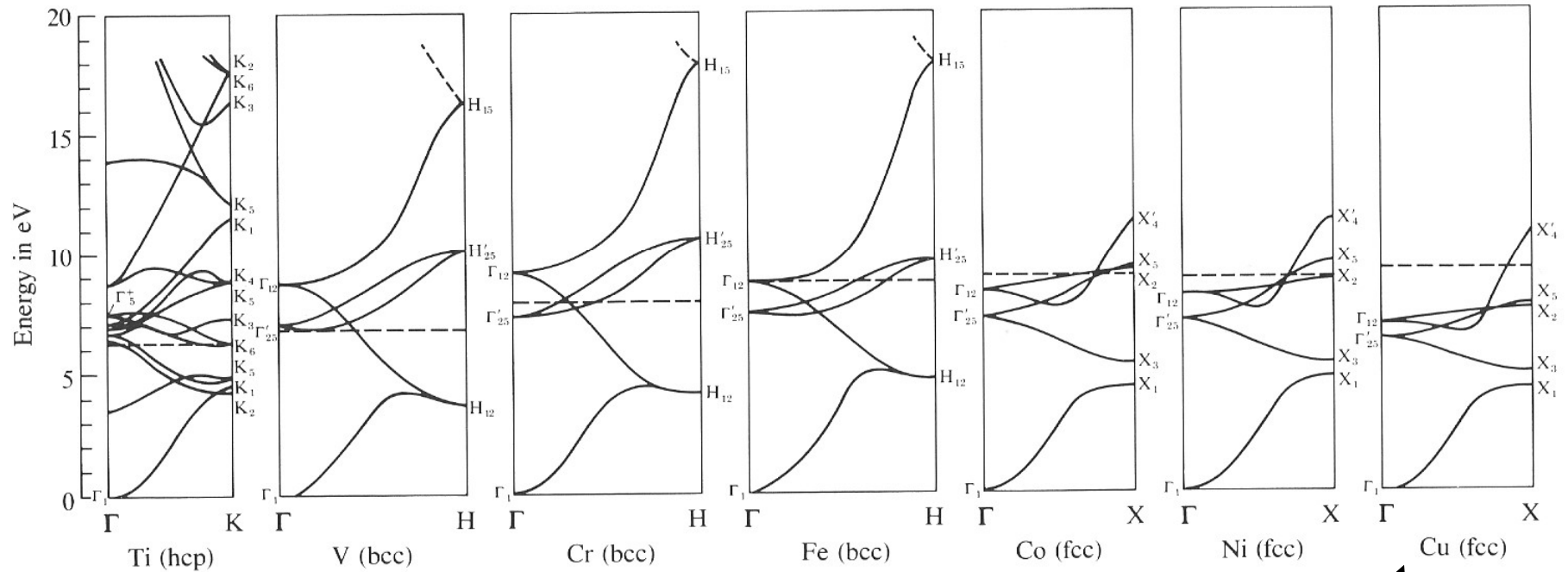


Materials Project



[http://lampx.tugraz.at/~hadley/ss1/bands/bandstructures/Cr/Cr\\_Bandstructure.html](http://lampx.tugraz.at/~hadley/ss1/bands/bandstructures/Cr/Cr_Bandstructure.html)

# Transition metals



hydrogen 1 <b>H</b> 1.0079																	helium 2 <b>He</b> 4.0026						
lithium 3 <b>Li</b> 6.941	beryllium 4 <b>Be</b> 9.0122																	boron 5 <b>B</b> 10.811	carbon 6 <b>C</b> 12.011	nitrogen 7 <b>N</b> 14.007	oxygen 8 <b>O</b> 15.999	fluorine 9 <b>F</b> 18.998	neon 10 <b>Ne</b> 20.180
sodium 11 <b>Na</b> 22.990	magnesium 12 <b>Mg</b> 24.305																	aluminium 13 <b>Al</b> 26.982	silicon 14 <b>Si</b> 28.086	phosphorus 15 <b>P</b> 30.974	sulfur 16 <b>S</b> 32.065	chlorine 17 <b>Cl</b> 35.453	argon 18 <b>Ar</b> 39.948
potassium 19 <b>K</b> 39.098	calcium 20 <b>Ca</b> 40.078	scandium 21 <b>Sc</b> 44.956	titanium 22 <b>Ti</b> 47.867	vanadium 23 <b>V</b> 50.942	chromium 24 <b>Cr</b> 51.996	manganese 25 <b>Mn</b> 54.938	iron 26 <b>Fe</b> 55.845	cobalt 27 <b>Co</b> 58.933	nickel 28 <b>Ni</b> 58.693	copper 29 <b>Cu</b> 63.546	zinc 30 <b>Zn</b> 65.39	gallium 31 <b>Ga</b> 69.723	germanium 32 <b>Ge</b> 72.61	arsenic 33 <b>As</b> 74.922	selenium 34 <b>Se</b> 78.96	bromine 35 <b>Br</b> 79.904	krypton 36 <b>Kr</b> 83.80						
rubidium 37 <b>Rb</b> 85.468	strontium 38 <b>Sr</b> 87.62	yttrium 39 <b>Y</b> 88.906	zirconium 40 <b>Zr</b> 91.224	niobium 41 <b>Nb</b> 92.906	molybdenum 42 <b>Mo</b> 95.94	technetium 43 <b>Tc</b> [98]	ruthenium 44 <b>Ru</b> 101.07	rhodium 45 <b>Rh</b> 102.91	palladium 46 <b>Pd</b> 106.42	silver 47 <b>Ag</b> 107.87	cadmium 48 <b>Cd</b> 112.41	indium 49 <b>In</b> 114.82	tin 50 <b>Sn</b> 118.71	antimony 51 <b>Sb</b> 121.76	tellurium 52 <b>Te</b> 127.60	iodine 53 <b>I</b> 126.90	xenon 54 <b>Xe</b> 131.29						
caesium 55 <b>Cs</b> 132.91	barium 56 <b>Ba</b> 137.33	57-70 *	lutetium 71 <b>Lu</b> 174.97	hafnium 72 <b>Hf</b> 178.49	tantalum 73 <b>Ta</b> 180.95	tungsten 74 <b>W</b> 183.84	rhenium 75 <b>Re</b> 186.21	osmium 76 <b>Os</b> 190.23	iridium 77 <b>Ir</b> 192.22	platinum 78 <b>Pt</b> 195.08	gold 79 <b>Au</b> 196.97	mercury 80 <b>Hg</b> 200.59	thallium 81 <b>Tl</b> 204.38	lead 82 <b>Pb</b> 207.2	bismuth 83 <b>Bi</b> 208.98	polonium 84 <b>Po</b> [209]	astatine 85 <b>At</b> [210]	radon 86 <b>Rn</b> [222]					
francium 87 <b>Fr</b> [223]	radium 88 <b>Ra</b> [226]	89-102 **	lawrencium 103 <b>Lr</b> [262]	rutherfordium 104 <b>Rf</b> [261]	dubnium 105 <b>Db</b> [262]	seaborgium 106 <b>Sg</b> [266]	bohrium 107 <b>Bh</b> [264]	hassium 108 <b>Hs</b> [269]	meitnerium 109 <b>Mt</b> [268]	ununnium 110 <b>Uun</b> [271]	ununium 111 <b>Uuu</b> [272]	ununium 112 <b>Uub</b> [277]	ununquadium 114 <b>Uuq</b> [289]										

d band metals, transition metals



\* Lanthanide series

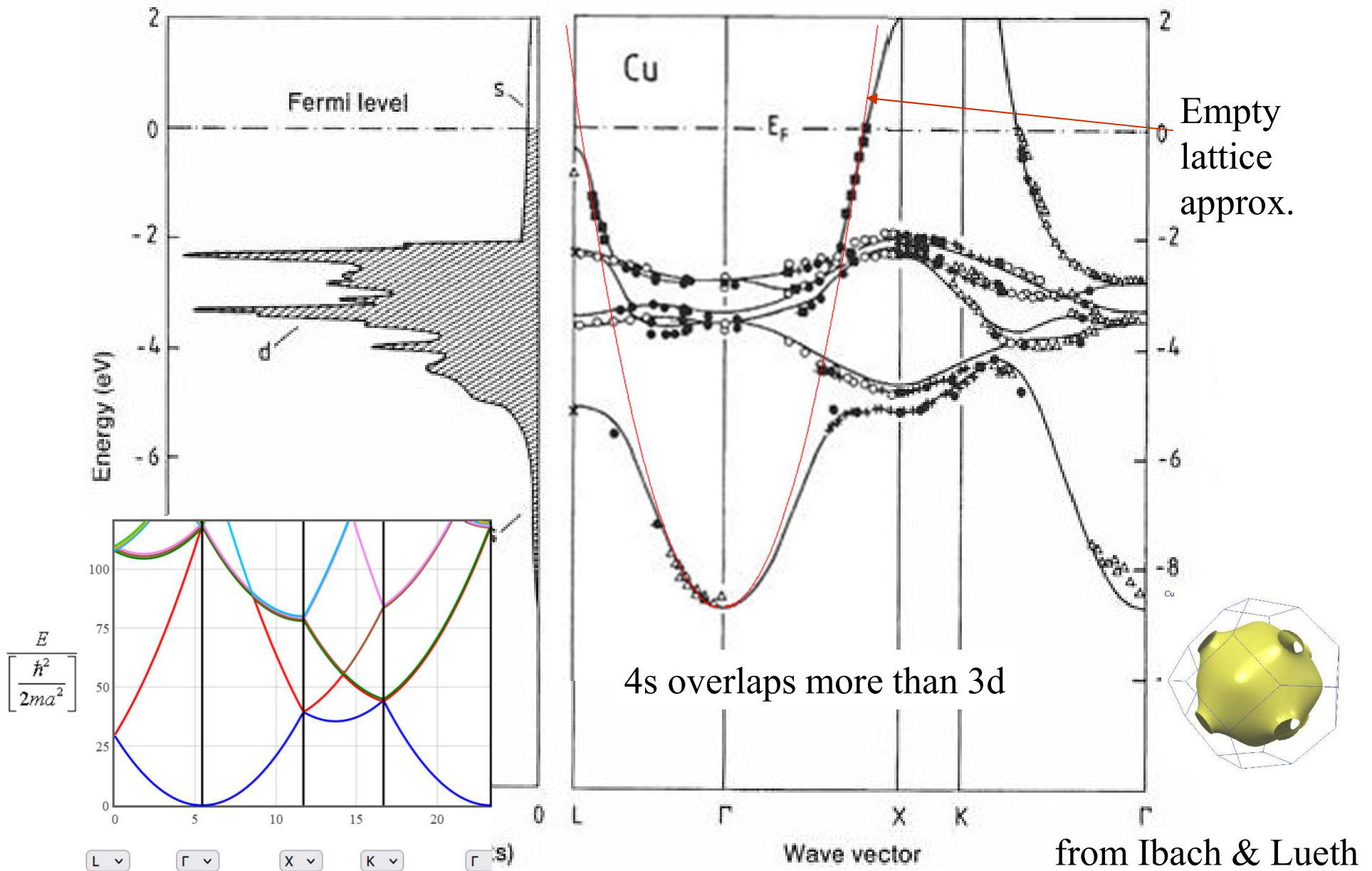
\*\* Actinide series

lanthanum 57 <b>La</b> 138.91	cerium 58 <b>Ce</b> 140.12	praseodymium 59 <b>Pr</b> 140.91	neodymium 60 <b>Nd</b> 144.24	promethium 61 <b>Pm</b> [145]	samarium 62 <b>Sm</b> 150.36	europium 63 <b>Eu</b> 151.96	gadolinium 64 <b>Gd</b> 157.25	terbium 65 <b>Tb</b> 158.93	dysprosium 66 <b>Dy</b> 162.50	holmium 67 <b>Ho</b> 164.93	erbium 68 <b>Er</b> 167.26	thulium 69 <b>Tm</b> 168.93	ytterbium 70 <b>Yb</b> 173.04
actinium 89 <b>Ac</b> [227]	thorium 90 <b>Th</b> 232.04	protactinium 91 <b>Pa</b> 231.04	uranium 92 <b>U</b> 238.03	neptunium 93 <b>Np</b> [237]	plutonium 94 <b>Pu</b> [244]	americium 95 <b>Am</b> [243]	curium 96 <b>Cm</b> [247]	berkelium 97 <b>Bk</b> [247]	californium 98 <b>Cf</b> [251]	einsteinium 99 <b>Es</b> [252]	fermium 100 <b>Fm</b> [257]	mendelevium 101 <b>Md</b> [258]	nobelium 102 <b>No</b> [259]

f band metals, rare earths

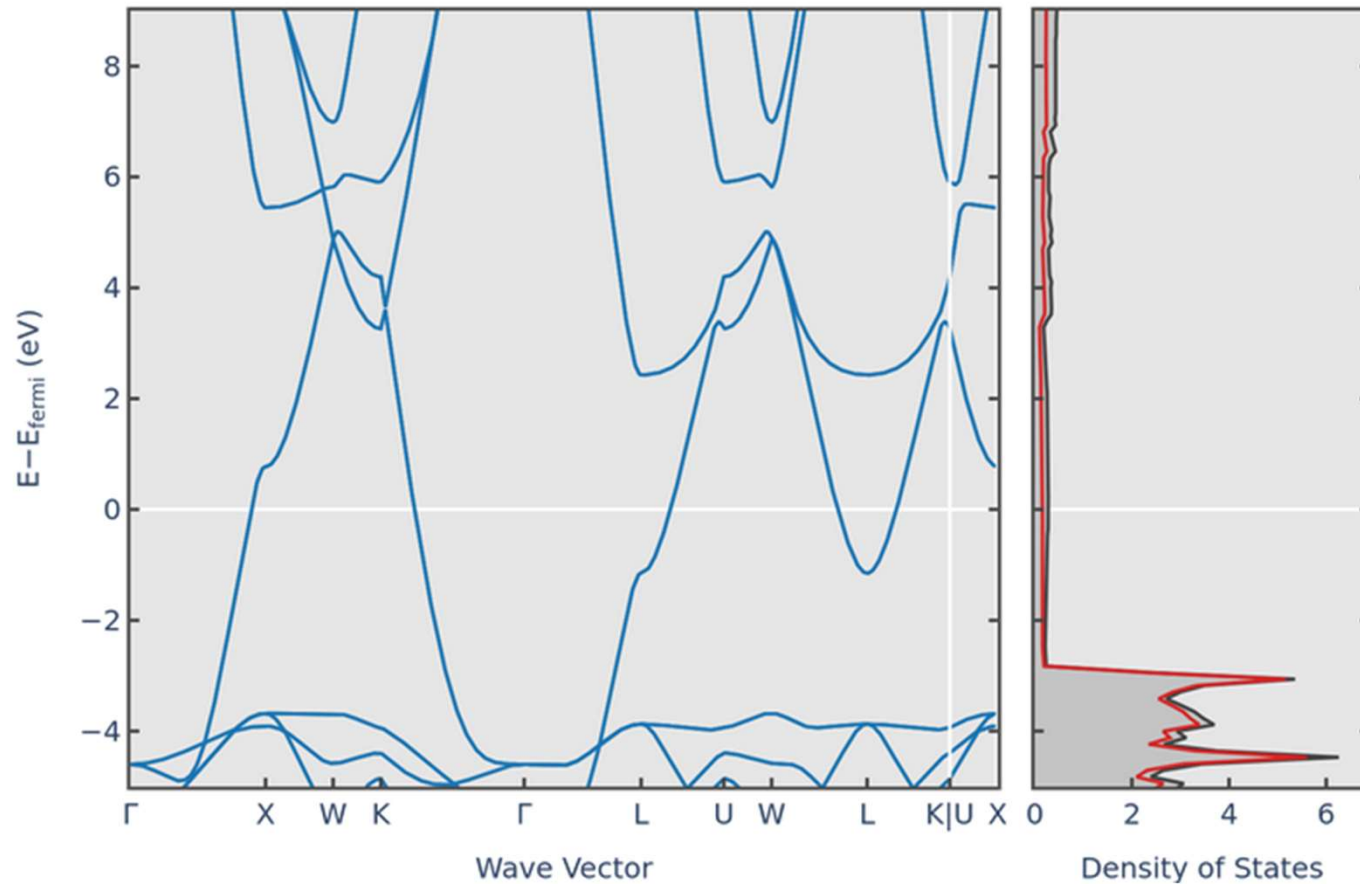
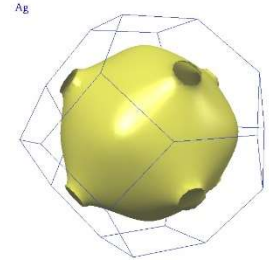


# Copper dispersion relation and density of states



# Silver

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# Gold

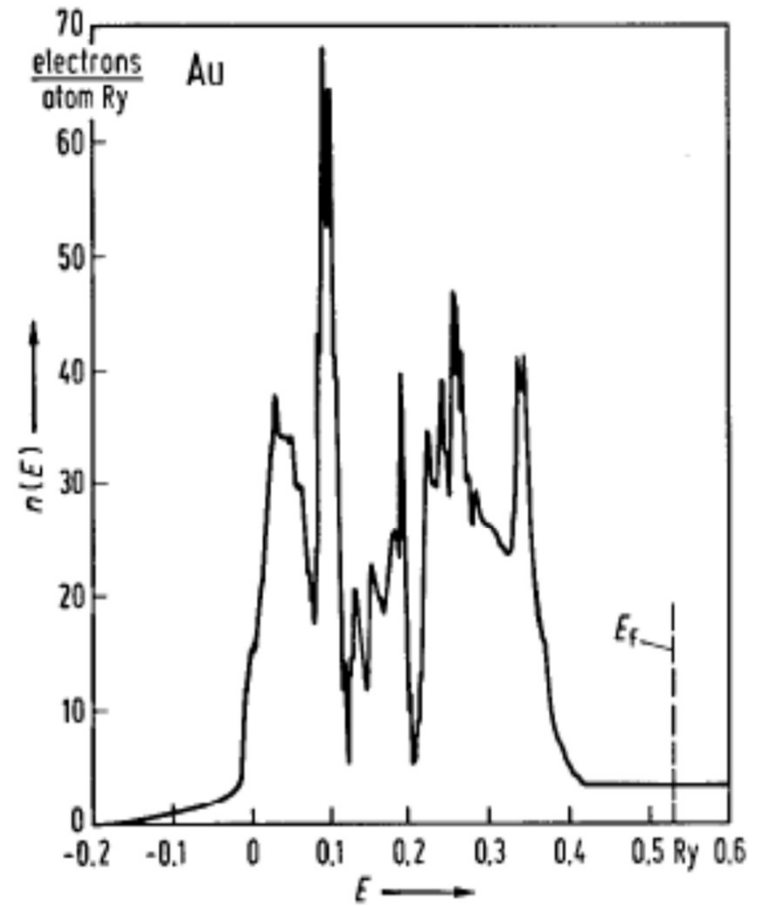
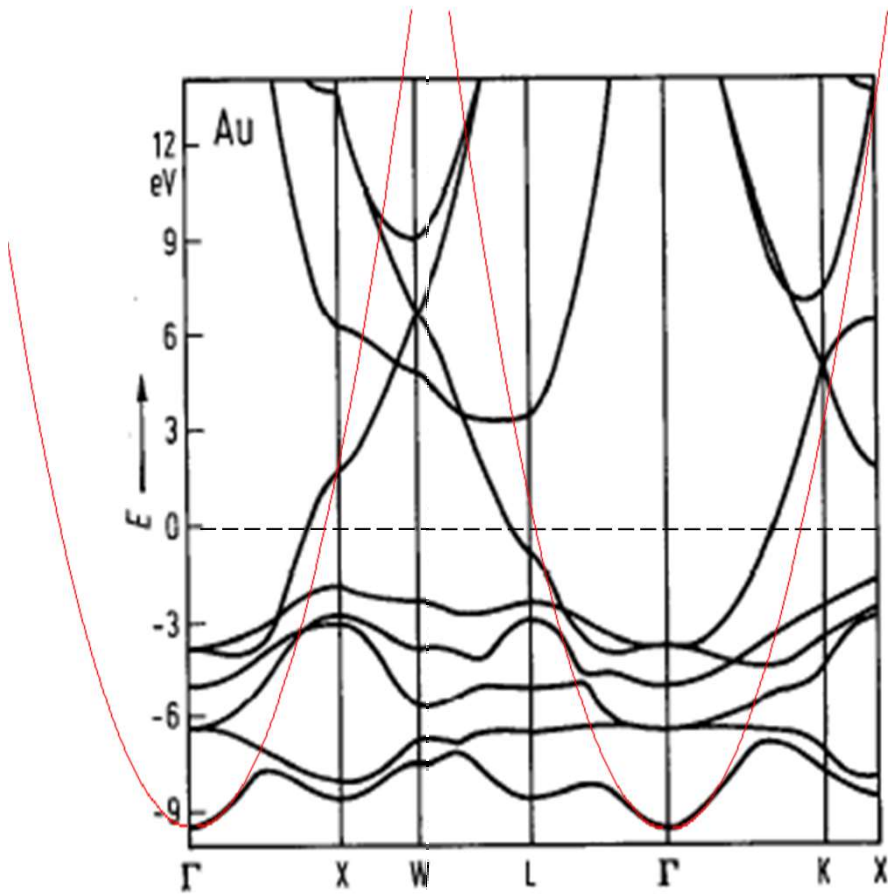
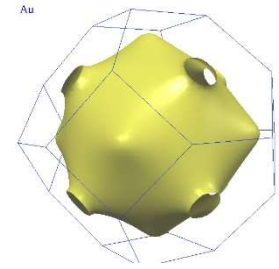
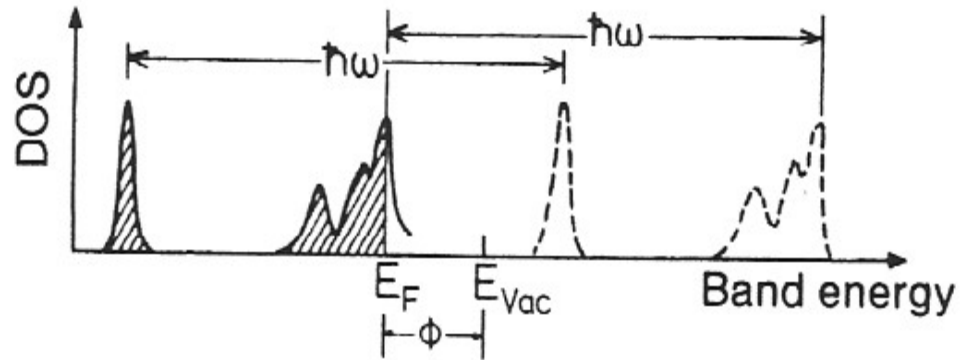
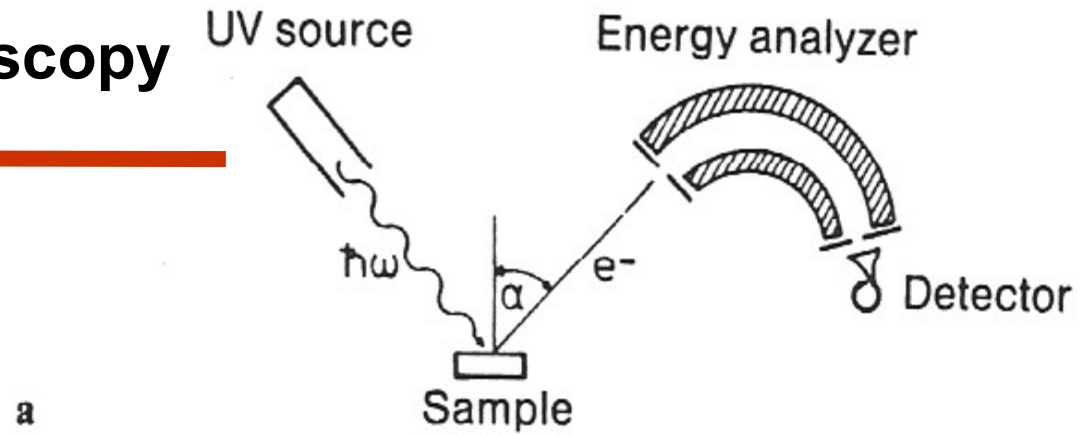


Fig. 9. Au. Density of states calculated from the energy bands in Fig. 4b. Au [71Chr2].

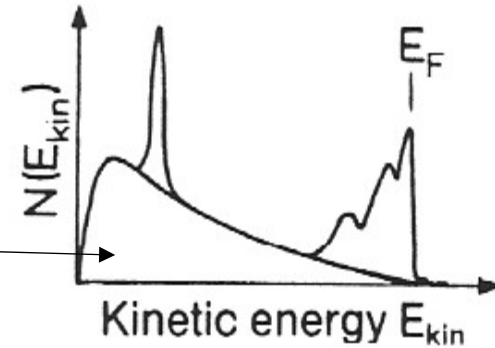
# Photoemission spectroscopy

UPS - Ultraviolet photoemission spectroscopy

Measure the density of states with photoemission spectroscopy



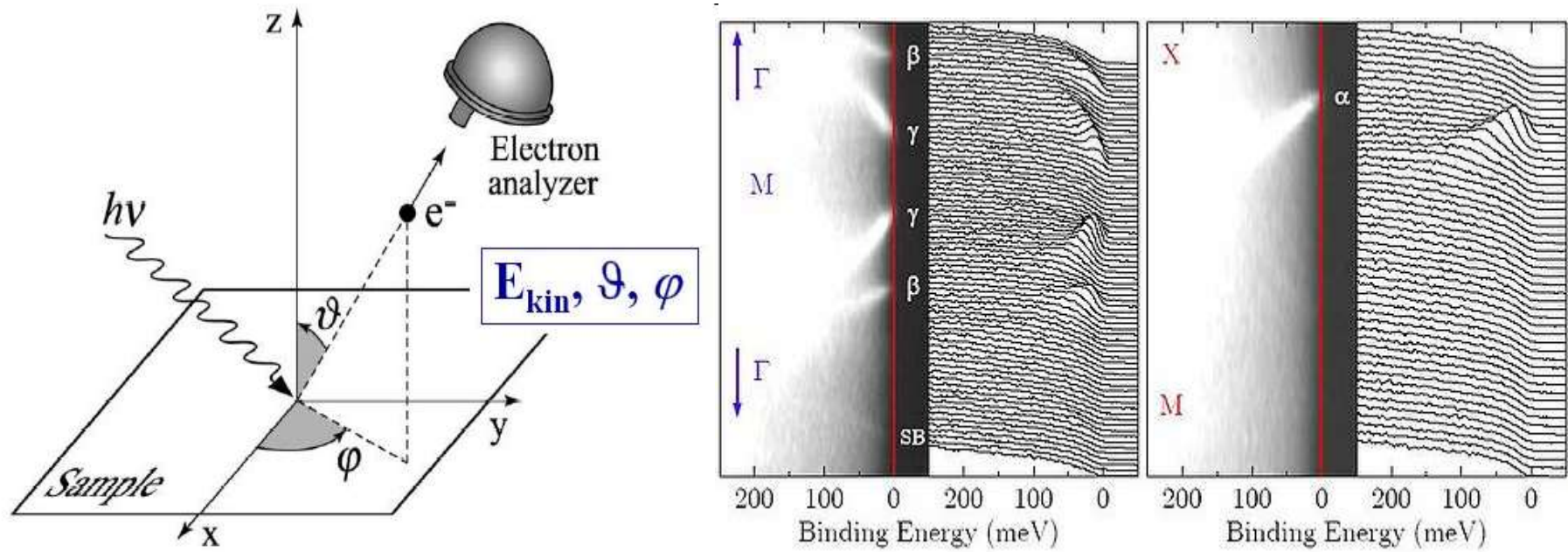
Secondary electrons



From: Ibach & Lueth

b

# Angle resolved photoemission spectroscopy (ARPES)

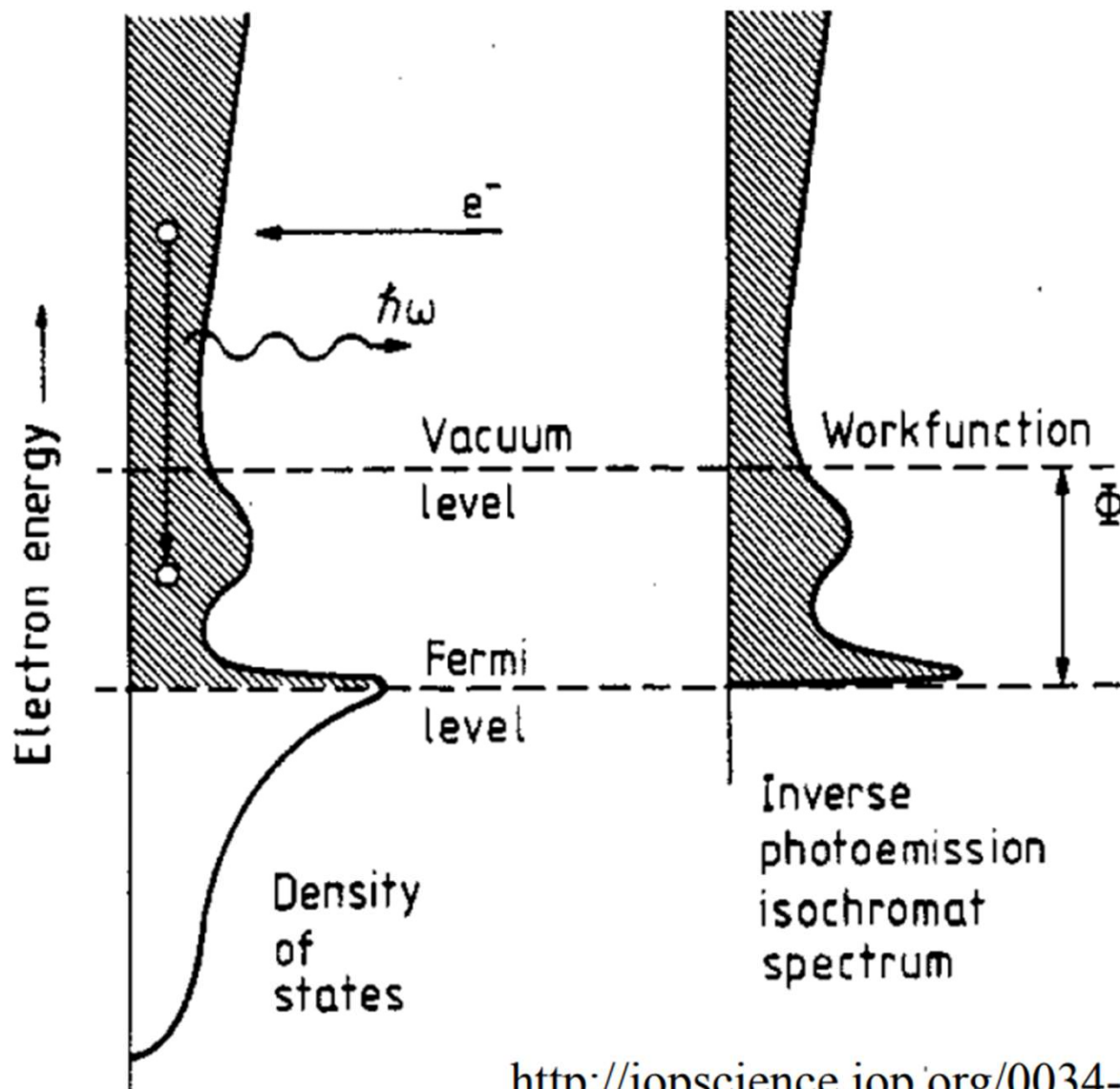


Measure the dispersion relation with angle resolved photoemission



# Inverse photoemission spectroscopy (IPES)

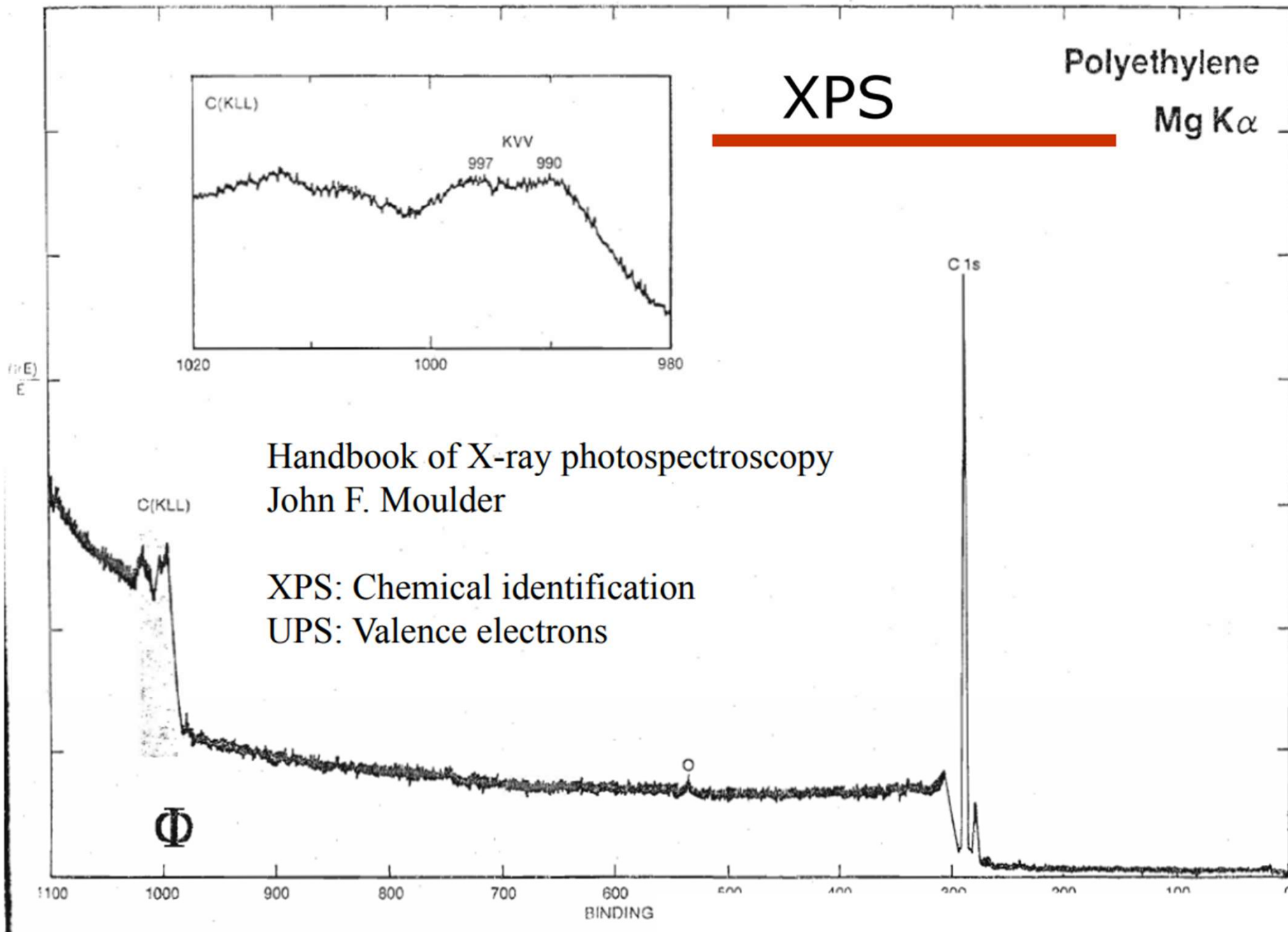
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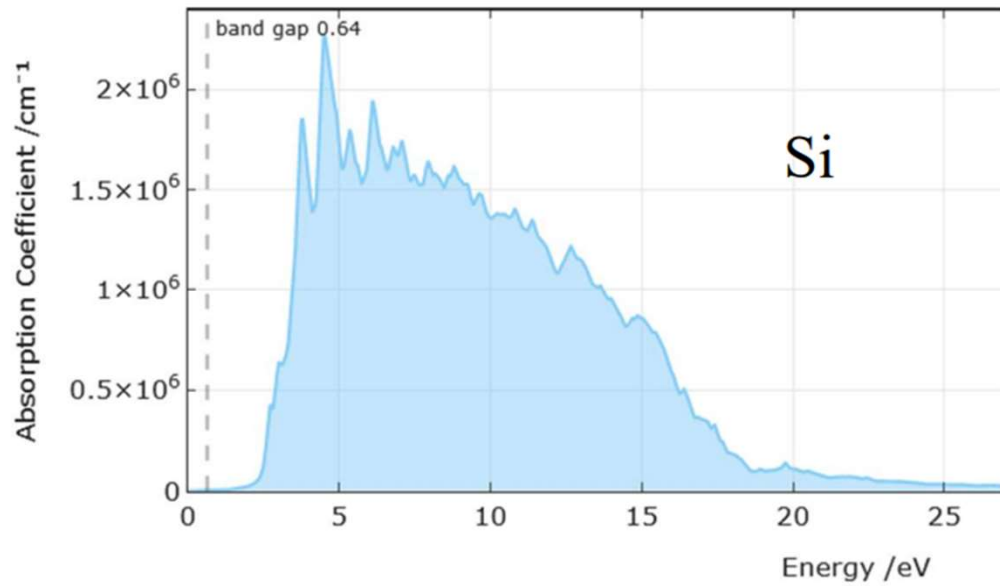
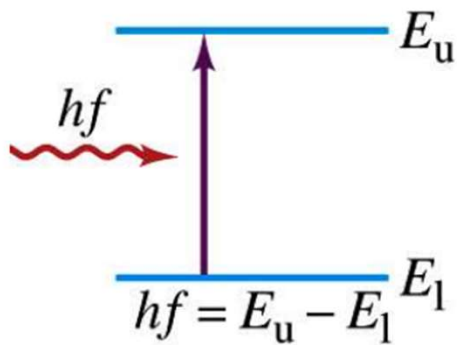
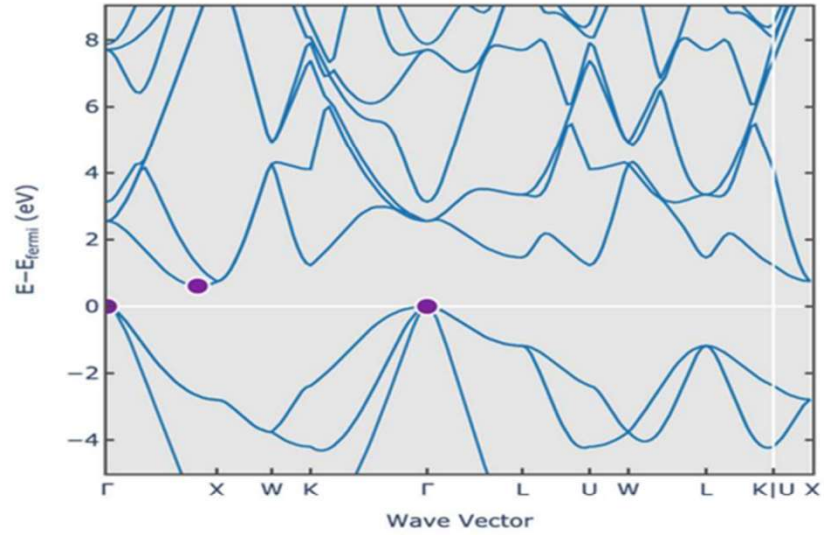
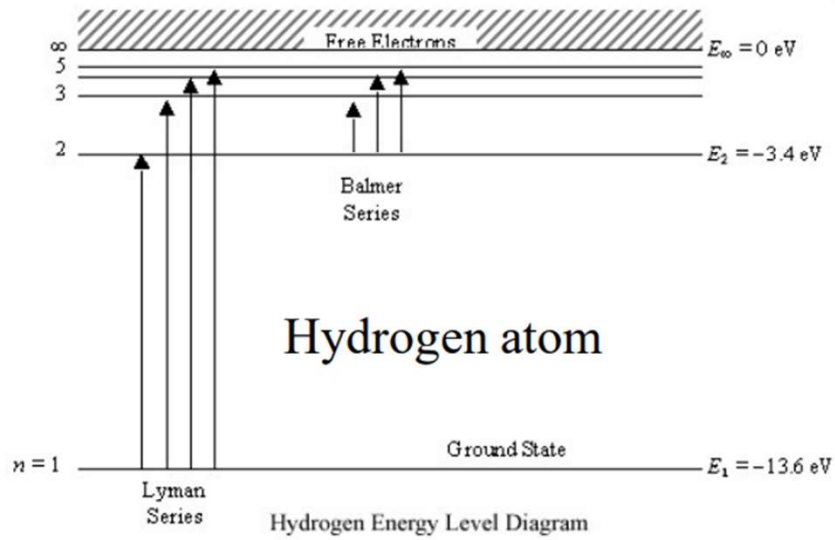
# XPS

Polyethylene

Mg K $\alpha$

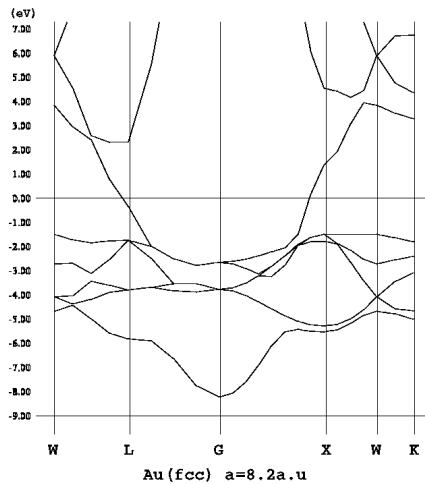


# Optical absorption

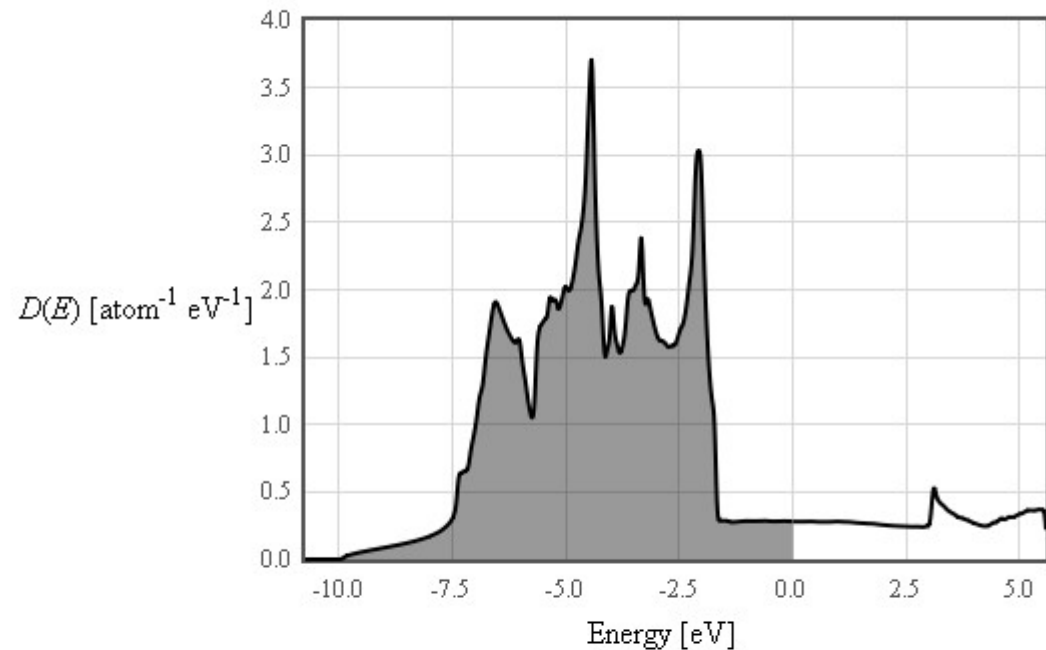


# Thermodynamic properties of metals

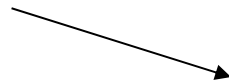
From the band structure measurements, we obtain the electron density of states.



Electron density of states for fcc gold



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



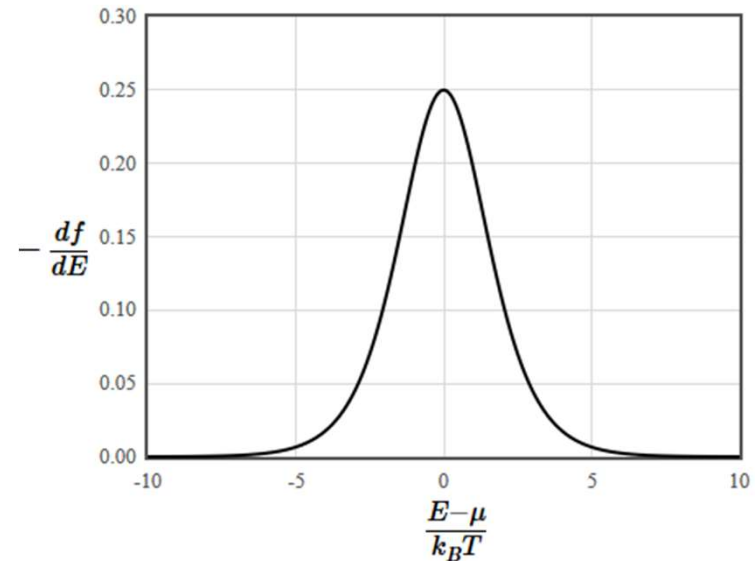
$E$ [eV]	$D(E)$ [ $\text{atom}^{-1} \text{eV}^{-1}$ ]
-10.74913	0
-10.73552	0
-10.72192	0

# Thermodynamic properties of metals

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$$n = \int_{-\infty}^{\infty} D(E) f(E) dE, \quad u = \int_{-\infty}^{\infty} ED(E) f(E) dE.$$

$$\int_{-\infty}^{\infty} H(E) f(E) dE$$



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

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

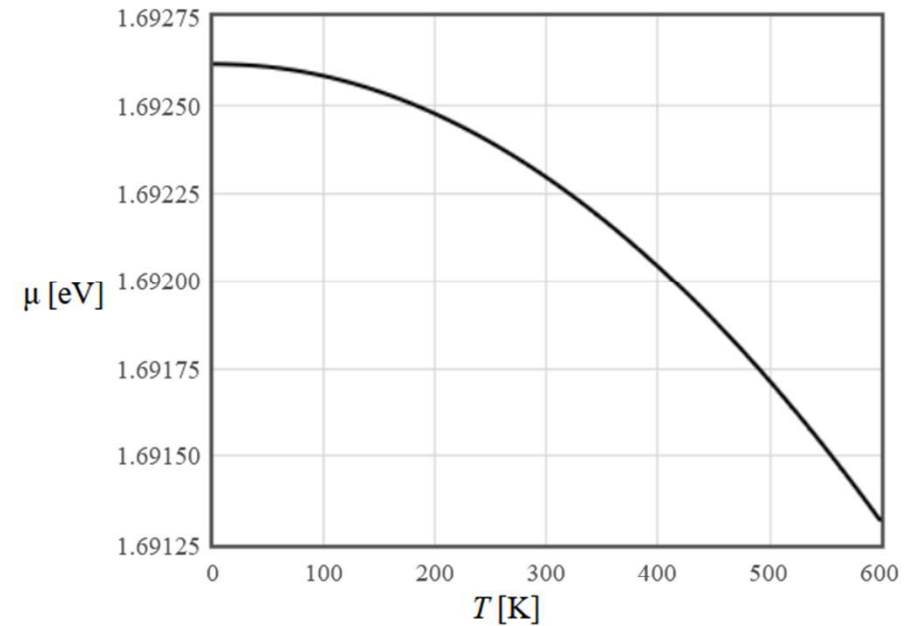
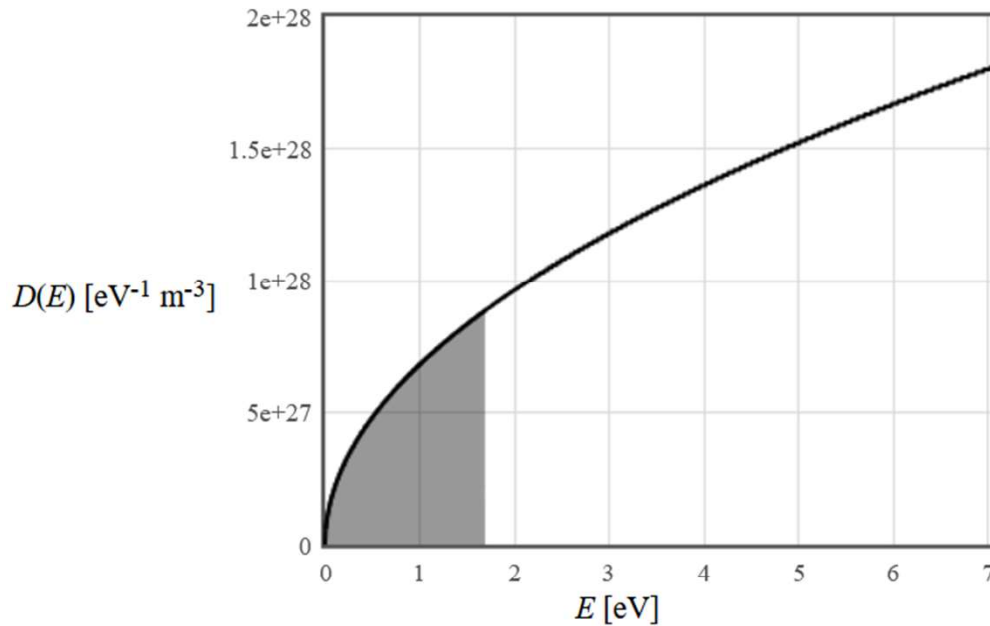
$$K(E) = \int_{-\infty}^E H(E') dE'.$$

<http://lampz.tugraz.at/~hadley/ss1/fermigas/sommerfeldtable/sommerfeld.php>

## Density of states → chemical potential for electrons in metals

The electron density  $n$  is the integral of the density of states  $D(E)$  times the probability that those states are occupied. The occupation probability is given by the Fermi function  $f(E)$ .

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



dimensionality:  1  2  3

number of electrons per primitive unit cell:  volume of a primitive unit cell:  m<sup>3</sup> electron  
density = 1.0000e+28 m<sup>-3</sup>

$T_{min}$ :  K  $T_{max}$ :  K

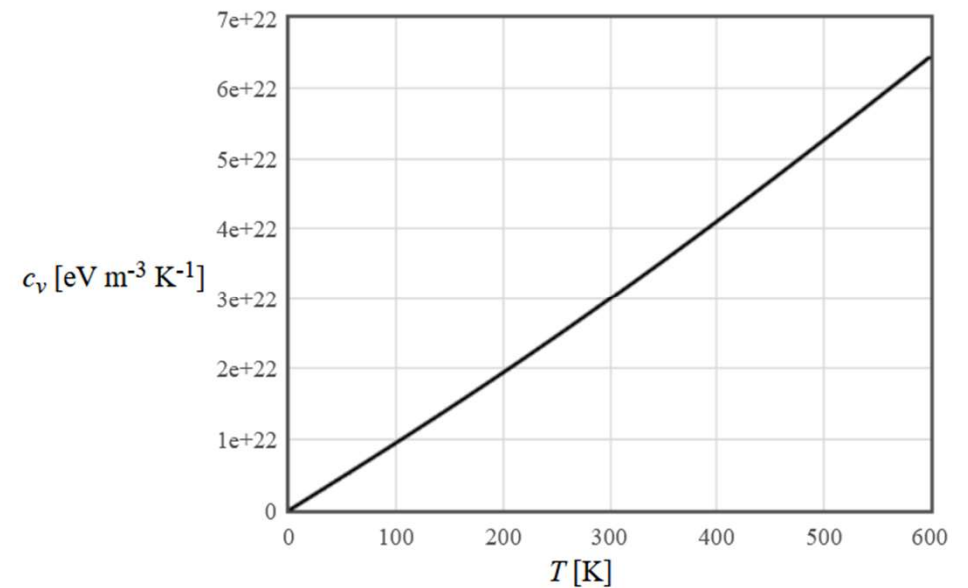
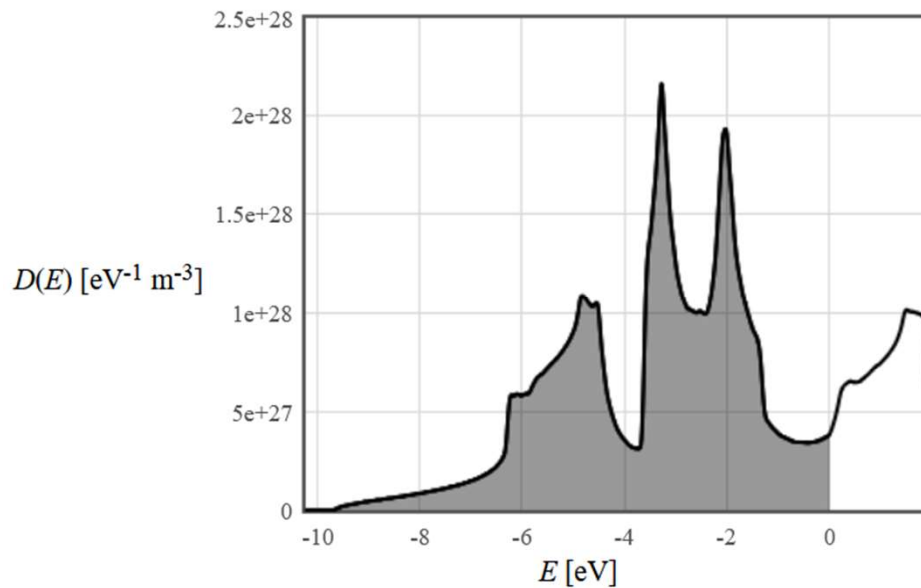
## Density of states → specific heat for electrons in metals

The specific heat  $c_v$  is the derivative of the internal energy density with respect to temperature.

$$c_v = \frac{du}{dT} = \frac{d}{dT} \int_{-\infty}^{\infty} ED(E) f(E) dE = \int_{-\infty}^{\infty} ED(E) \frac{df(E)}{dT} dE.$$

Here  $E$  is the energy,  $D(E)$  is the density of states, and  $f(E)$  is the Fermi function. The derivative of the Fermi function is,

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



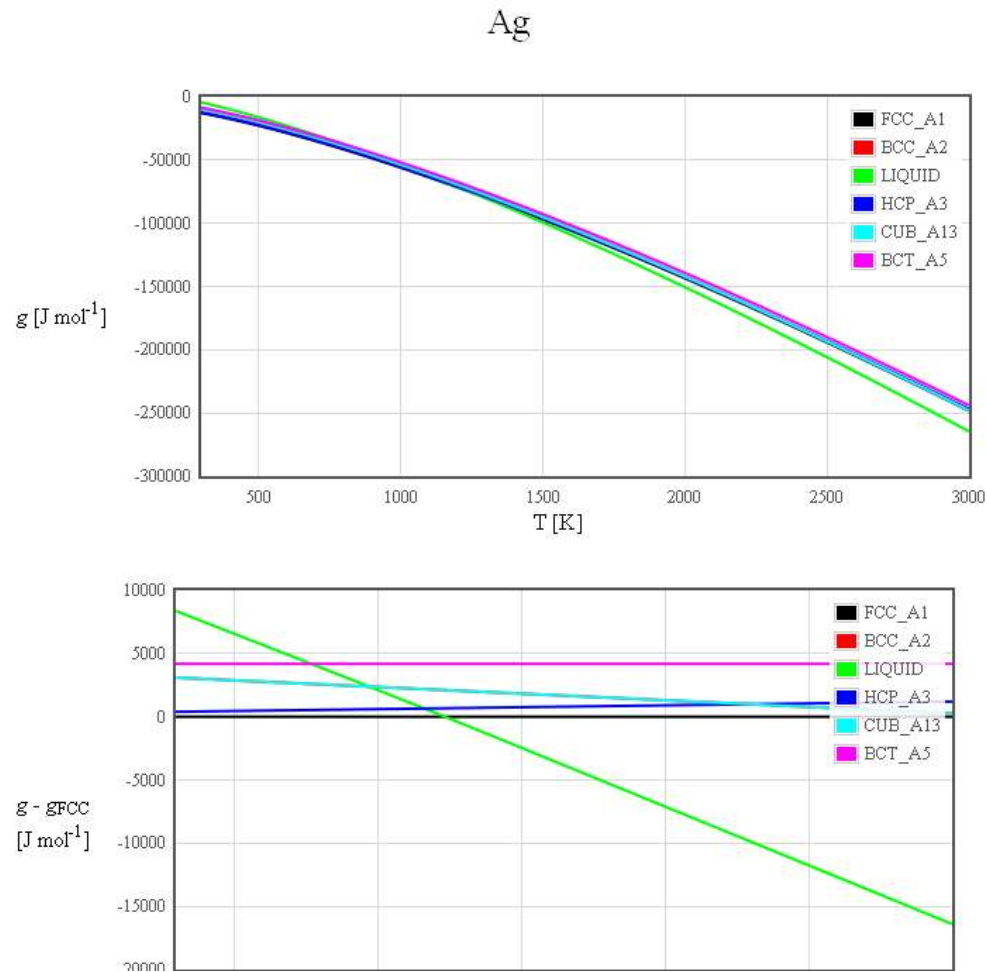
# SGTE data for pure elements

## SGTE thermodynamic data

The [Scientific Group ThermoData Europe SGTE](http://www.sciencedirect.com/science/article/pii/036459169190030N) maintains thermodynamic databanks for inorganic and metallurgical systems. Data from their 'pure element database' is plotted below.

Typically, experiments are performed at constant pressure  $p$ , temperature  $T$ , and number  $N$ . Under these conditions, the system will go to the minimum of the Gibbs energy  $G = U + pV - TS$ . Here  $U$  is the internal energy,  $V$  is the volume, and  $S$  is the entropy. The top plot is the Gibbs energy per mole  $g = u + p\nu - Ts$ , where  $u$  is the internal energy per mole,  $\nu$  is the volume per mole, and  $s$  is the entropy per mole.

Ag	Al	Am	As
Au	B	Ba	Be
Bi	C	Ca	Cd
Ce	Co	Cr	Cs
Cu	Dy	Er	Eu
Fe	Ga	Gd	Ge
Hf	Hg	Ho	In
Ir	K	La	Li
Lu	Mg	Mn	Mo
N	Na	Nb	Nd
Ni	Np	O	Os
P	Pa	Pb	Pd
Pr	Pt	Pu	Rb
Re	Rh	Ru	S
Sb	Sc	Se	Si
Sm	Sn	Sr	Ta
Tb	Tc	Te	Th
Ti	Tl	Tm	U
V	W	Y	Yb
Zn	Zr		



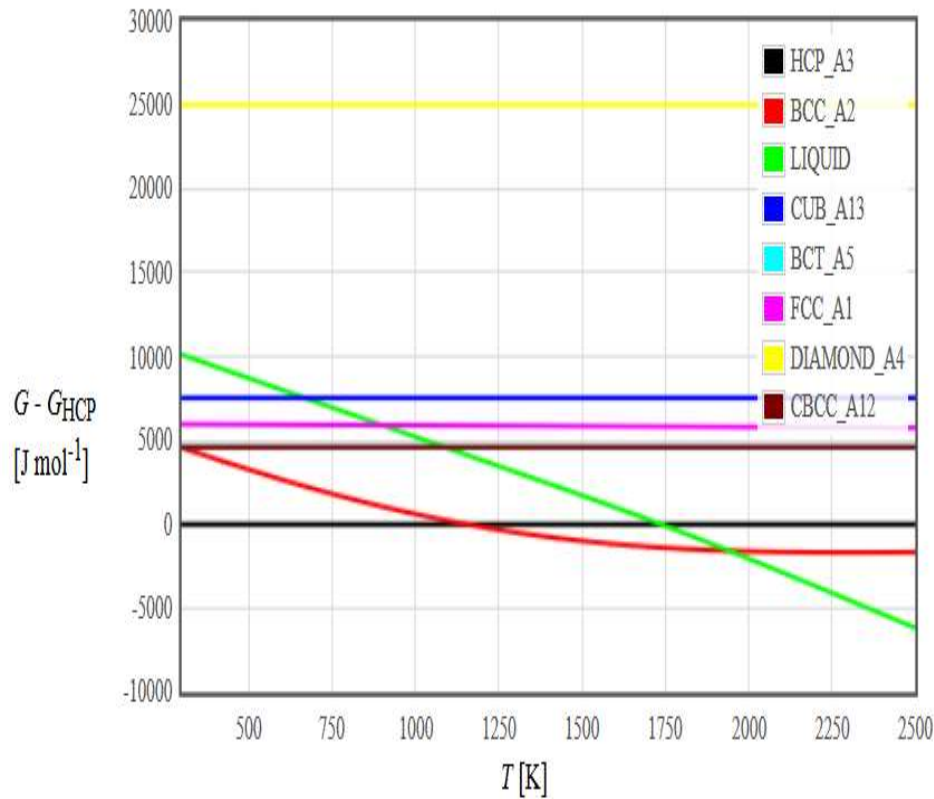
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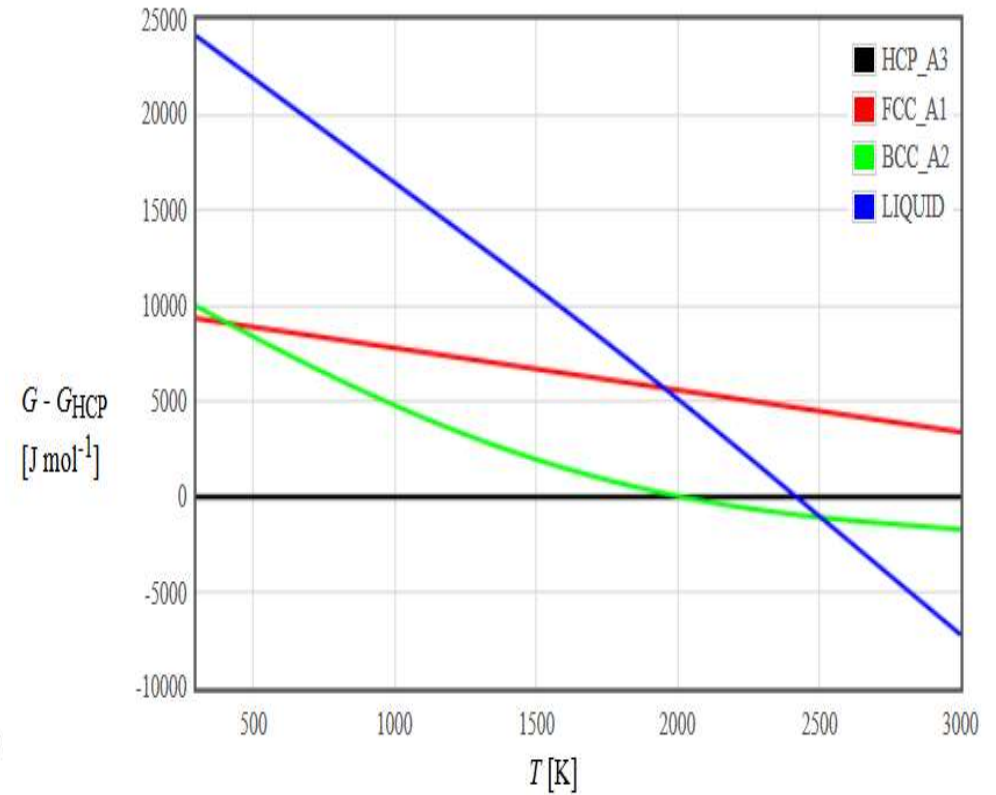


# Close packed → bcc

Ti



Hf



Close packed → bcc: Am, Be, Ca, Gd, Nd, Pr, Hf, Sc, Sm, Sr, Ti, Tb, Th, Tl, Y, Yb, Zr

<http://lampx.tugraz.at/~hadley/ss1/materials/sgte/SGTE.html>

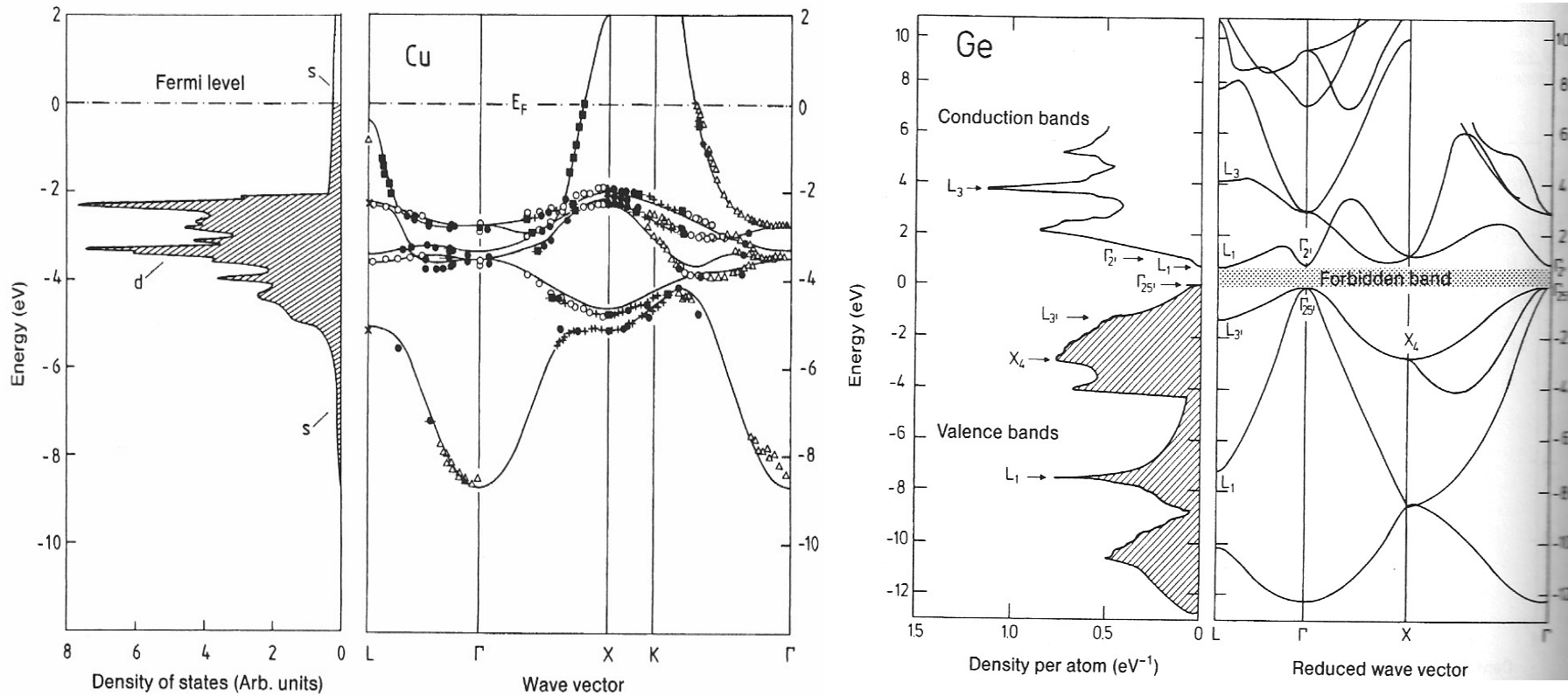
# Sommerfeld expansion for metals

Approximate the density of states with  $D(E_F)$  and  $D'(E_F)$ .

<p><b>Chemical potential <math>\mu</math></b> Implicitly defined by</p> $n = \int_{-\infty}^{\infty} D(E)f(E)dE$	$\mu \approx E_F - \frac{\pi^2}{6}(k_B T)^2 \frac{D'(E_F)}{D(E_F)} \text{ [J]}$	<p><b>Entropy</b></p> $s = \int \frac{c_v}{T} dT$ $s \approx \frac{\pi^2 D(E_F)}{3} k_B^2 T \text{ [J m}^{-3} \text{ K}^{-1}]$
<p><b>Internal energy</b></p> $u = \int_{-\infty}^{\infty} ED(E)f(E) dE$	$u \approx \int_{-\infty}^{E_F} ED(E)dE + \frac{\pi^2 D(E_F)}{6} (k_B T)^2 \text{ [J m}^{-3}]$	<p><b>Helmholtz free energy</b></p> $f = u - Ts$ $f \approx \int_{-\infty}^{E_F} ED(E)dE - \frac{\pi^2 D(E_F)}{6} (k_B T)^2 \text{ [J m}^{-3}]$
<p><b>Specific heat</b></p> $c_v = \left( \frac{du}{dT} \right)_{V=\text{const}}$	$c_v \approx \frac{\pi^2 D(E_F)}{3} k_B^2 T \text{ [J m}^{-3} \text{ K}^{-1}]$	

<http://lampz.tugraz.at/~hadley/ss1/fermigas/sommerfeldtable/sommerfeld.php>

# Metals, semiconductors, and insulators



Insulators: band gap  $> 3$  eV

From Ibach & Lueth