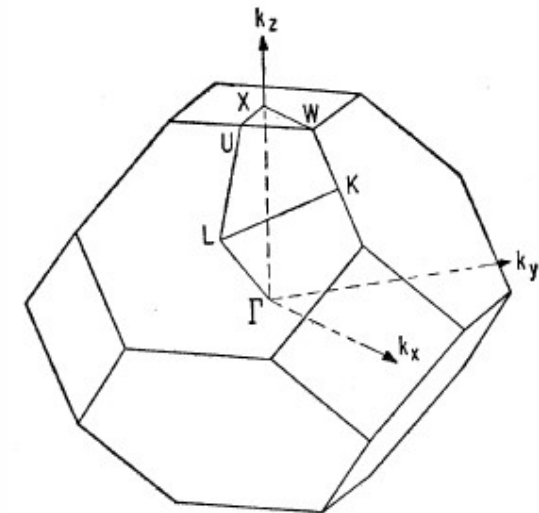
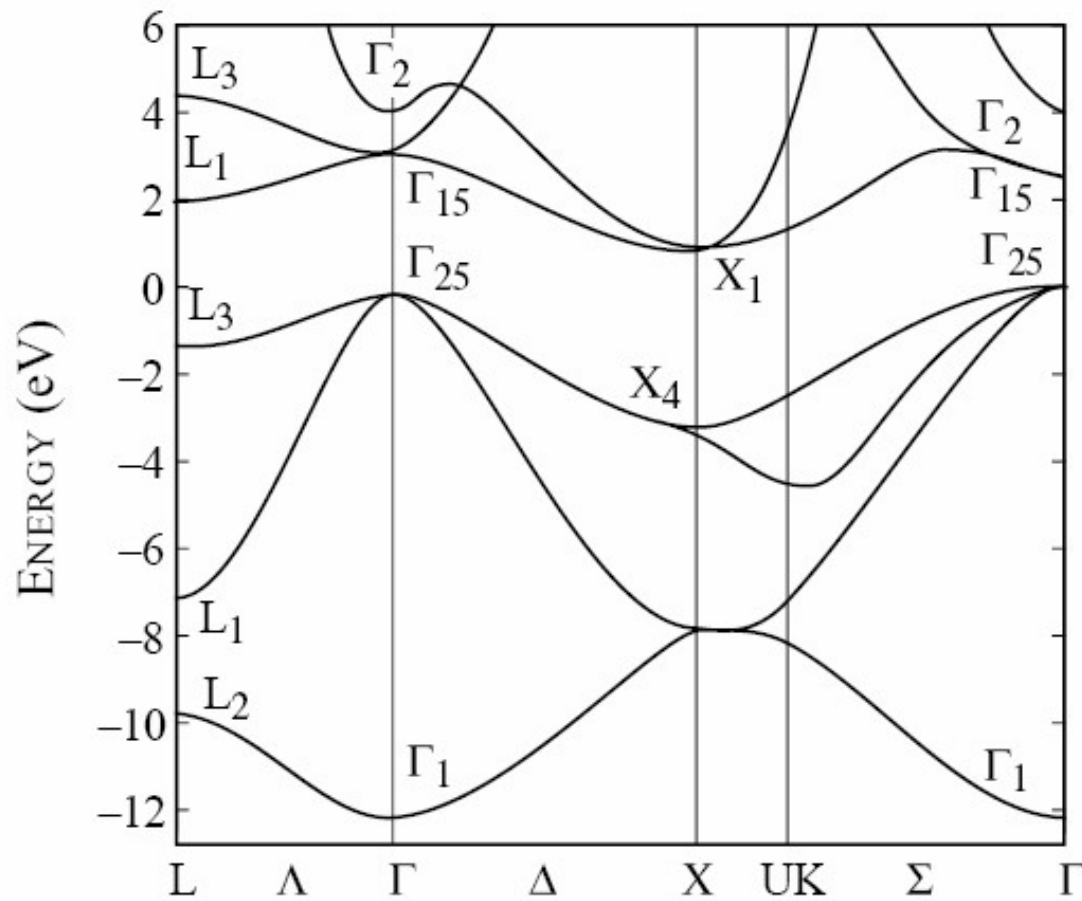


# Electrons

---

# Electron Band Theory

Calculate the dispersion relation for electrons in a crystal



silicon

# 2N states per Brillouin zone

---

A crystal  $L \times L \times L$  has  $N = \frac{L^3}{a^3}$  primitive unit cells.

The first Brillouin zone contains  $N = \frac{\left(\frac{2\pi}{a}\right)^3}{\left(\frac{2\pi}{L}\right)^3} = \frac{L^3}{a^3}$   $k$  points.

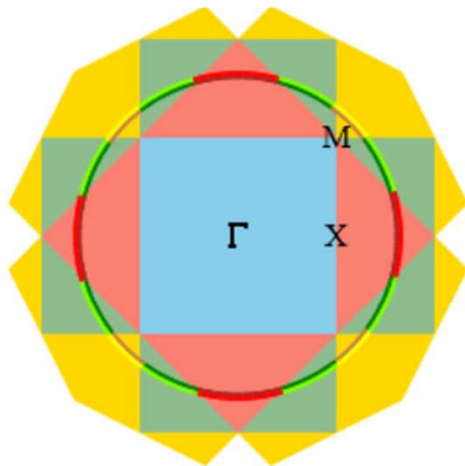
Each  $k$  state can hold 2 electrons (spin).

There are  $2N$  electron states per Brillouin zone.

$2N$  electron states per band

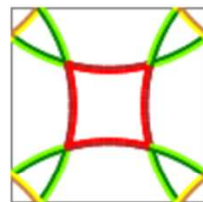
# Fermi surface of a two-dimensional square lattice

$n = 4.2$   -  + electrons/unit cell  
 $\frac{k_F a}{\pi} = 1.635$      $\frac{E_F}{\left[\frac{\hbar^2 \pi^2}{2ma^2}\right]} = 2.674$

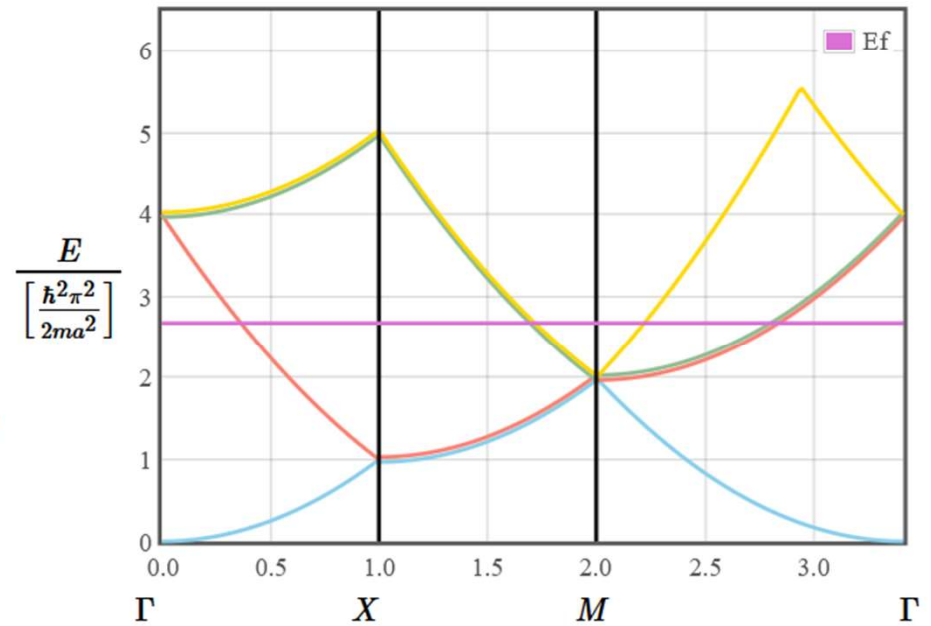


■ 1 Bz    ■ 2 Bz    ■ 3 Bz    ■ 4 Bz

Extended Zone Scheme



Reduced Zone Scheme



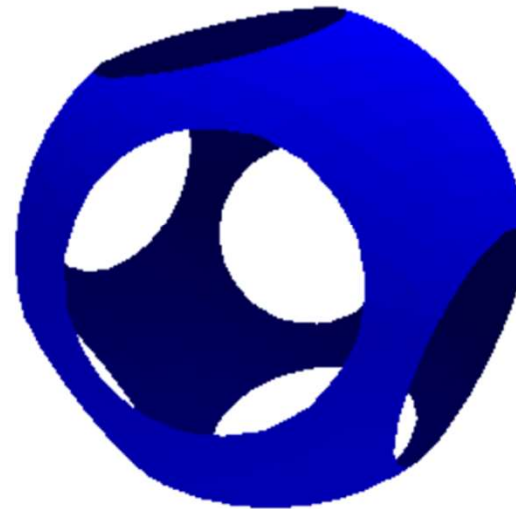
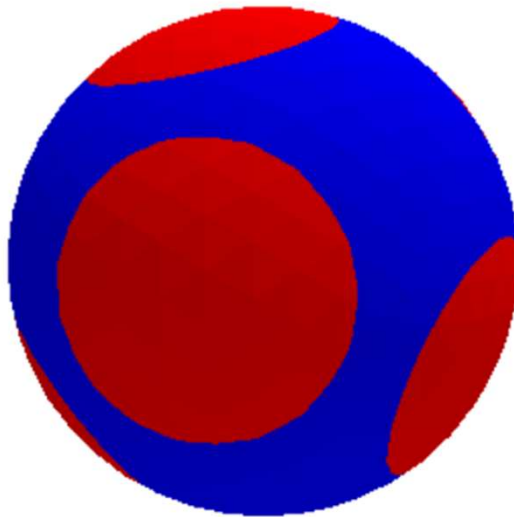
# Fermi Surfaces

$n = 2$     electrons/unit cell

$$k_F = (3\pi^2 n)^{1/3} = 3.90$$

Lattice:  Simple Cubic  Body Centered Cubic  Face Centered Cubic  Hexagonal Close Pack  $\frac{c}{a} = \sqrt{\frac{8}{3}}$

Brillouinzone	1	2	3	4
Outside Color	<input type="checkbox"/> Blue	<input type="checkbox"/> Red	<input type="checkbox"/> Yellow	<input type="checkbox"/> Green
Inside Color	<input type="checkbox"/> Dark Blue	<input type="checkbox"/> Dark Red	<input type="checkbox"/> Dark Yellow	<input type="checkbox"/> Dark Green
Show	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>



[http://lampx.tugraz.at/~hadley/ss2/fermisurface/3d\\_fermisurface/index.html](http://lampx.tugraz.at/~hadley/ss2/fermisurface/3d_fermisurface/index.html)

# Band structure calculations

---

Knowing how the atoms are arranged, calculate the electron states

Density Functional Theory (DFT)

Plane wave method

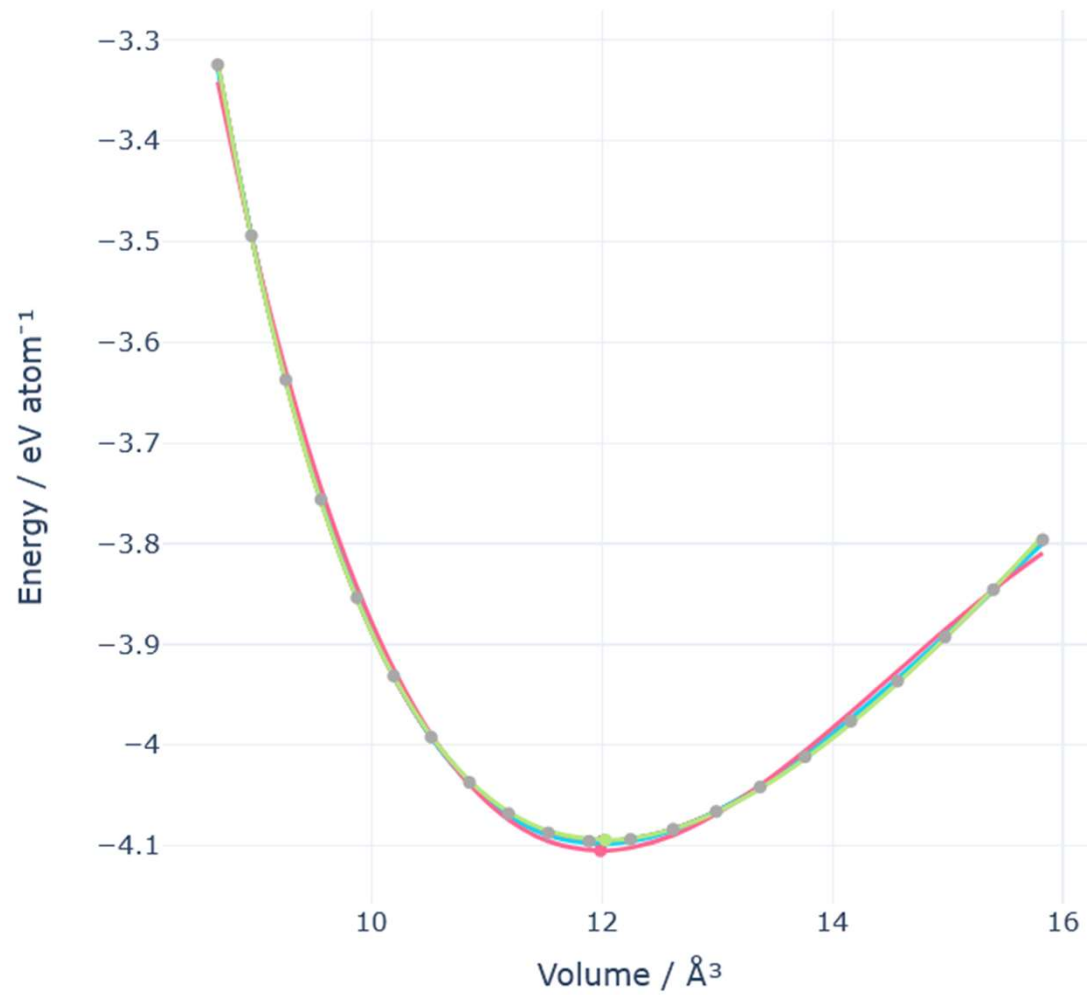
Tight binding

$$H = - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_a \frac{\hbar^2}{2m_a} \nabla_a^2 - \sum_{a,i} \frac{Z_a e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_a|} + \sum_{i < j} \frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|} + \sum_{a < b} \frac{Z_a Z_b e^2}{4\pi\epsilon_0 |\vec{r}_a - \vec{r}_b|}$$

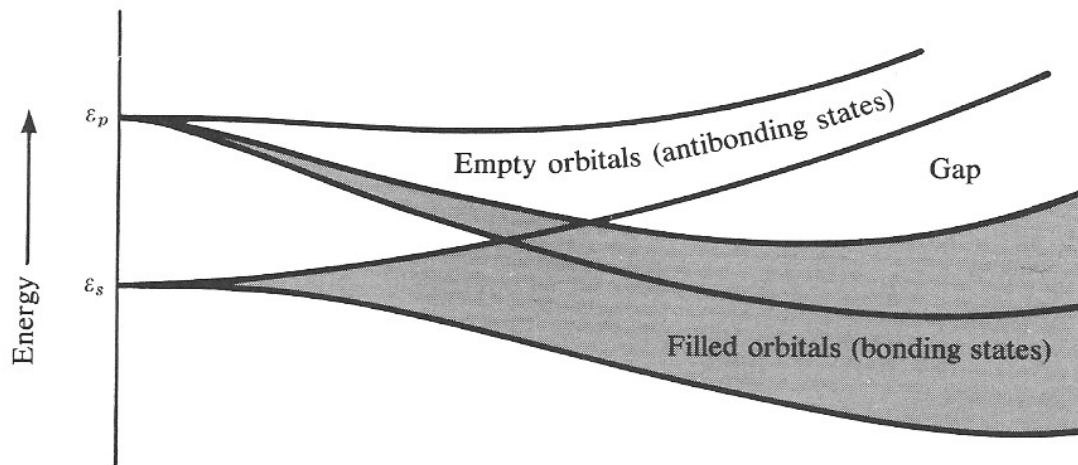
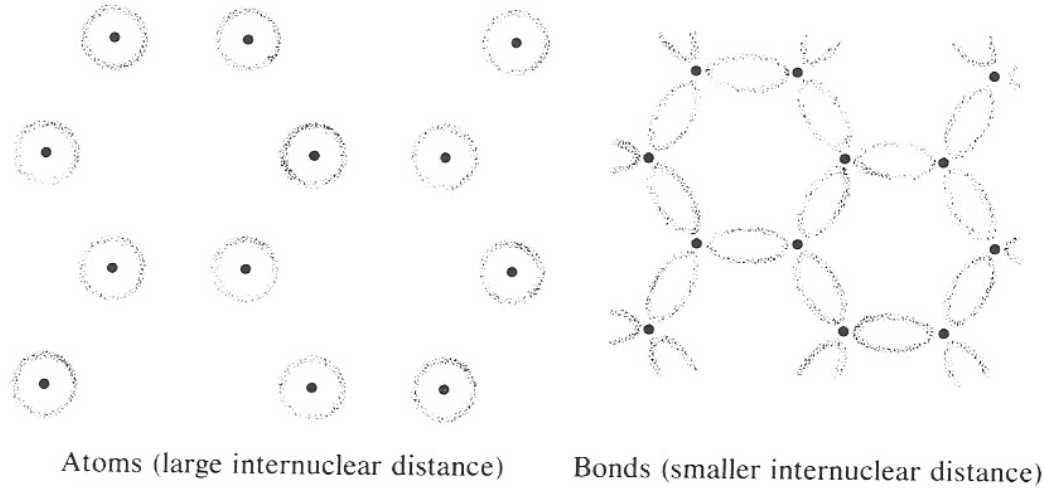
$$E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

# Band structure calculations

---



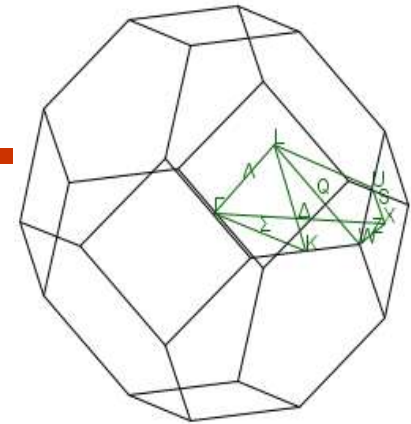
# Tight binding



Harrison, Electronic Structure, Freeman 1980

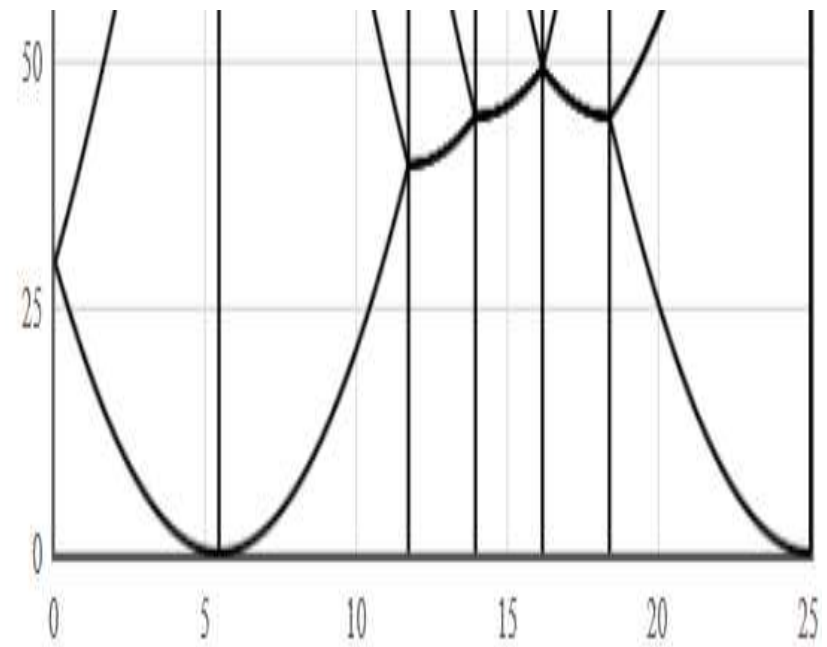
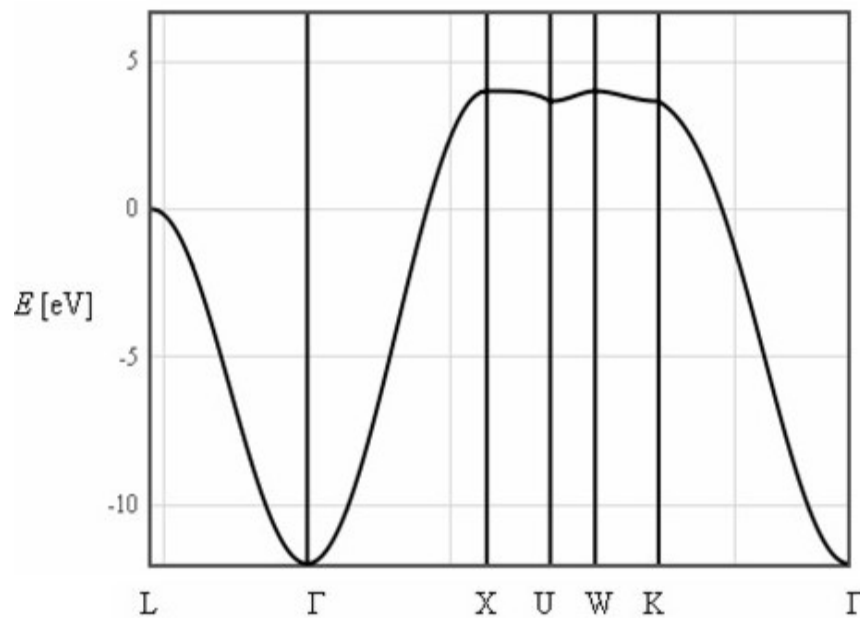


# Tight binding, fcc



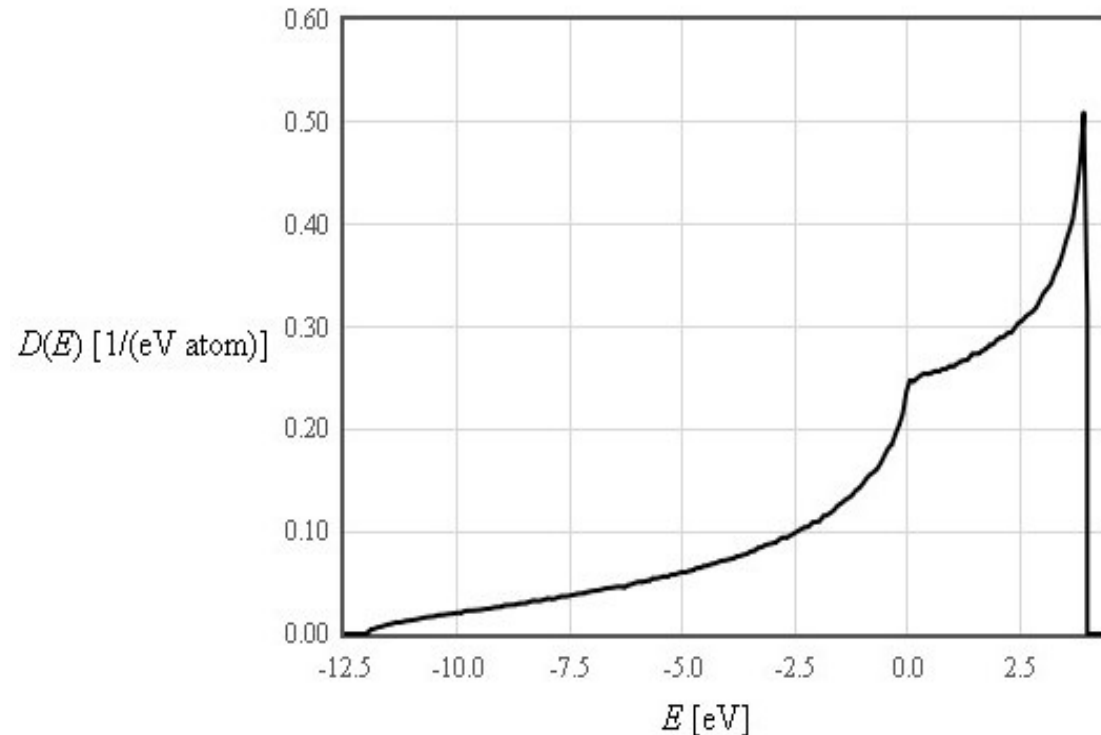
$$E = \varepsilon - t \sum_{lmn} e^{i\vec{k} \cdot \vec{\rho}_{lmn}}$$

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



# Density of states (fcc)

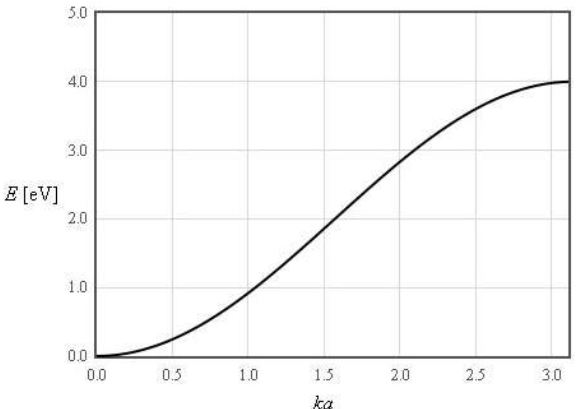
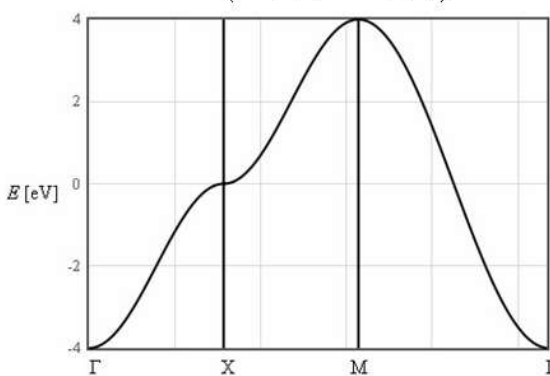
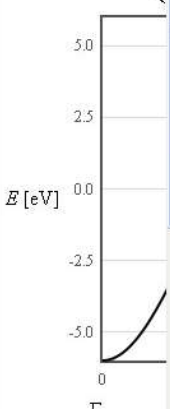
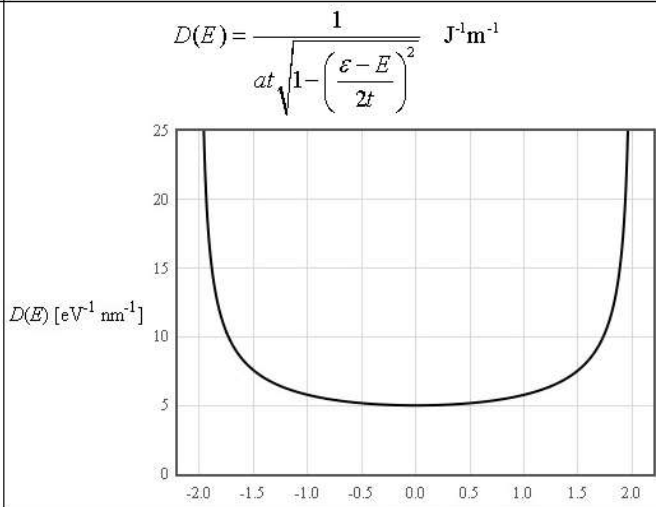
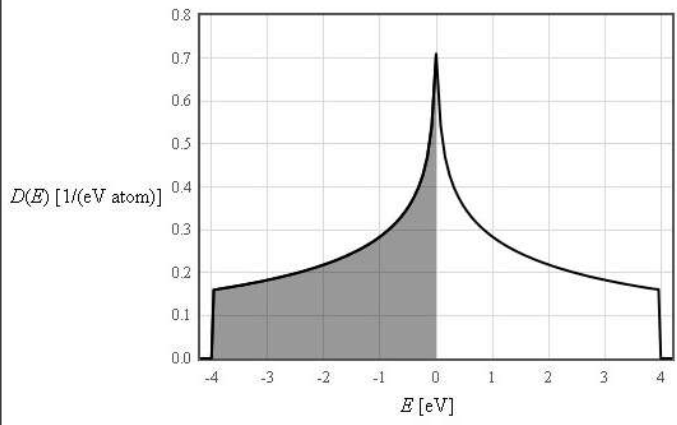
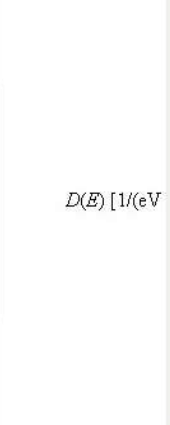
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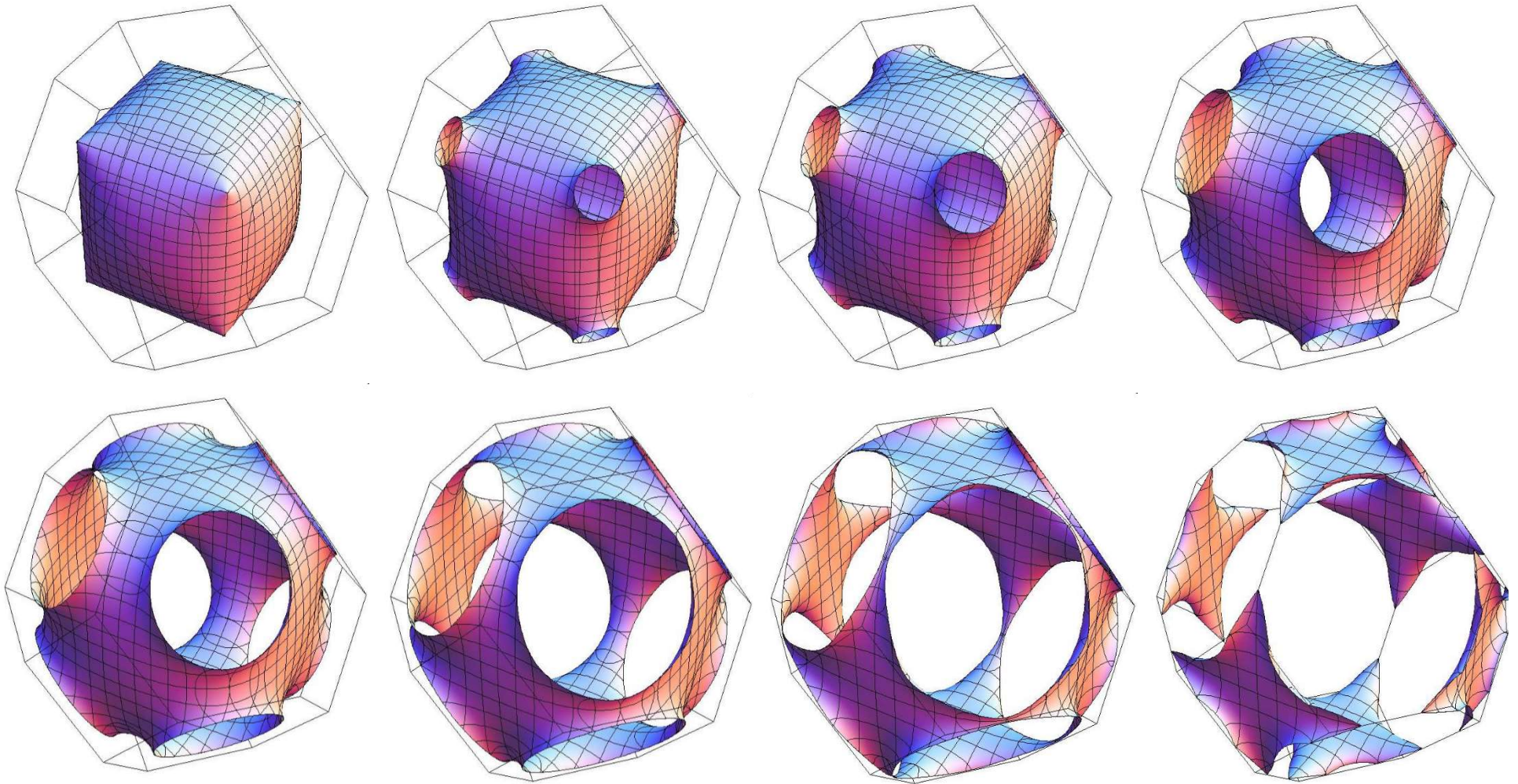
Calculate the energy for every allowed  $k$  in the Brillouin zone

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

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

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

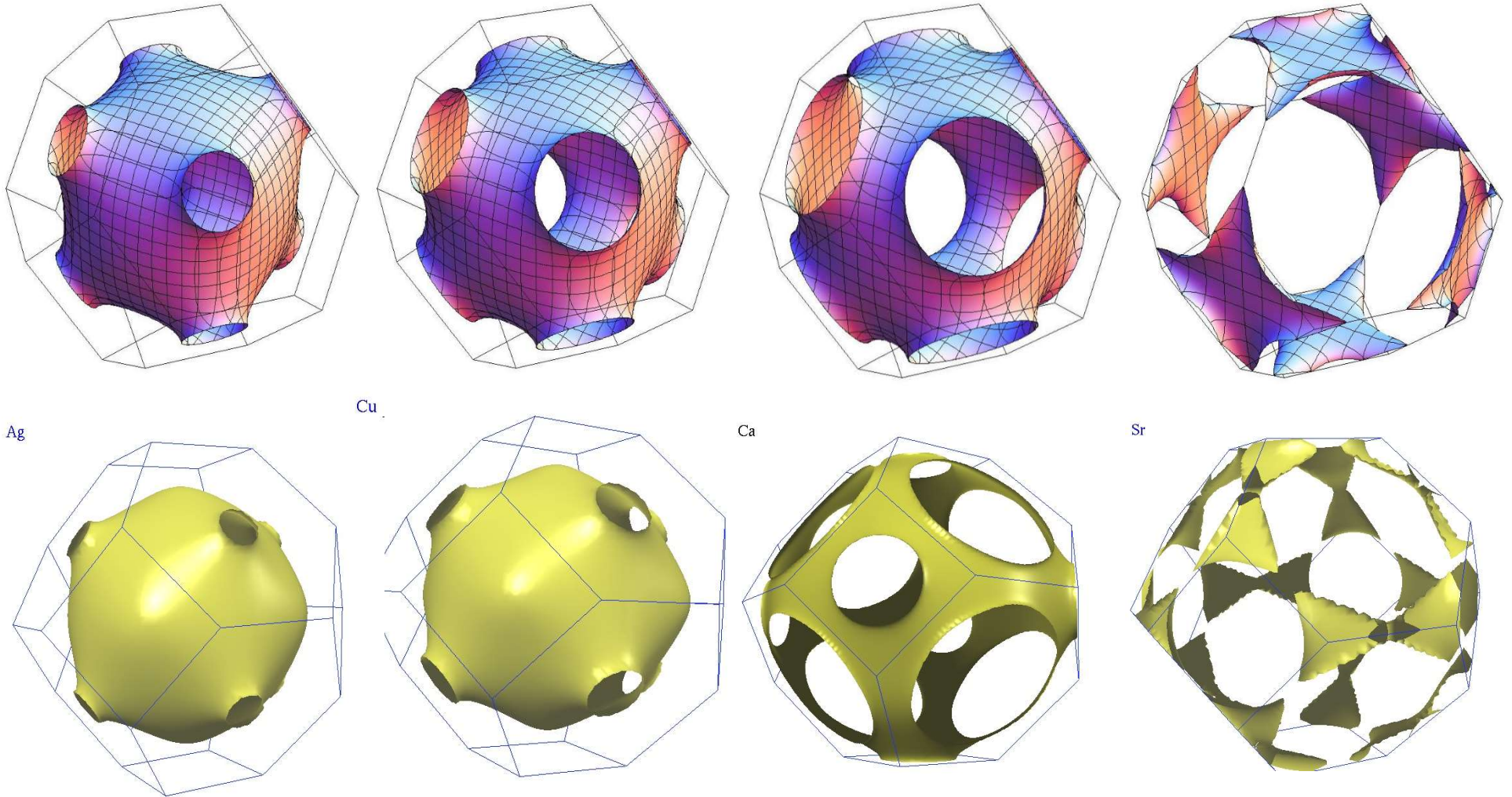
# Tight binding, fcc



Christian Gruber, 2008



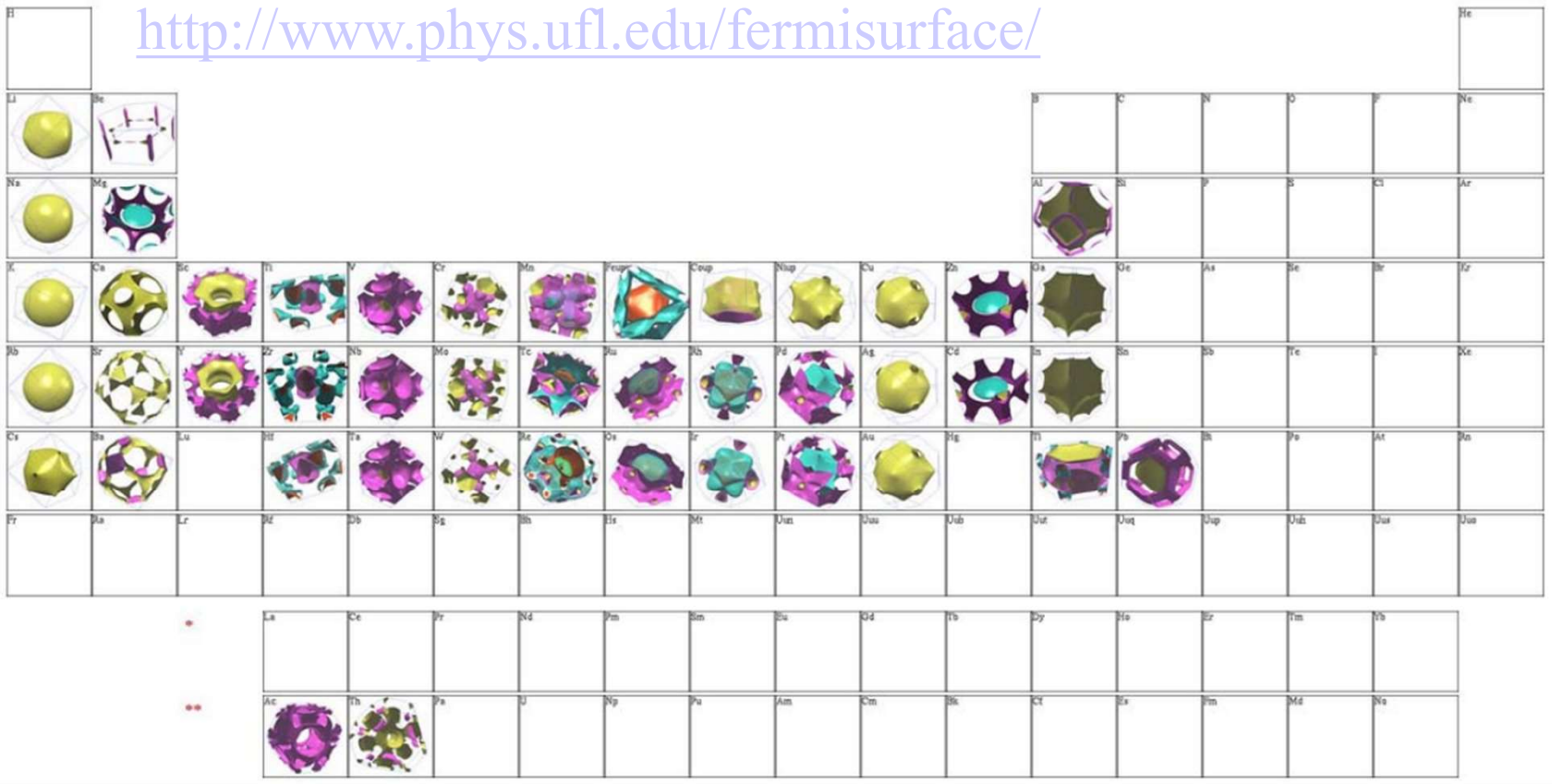
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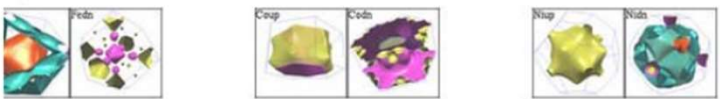
<http://www.phys.ufl.edu/fermisurface/>

1A 2A 3B 4B 5B 6B 7B 8 1B 2B 3A 4A 5A 6A 7A NG

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



magnets :



native Structures :



[Simple Periodic Table with the electronic band structure of each element]

<a href="#">H</a>																						<a href="#">He</a>
<a href="#">Li</a>	<a href="#">Be</a>									<a href="#">B</a>	<a href="#">C</a>	<a href="#">N</a>	<a href="#">O</a>	<a href="#">F</a>	<a href="#">Ne</a>							
<a href="#">Na</a>	<a href="#">Mg</a>									<a href="#">Al</a>	<a href="#">Si</a>	<a href="#">P</a>	<a href="#">S</a>	<a href="#">Cl</a>	<a href="#">Ar</a>							
<a href="#">K</a>	<a href="#">Ca</a>	<a href="#">Sc</a>	<a href="#">Ti</a>	<a href="#">V</a>	<a href="#">Cr</a>	<a href="#">Mn</a>	<a href="#">Fe</a>	<a href="#">Co</a>	<a href="#">Ni</a>	<a href="#">Cu</a>	<a href="#">Zn</a>	<a href="#">Ga</a>	<a href="#">Ge</a>	<a href="#">As</a>	<a href="#">Se</a>	<a href="#">Br</a>	<a href="#">Kr</a>					
<a href="#">Rb</a>	<a href="#">Sr</a>	<a href="#">Y</a>	<a href="#">Zr</a>	<a href="#">Nb</a>	<a href="#">Mo</a>	<a href="#">Tc</a>	<a href="#">Ru</a>	<a href="#">Rh</a>	<a href="#">Pd</a>	<a href="#">Ag</a>	<a href="#">Cd</a>	<a href="#">In</a>	<a href="#">Sn</a>	<a href="#">Sb</a>	<a href="#">Te</a>	<a href="#">I</a>	<a href="#">Xe</a>					
<a href="#">Cs</a>	<a href="#">Ba</a>	<a href="#">La</a>	<a href="#">Hf</a>	<a href="#">Ta</a>	<a href="#">W</a>	<a href="#">Re</a>	<a href="#">Os</a>	<a href="#">Ir</a>	<a href="#">Pt</a>	<a href="#">Au</a>	<a href="#">Hg</a>	<a href="#">Tl</a>	<a href="#">Pb</a>	<a href="#">Bi</a>	<a href="#">Po</a>	<a href="#">At</a>	<a href="#">Rn</a>					

[png images, less than about 20 kb](Start 2/2, 2006)(Update 7/30, 2020)

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Materials Explorer

App by Materials Project

References

Search for materials information by chemistry, composition, or property.

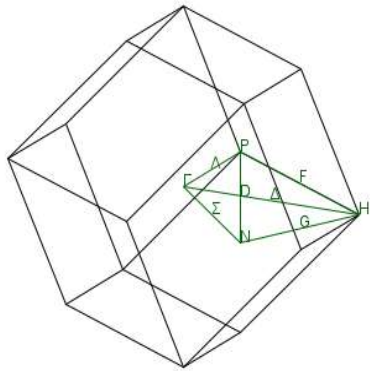
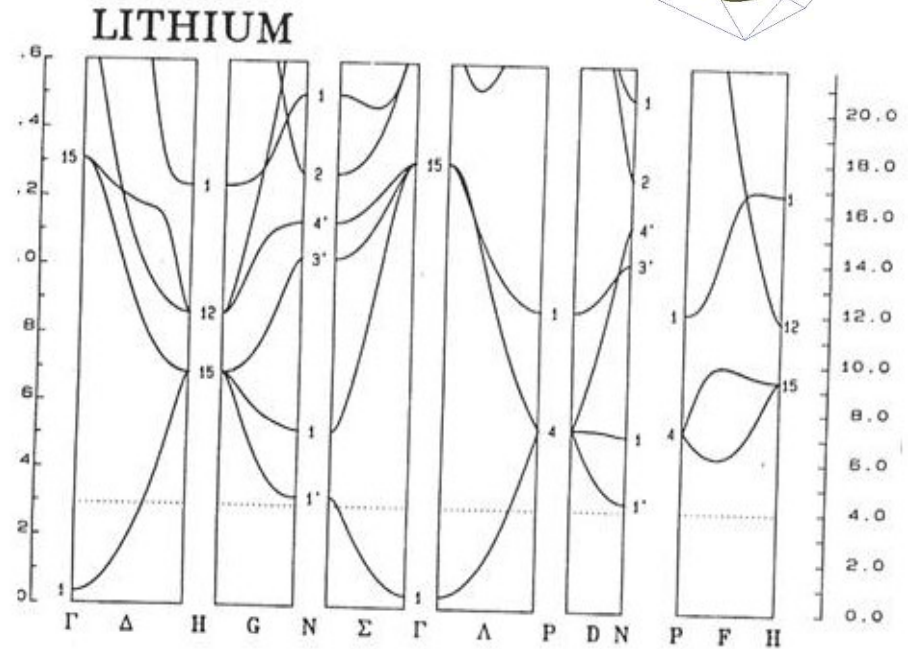
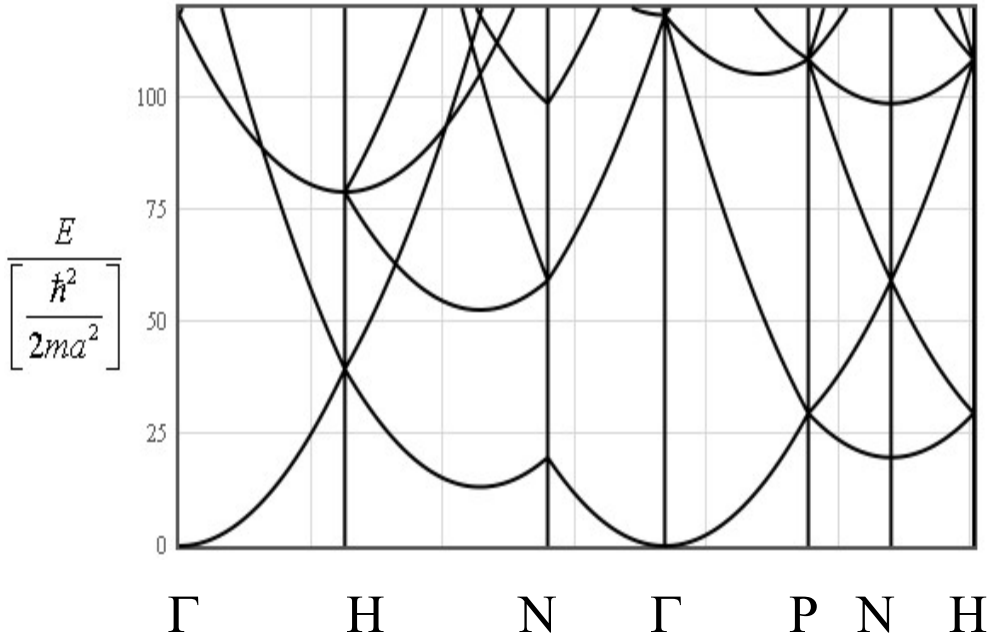
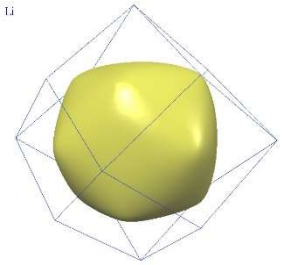
Materials

e.g. Li-Fe or Li,Fe or Li3Fe or mp-19017

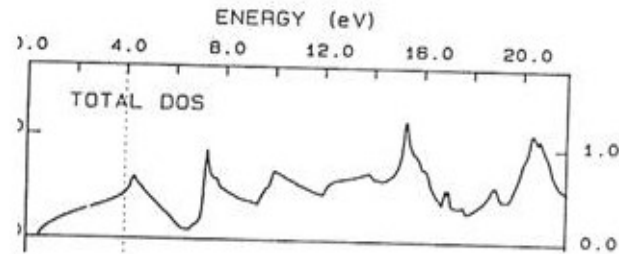
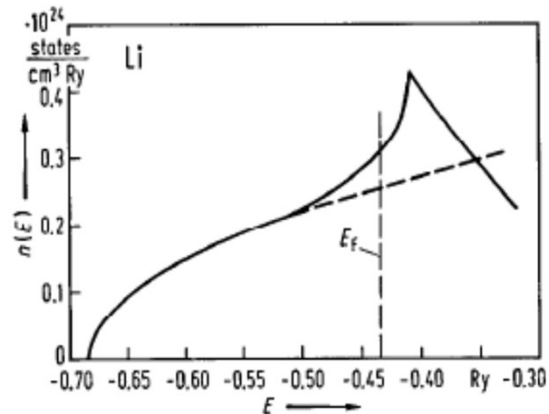
H																						He
Li	Be																					
Na	Mg																					
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr					
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe					
Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn					
Fr	Ra	Ac-Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og					
		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu						
		Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr						



# Lithium bcc



Density of states





# Sodium

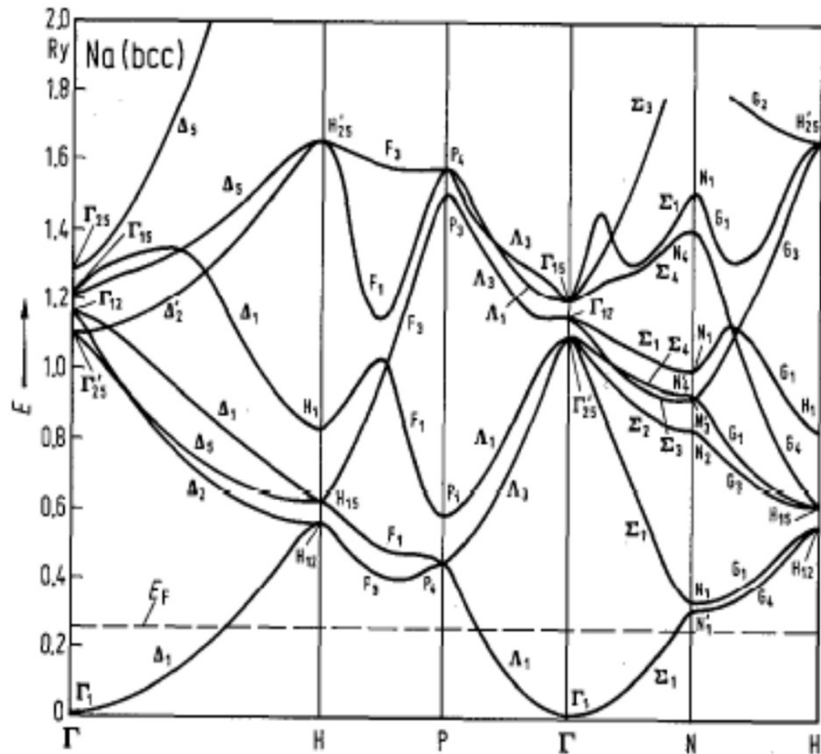
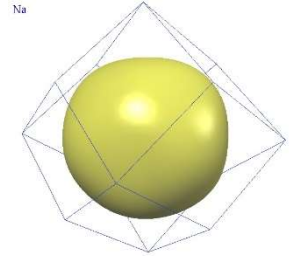
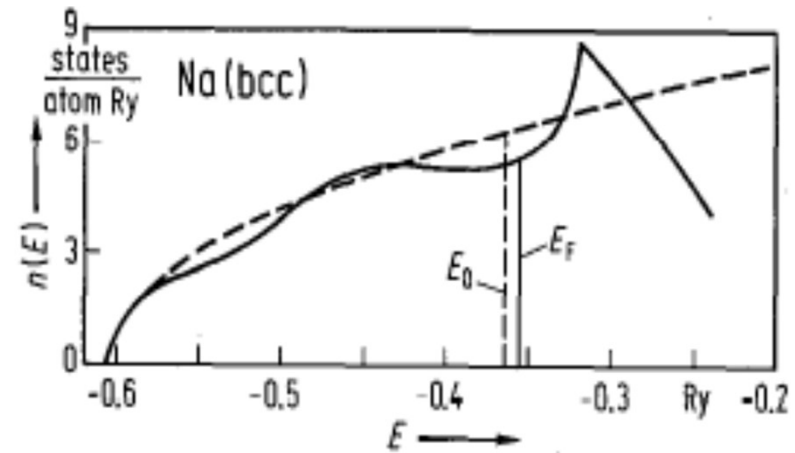
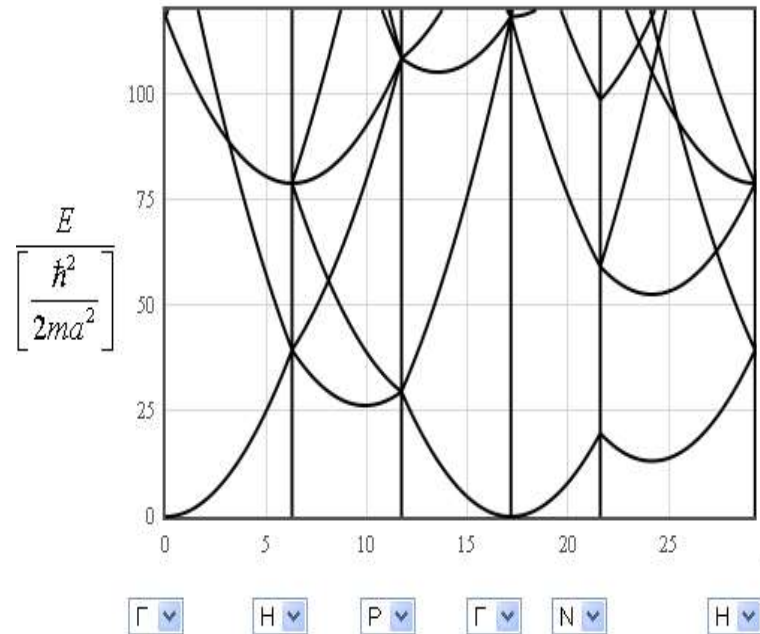
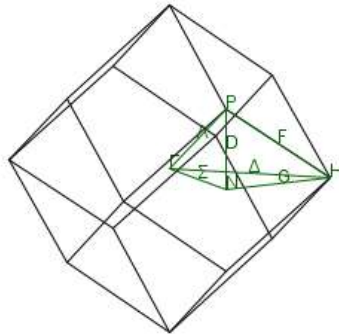
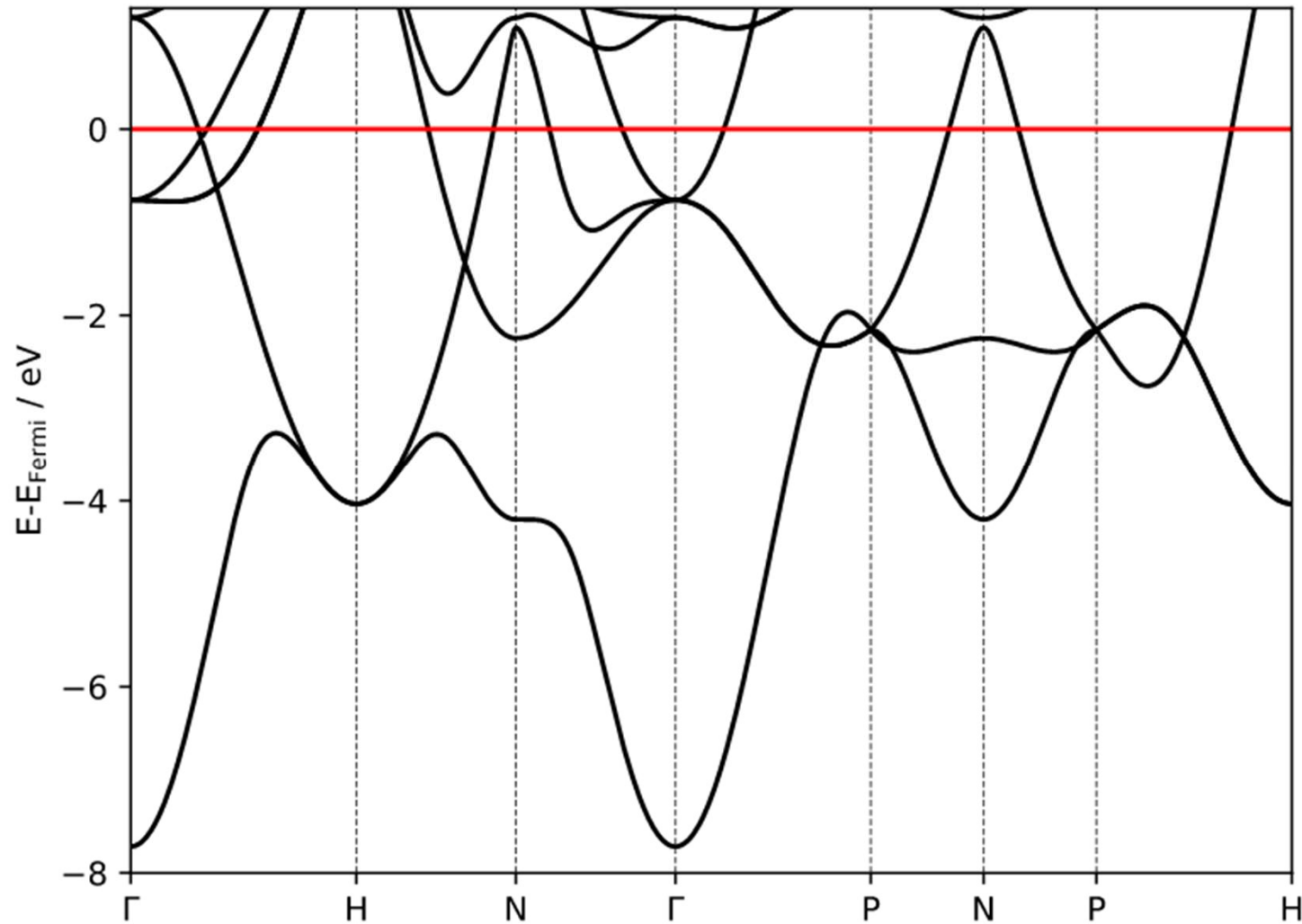
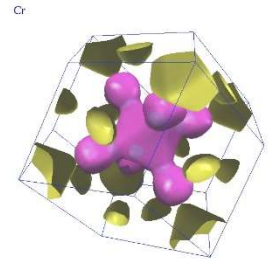


Fig. 6. Na (bcc). Energy bands calculated using the APW method by Gupta (quoted in [73Haa]).

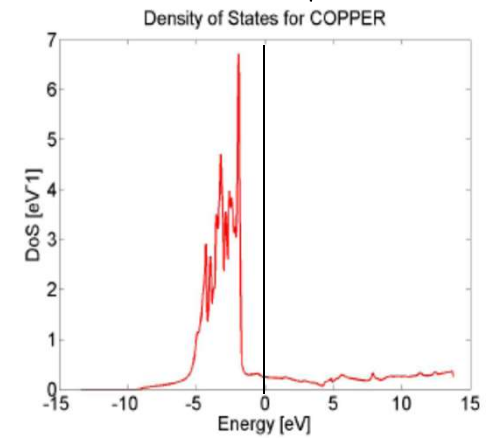
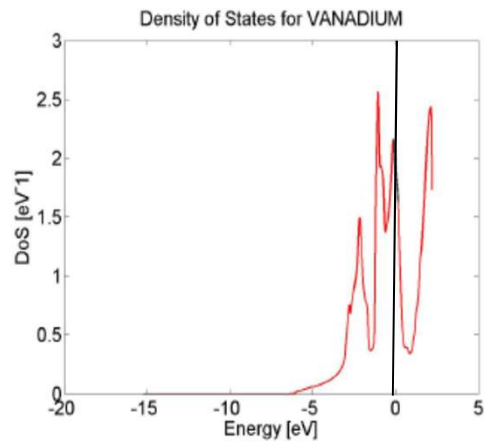
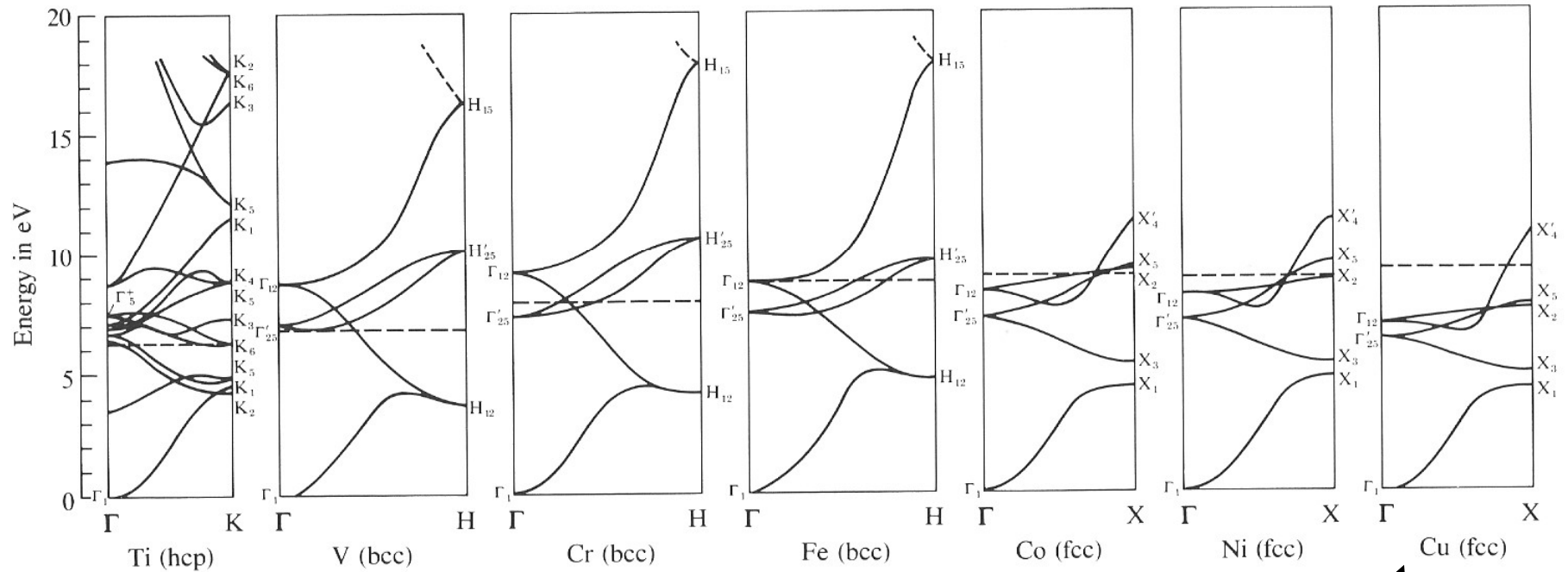


# Bandstructure of bcc chromium (Cr)



[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

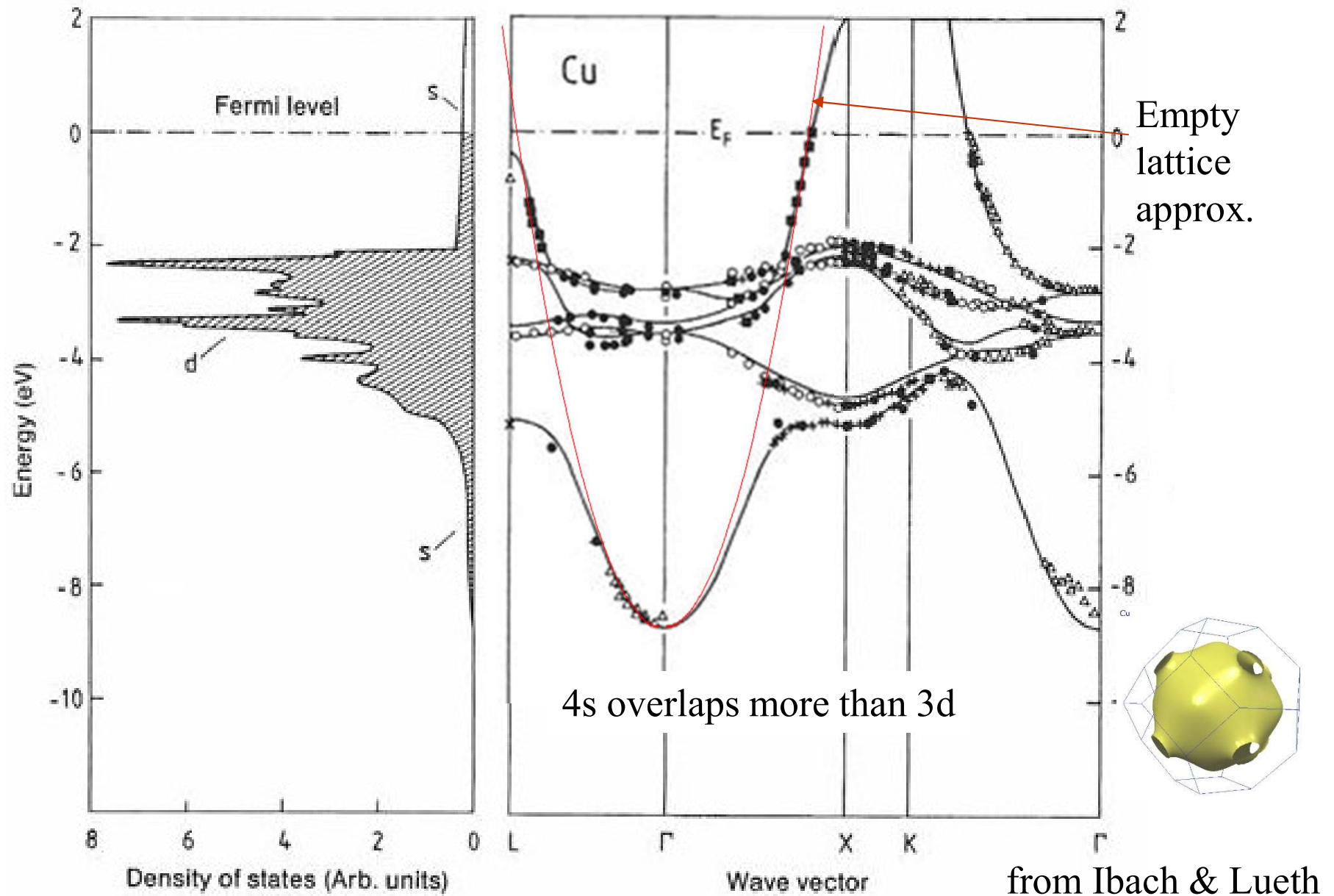
\*\* Actinide series

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

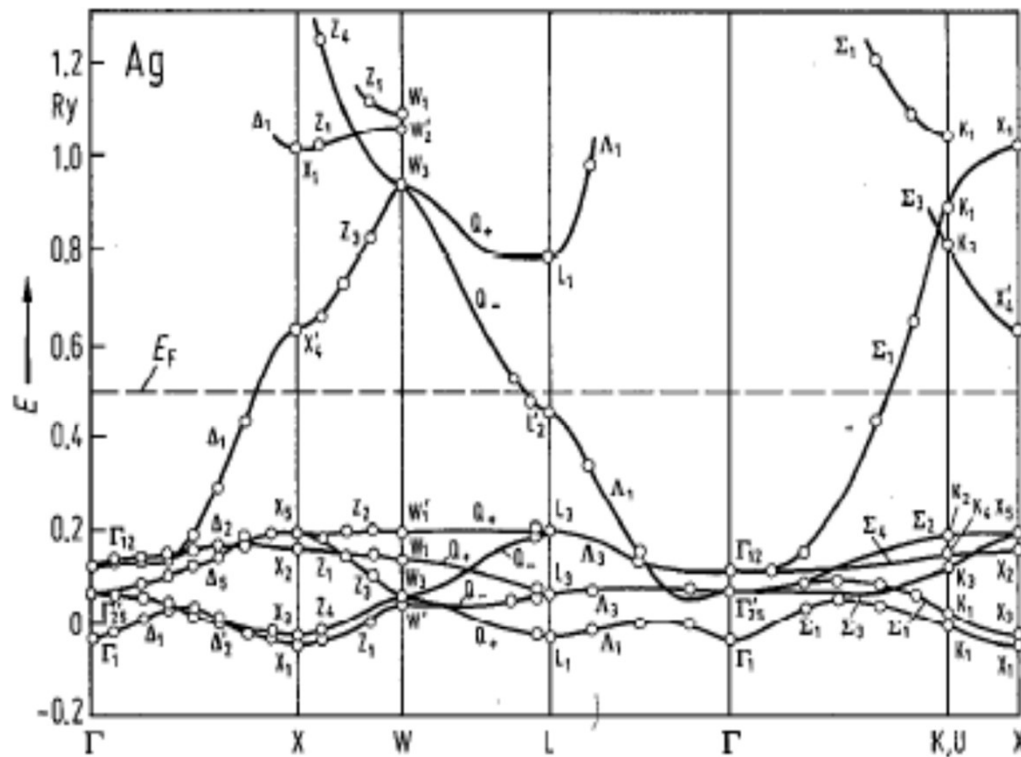
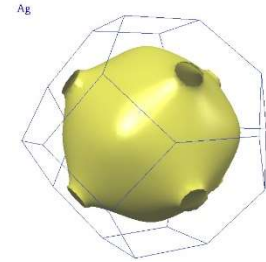


Fig. 3. Ag. Energy bands calculated using the APW method [69Chr].

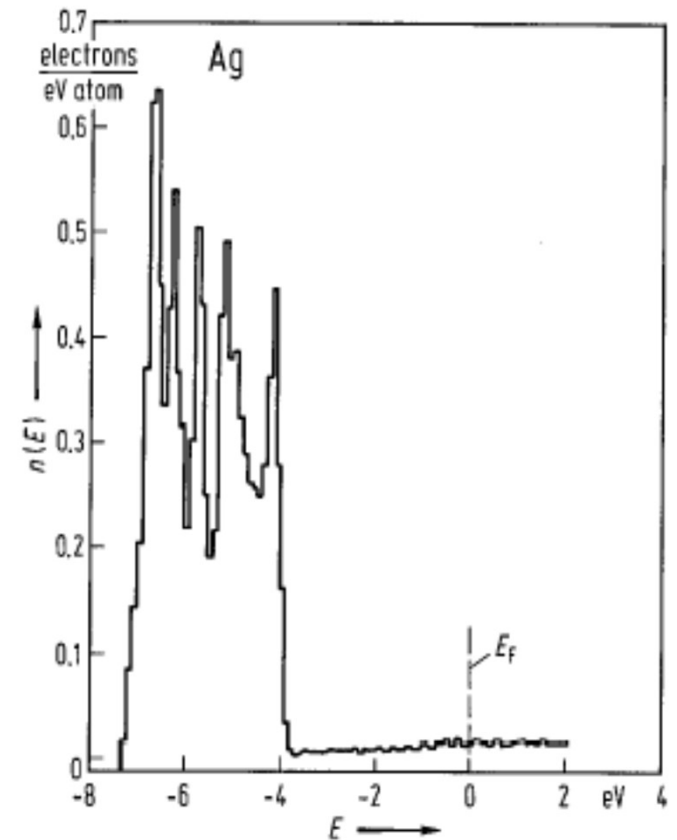


Fig. 15. Ag. Density of states calculated from the energy bands in Fig. 10. Ag [75Fon].



# Gold

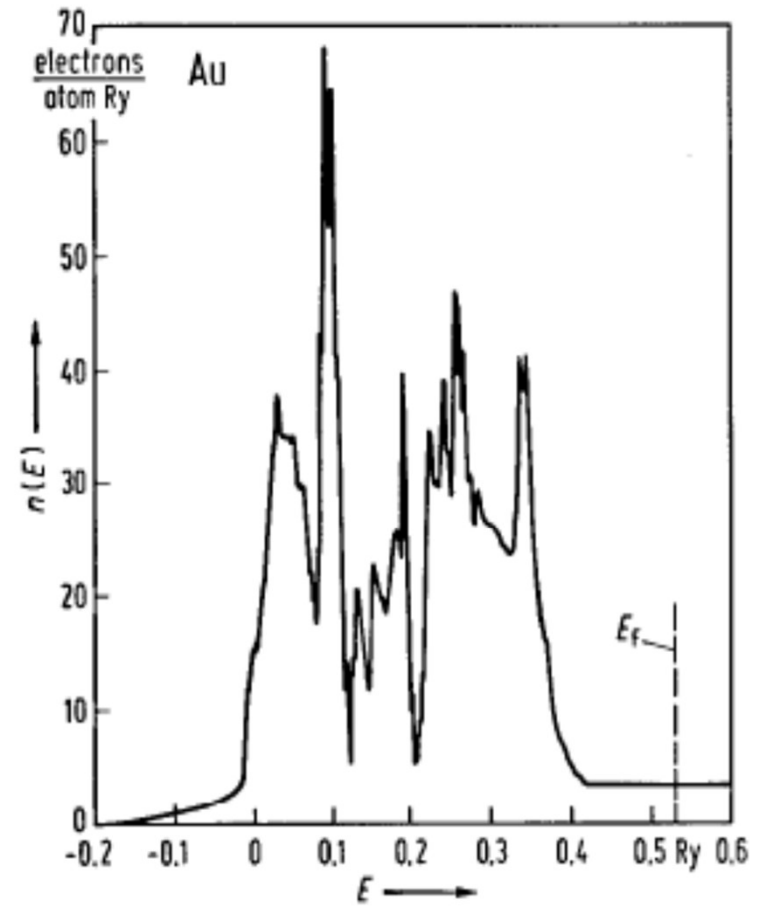
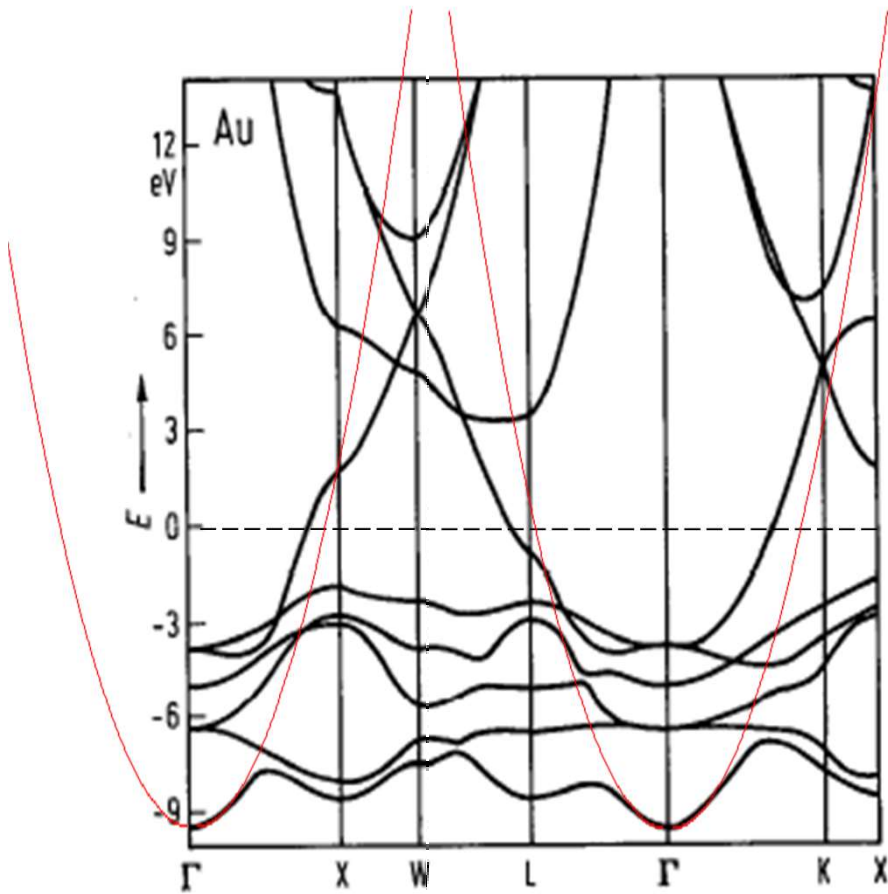
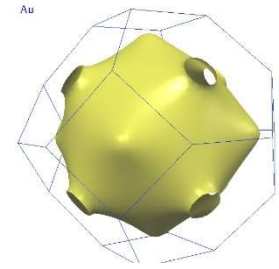
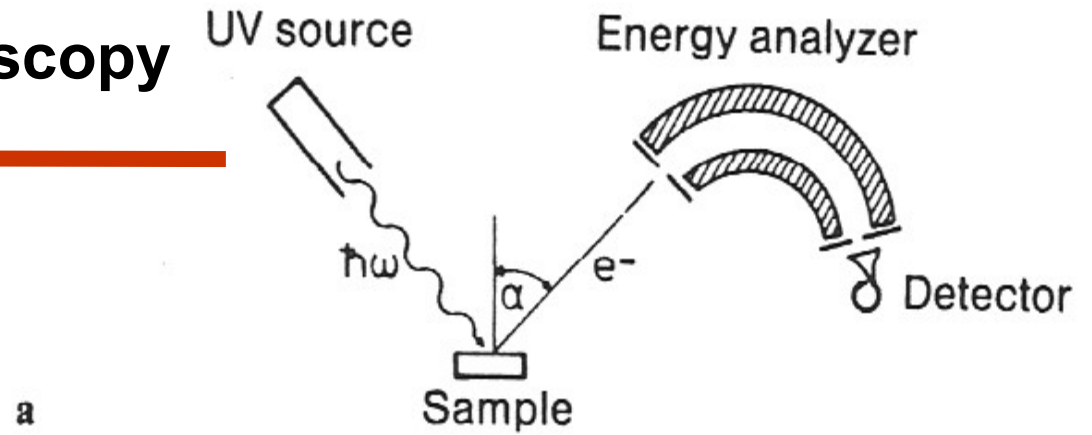


Fig. 9. Au. Density of states calculated from the energy bands in Fig. 4b. Au [71Chr2].

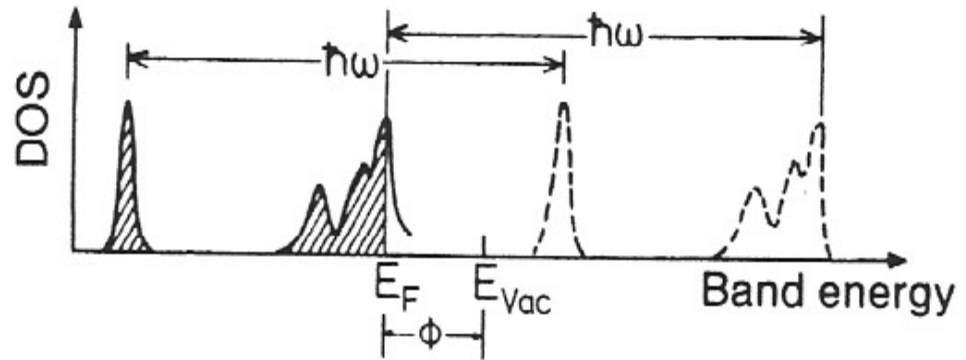
# Photoemission spectroscopy

UPS - Ultraviolet photoemission spectroscopy

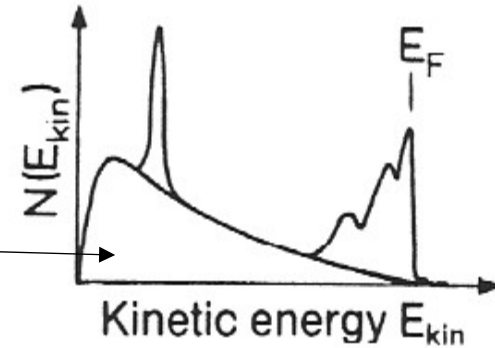
Measure the density of states with photoemission spectroscopy



a



Secondary electrons



Binding energy

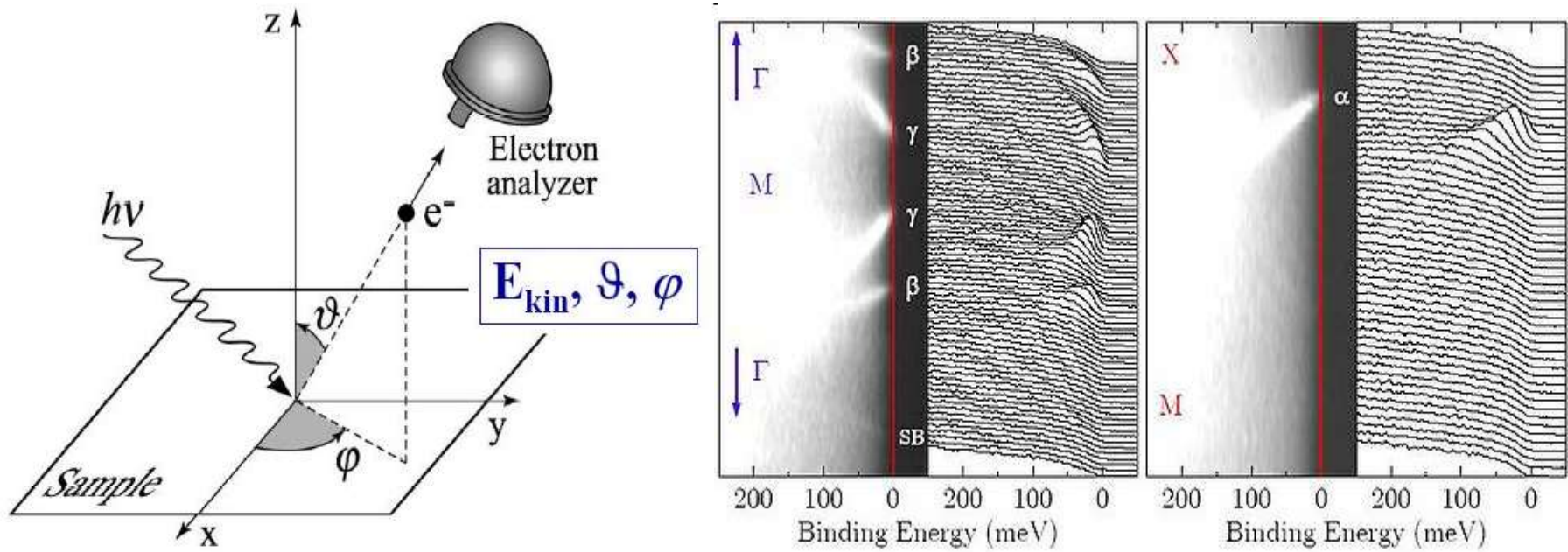
From: Ibach & Lueth

b



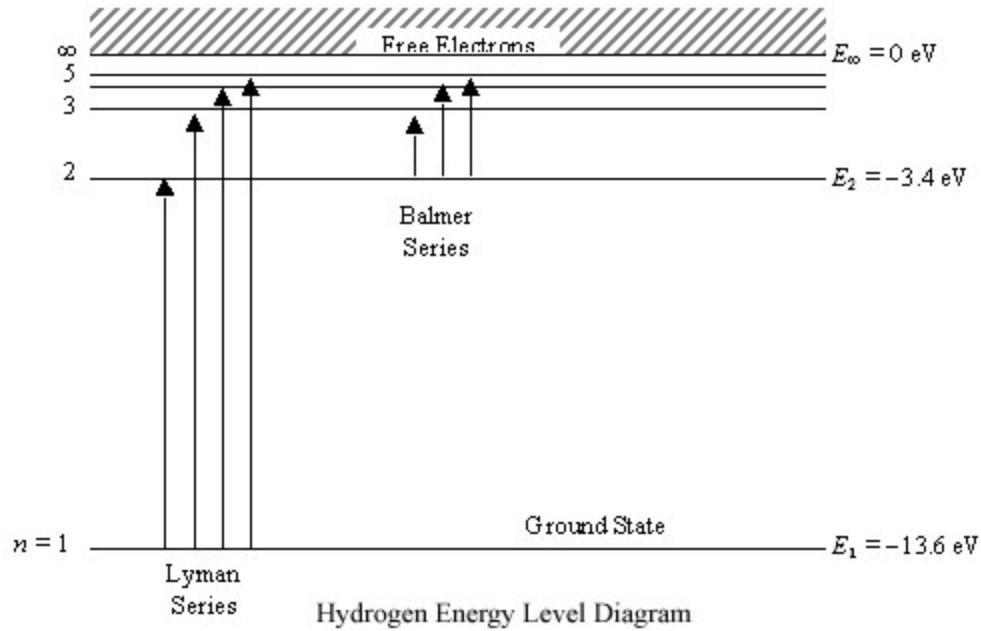
# Angle resolved photoemission spectroscopy (ARPES)

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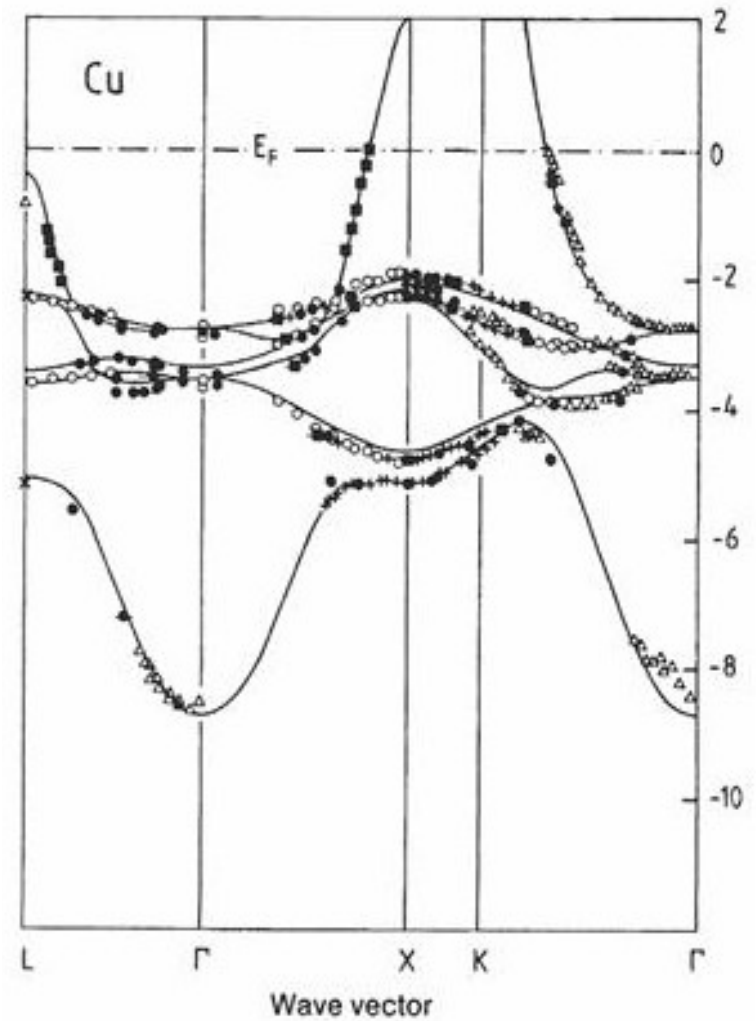
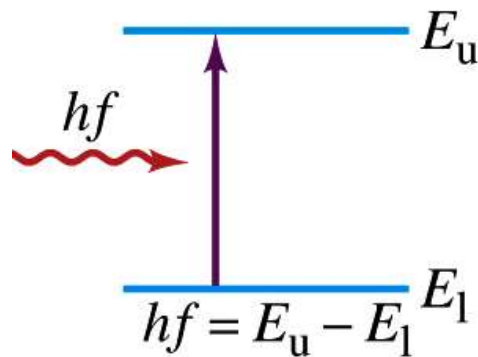


Measure the dispersion relation with angle resolved photoemission

# Optical absorption



Hydrogen atom

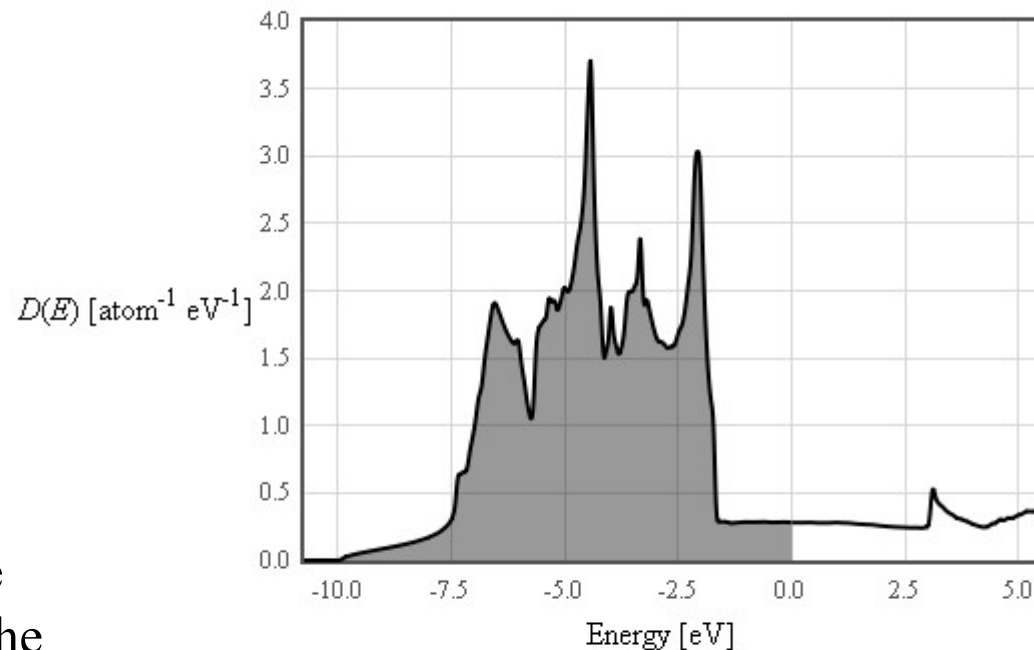


Copper fcc crystal

# 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

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

<b>Entropy</b> $s = \int \frac{c_v}{T} dT$	$s \approx \frac{\pi^2 D(E_F)}{3} k_B^2 T \text{ [J m}^{-3} \text{ K}^{-1}\text{]}$
<b>Helmholtz free energy</b> $f = u - Ts$	$f \approx \int_{-\infty}^{E_F} ED(E)dE - \frac{\pi^2 D(E_F)}{6} (k_B T)^2 \text{ [J m}^{-3}\text{]}$

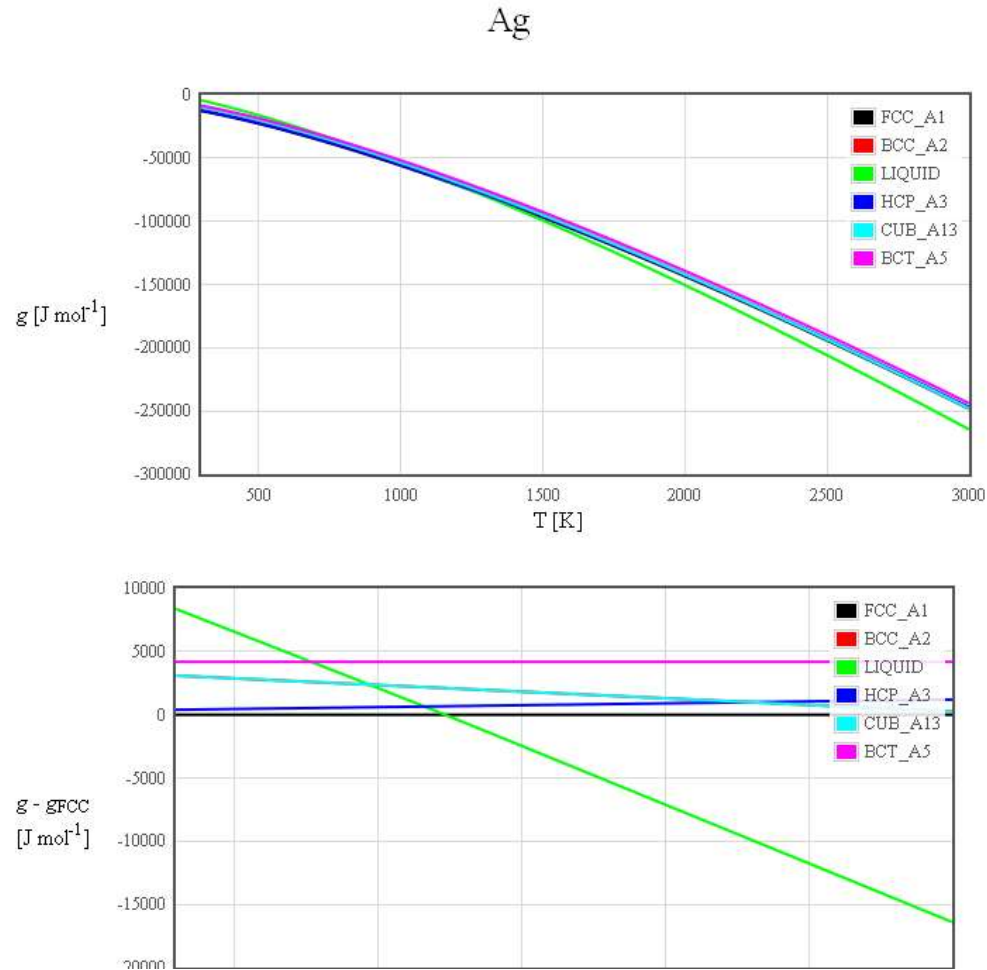
# SGTE data for pure elements

## 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.

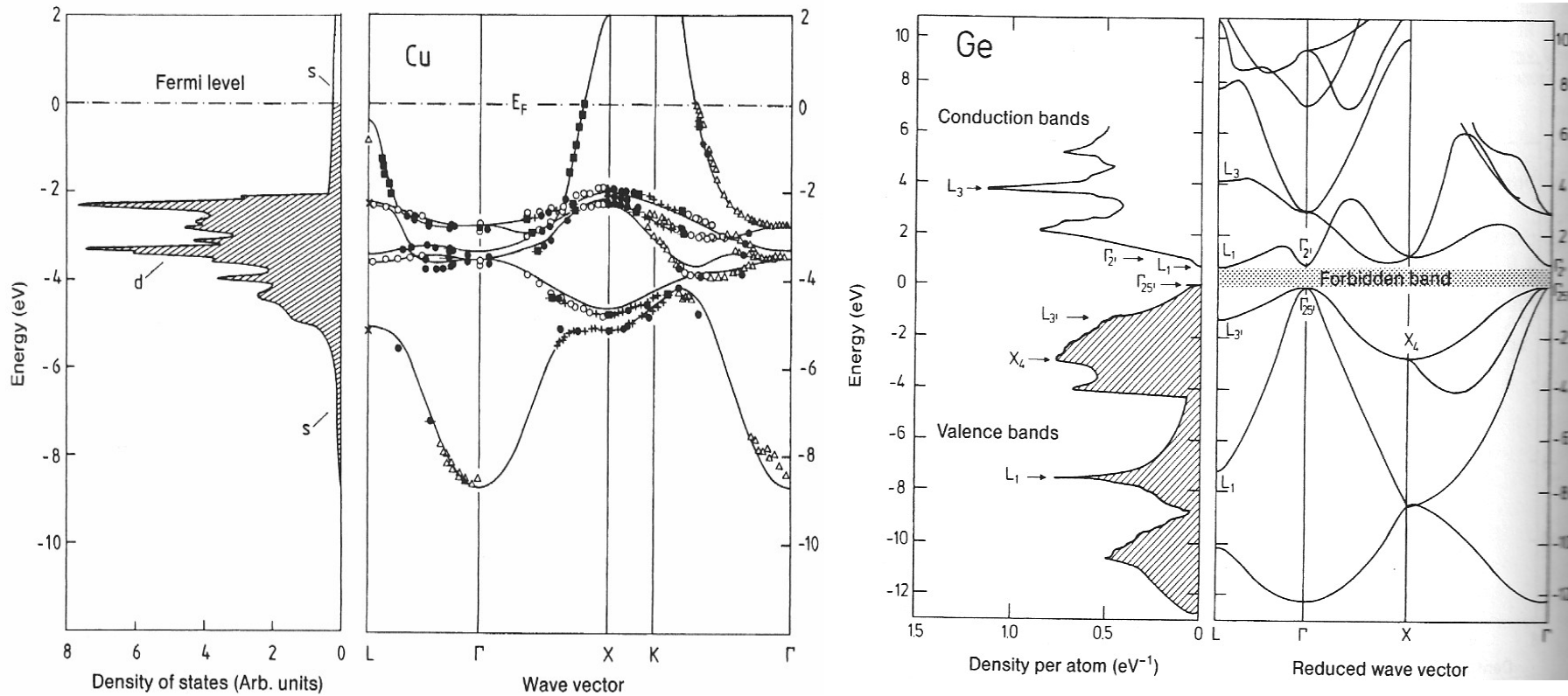
Ag	Al	Am	As
Au	B	Ba	Be
Bi	C	Ca	Cd
Ce	Co	Cr	Cs
Cu	Dy	Er	Eu
Fe	Ga	Gd	Ge
Hf	Hg	Ho	In
Ir	K	La	Li
Lu	Mg	Mn	Mo
N	Na	Nb	Nd
Ni	Np	O	Os
P	Pa	Pb	Pd
Pr	Pt	Pu	Rb
Re	Rh	Ru	S
Sb	Sc	Se	Si
Sm	Sn	Sr	Ta
Tb	Tc	Te	Th
Ti	Tl	Tm	U
V	W	Y	Yb
Zn	Zr		



<http://www.sciencedirect.com/science/article/pii/036459169190030N>

<http://www.sciencedirect.com/science/article/pii/036459169190030N>

# Metals, semiconductors, and insulators



Insulators: band gap  $> 3$  eV

From Ibach & Lueth