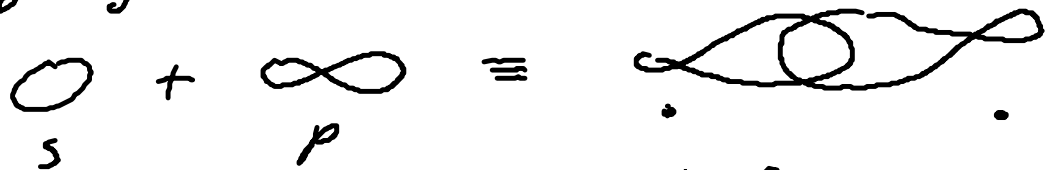


# Covalent bonding cont.

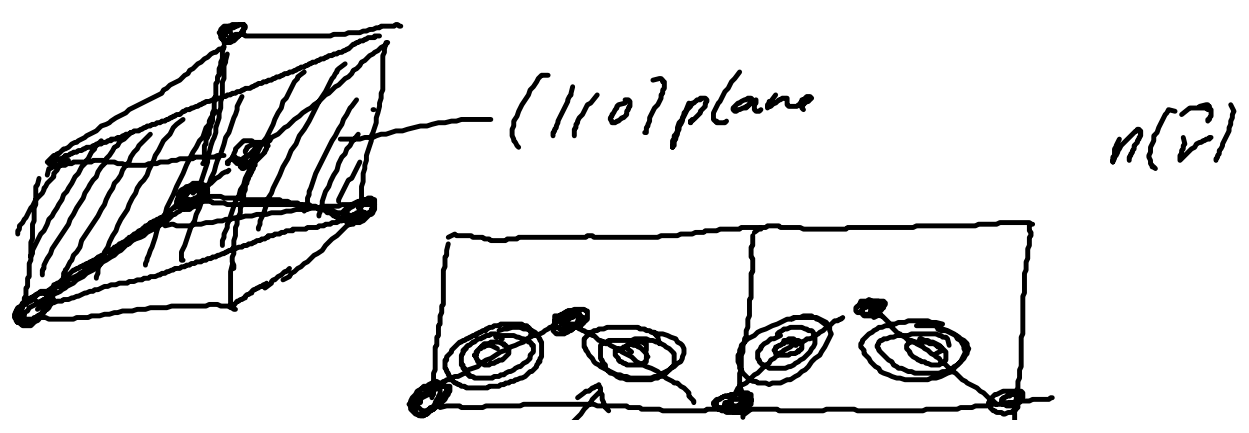
$sp^3$  hybrids



4  $sp^3$  orbitals  $\neq 109,47^\circ$

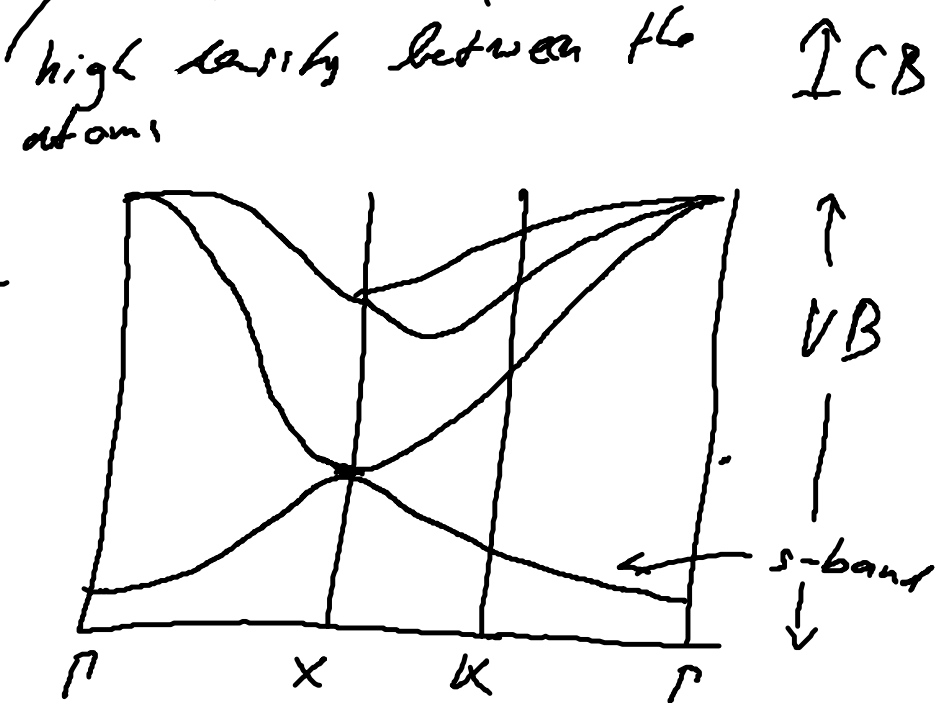
Best localization (narrowest lobes) is found in carbon. Reason: 2p shell is the first p-shell  $\Rightarrow$  there are no p-states in the core;  $\Rightarrow$  no nodes in the core region

Si and Ge: wider lobes

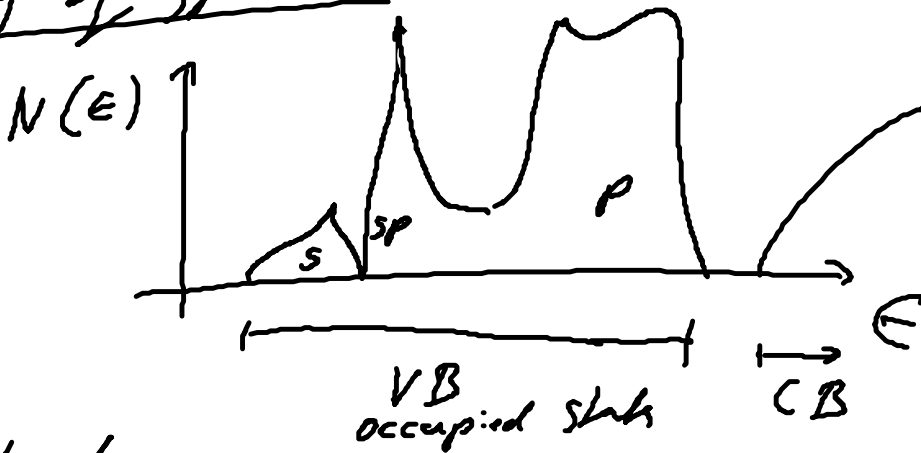


C, Si, Ge  
Si band structure

diamond structure  
≡ fcc structure  
with units  
of two atoms



Density of states



Band structure

& DOS look similar for C, Si, Ge

Comparison with other semiconductors

II	III	IV	V	IV
	B	C	N	
	Al	Si	P	
Zn	Ga	Ge	As	Se
				II-VI

Ge:  $n(v)$  symmetric between two Ge atoms

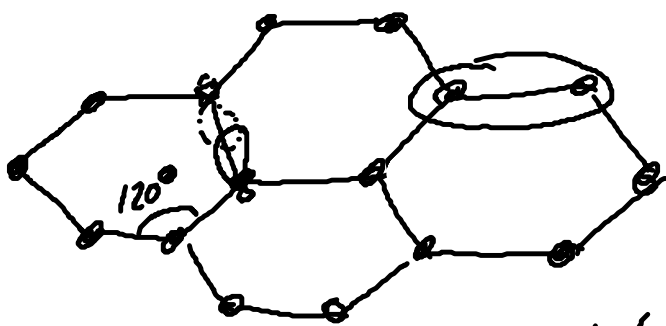
GaAs: qualitatively similar to Ge but  $n(v)$ -peak shifted towards As

Zn Se: looks really very much ionic:

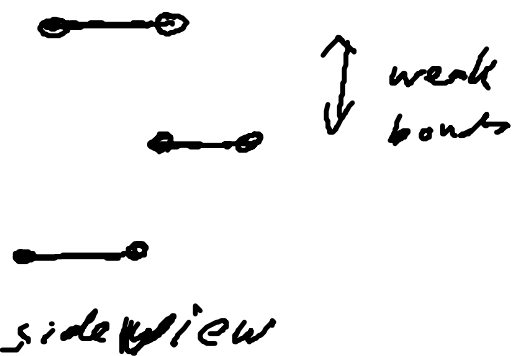


Carbon also can form  $sp^2$  hybrids

$$\begin{aligned} \phi_1 &= \frac{1}{\sqrt{3}}s + \frac{\sqrt{2}}{\sqrt{3}}p_x \\ \phi_2 &= \frac{1}{\sqrt{3}}s - \frac{1}{\sqrt{6}}p_x + \frac{1}{\sqrt{2}}p_y \\ \phi_3 &= \frac{1}{\sqrt{3}}s - \frac{1}{\sqrt{6}}p_x - \frac{1}{\sqrt{2}}p_y \\ \phi_4 &= p_z \end{aligned}$$



top view at graphite



very short & strong bonds in the layer (intra layer);  
very weak inter layer bonds.

Figure Theory vs exp.

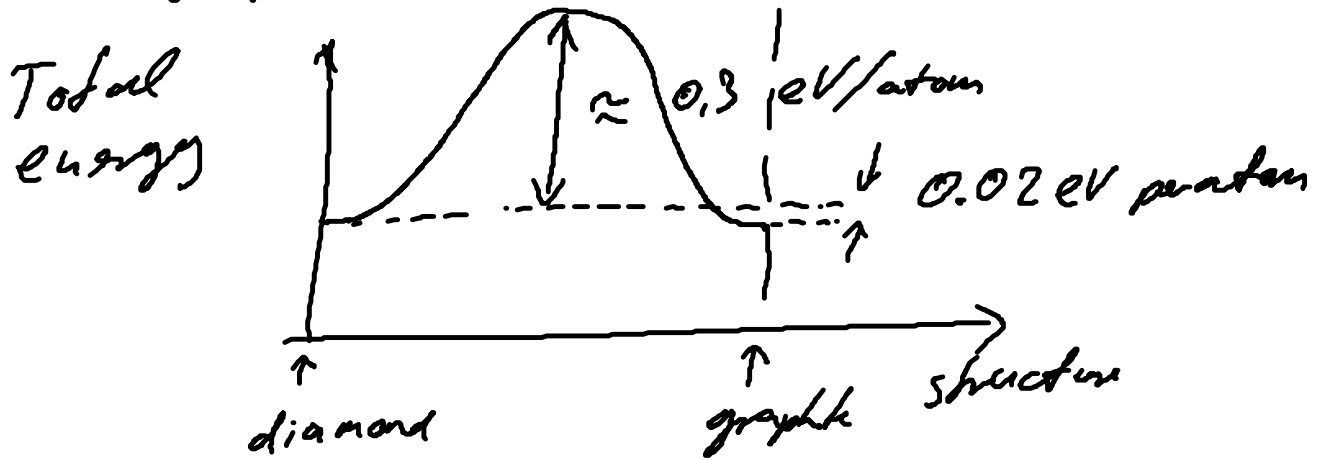
⇒ strong covalent, very directional bonds,  
electron density between layers is

very low.

graphite has higher volume  
than diamond ( $\approx$  Faktor 1.7)

crystal structure of carbon:

graphite has the lowest energy



barrier of 0.3 eV is not much.

However all atoms move simultaneously  
the result is a huge barrier.

graphite exists for C but not for Si, Ge  
large interlayer spacing  $\Rightarrow$  intercalation  
e.g. Li-Batteries: cathode  $\equiv$  graphite

it is possible to peel off a single of  
graphite.

truly 2 Dim. System.

a lot physics

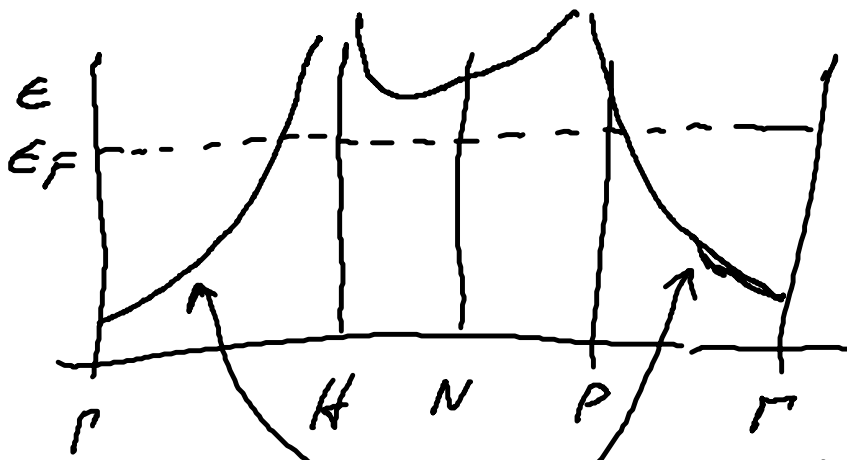
# "graphene"

## 6.5 Metallic bonding

metals typically have a close packed structure  
(fcc, hcp, bcc)

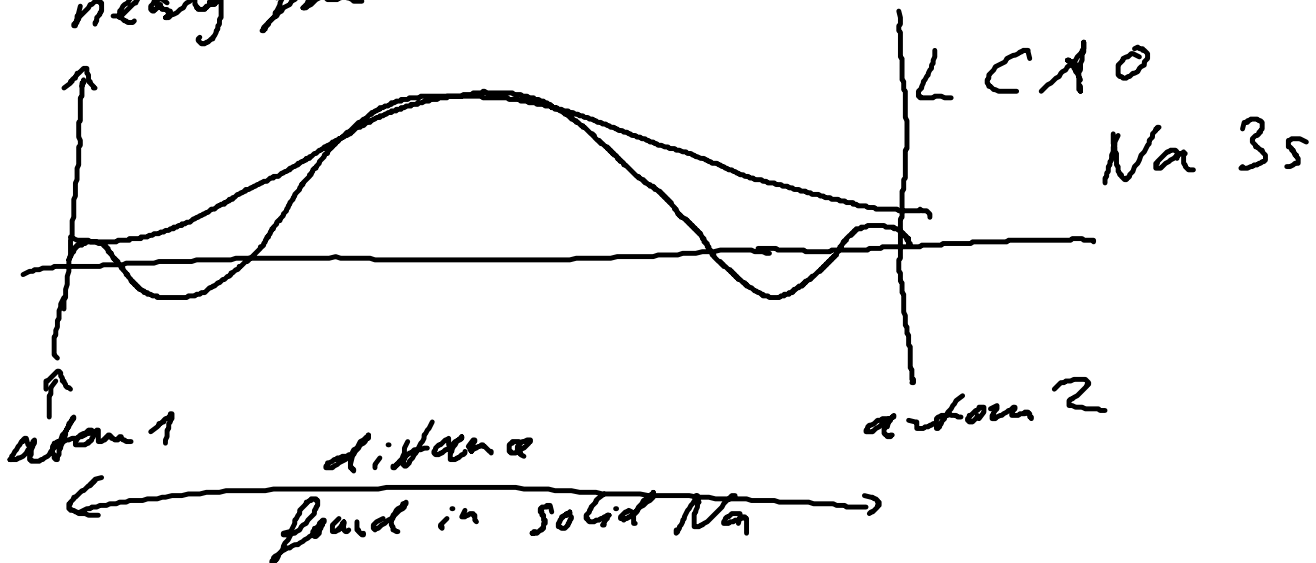
At first alkali metals: group I,  
Li, Na, K, Rb, Cs (except hydrogen)

one valence electron: Li: 2s  
Na: 3s  
↓  
etc.



alkali metals  
assume the bcc  
structure

free electron par  
nearly free electron bandstructure



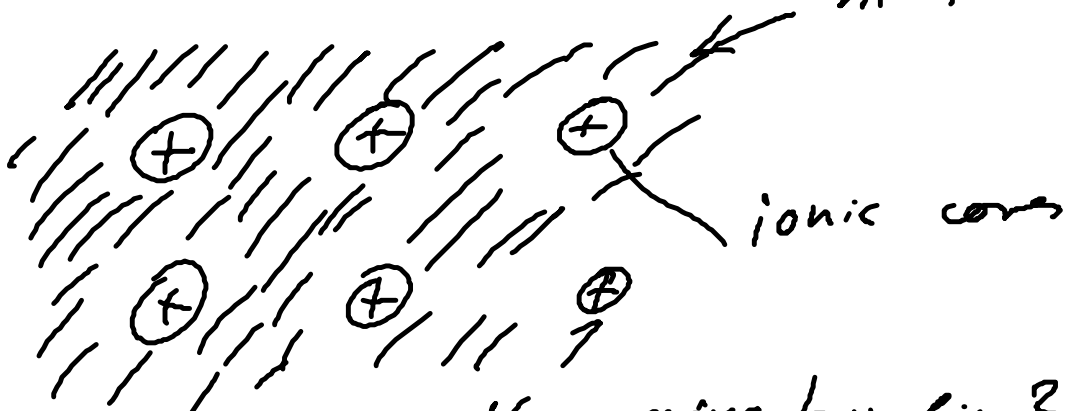
very large overlaps between  $s$ -orbitals,  
at centered at neighboring.

$\Rightarrow$  broad bands

Schematic picture of electrons & nuclei

in alkali metal crystals

$n(\vec{r}) \approx \text{constant}$



free? how does this give bonding?

for sure this is not directional.

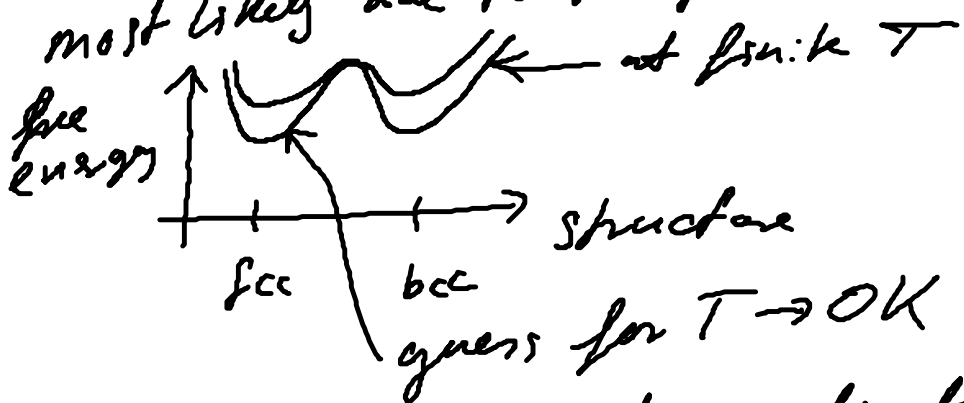
$\Rightarrow$  easy displacement of individual atoms  
 $\Rightarrow$  elastic and ductile

unoccupied states exist immediately  
above the the highest occupied state

$\Rightarrow$  electric field can induce a current flow

$\Rightarrow$  metals are electrons conductors.

delocalized bonds are expected to result in the closest packing: fcc, hcp  
 alkali metals are bcc — why?  
 most likely due to temperature



How can  $n(\vec{r}) \approx \text{const.}$  approximate bonding?

$$E = T_S [n] + \int n(\vec{r}) n(\vec{r}') d^3r + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \int \frac{n(\vec{r}) n(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r d^3r'$$

$$E_{xc}[n] + \underbrace{E^{\text{ion-ion}}}_{\substack{\text{ion-ion} \\ \text{MM} \\ \sum_{I, J} \\ I \neq J} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|}}$$

$$n(\vec{r}) = \text{const} = \frac{N}{V_0}$$

alkalis: one valence electron per atom:  $N = M$

evaluate  $\frac{E^{\text{Coulomb}}}{N}$  for bcc structure

$$= -24.35 \left( \frac{a_B}{r_s} \right) eV$$

$a_B = \text{bohr radius}$

$r_s = \text{density parameter} : \frac{4}{3} \pi r_s^3 = \frac{1}{n}$

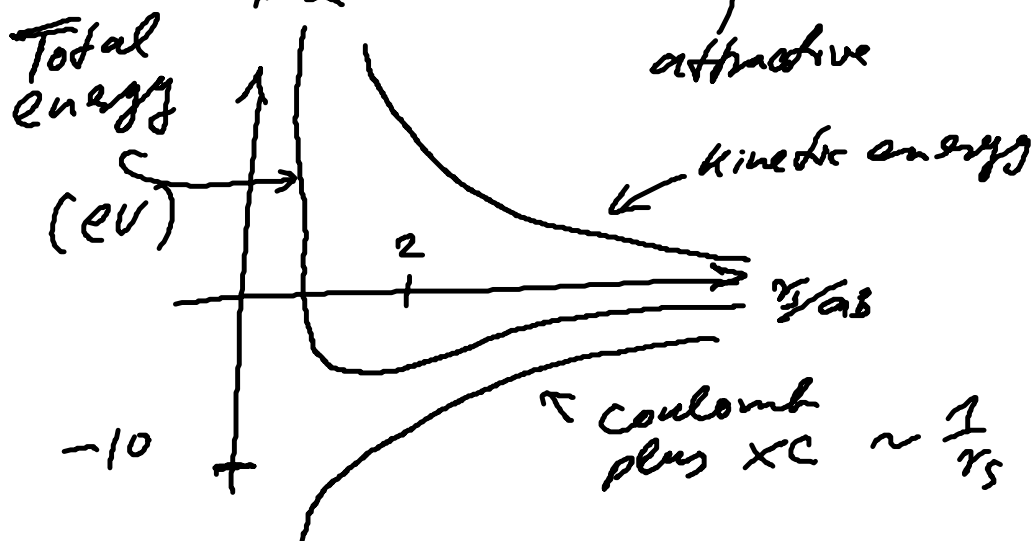
attractive

$$\frac{1}{M} T_S [u] = \frac{\hbar^2}{2m} \uparrow \text{spin} \quad 2 \quad \frac{1}{M} \quad \frac{V_g}{(2\pi)^3} \quad \left. \vphantom{\frac{1}{M} T_S [u]} \right\} k_F \quad k^2 \quad d^3k$$

$$= + 30.1 \left( \frac{a_B}{r_s} \right)^2 \text{ eV}$$

$$E_{xc} [u] \sim n^{2/3} \quad \rightarrow \quad - 8.33 \left( \frac{a_B}{r_s} \right) \text{ eV}$$

wing  $\times 2$  with  $\alpha = 2/3$



we did slightly better than jellium

$v(r)$  was not constant  
but  $n(r^3)$  was constant

$\Rightarrow$  already the crudest model of delocalized electrons leads to bonding.

Qualitative picture is o.k.  
quantitatively not acceptable



"theory"  $\Rightarrow \frac{r_s}{a_B} \approx 1.9$

Li, Na, K ... real metal  
 $\frac{r_s}{a_B}$  3,27 (Li) ... 5,75 (Cs)

$\Rightarrow$  we need a good calculation of  $v(\vec{r})$  and  $u(\vec{r})$  to get things right.

Transition metals (TM)

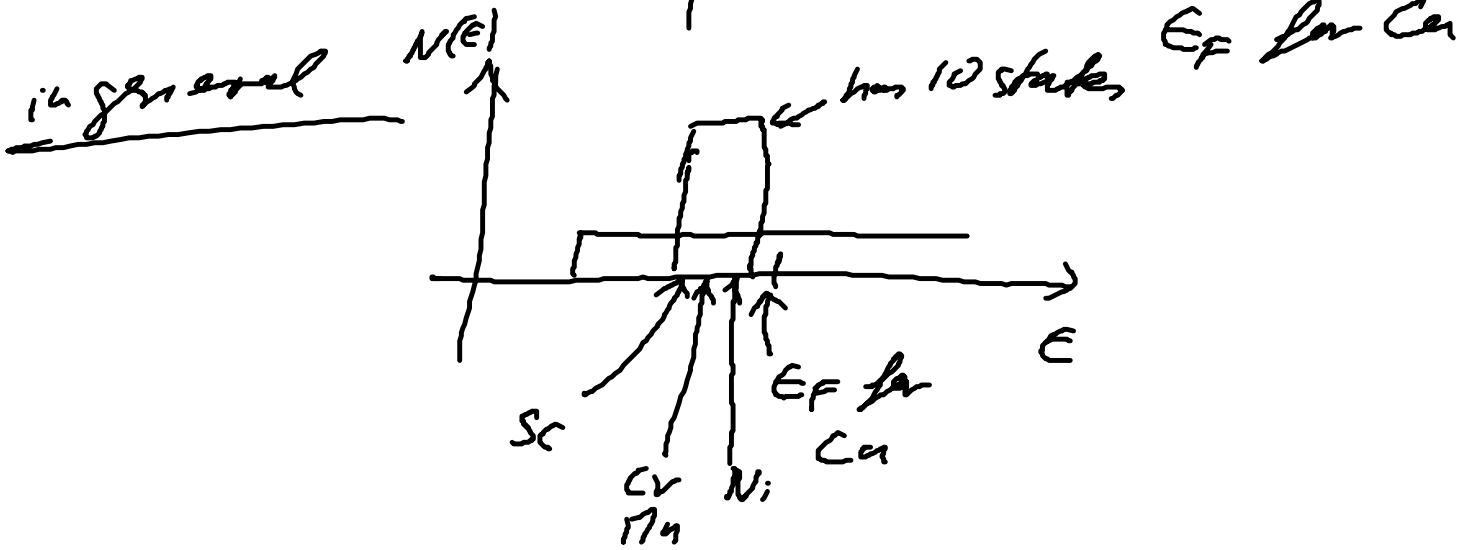
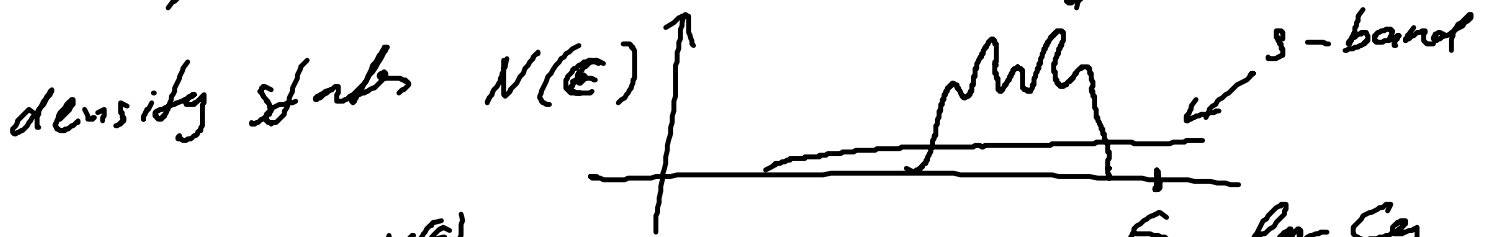
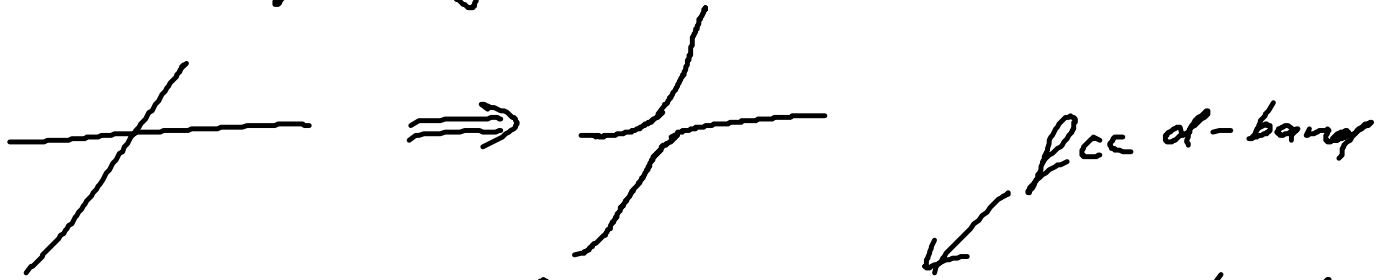
much stronger bond than alkalis  
 alkalis  $E^{col} \approx 7eV$   
 TM ... 8.9eV for W.

Reason:  
partially  
covalent

Band structure of Cu (Ag, Au nearly the same) fcc



s-band and d-bands "cross"  
 if same symmetry "avoided crossing"



atomic behavior

3d atoms

Sc	$3d^1 4s^2$
Ti	$3d^2 4s^2$
..	$3d^3 4s^2$

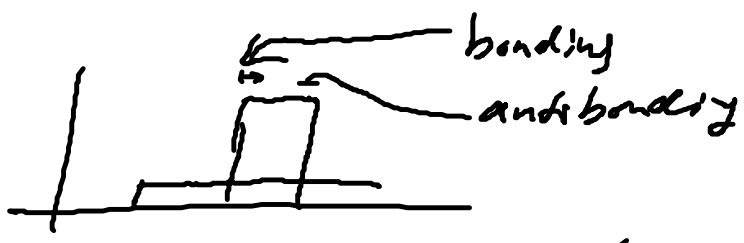
all TMs

have  $V_{xy}$

V	$3d^5 4s^1$
Cr	$3d^5 4s^1$
Mn	$3d^5 4s^2$
Fe	$3d^6 4s^1$
Co	$3d^7 4s^2$
Ni	$3d^8 4s^2$
Cu	$3d^{10} 4s^1$

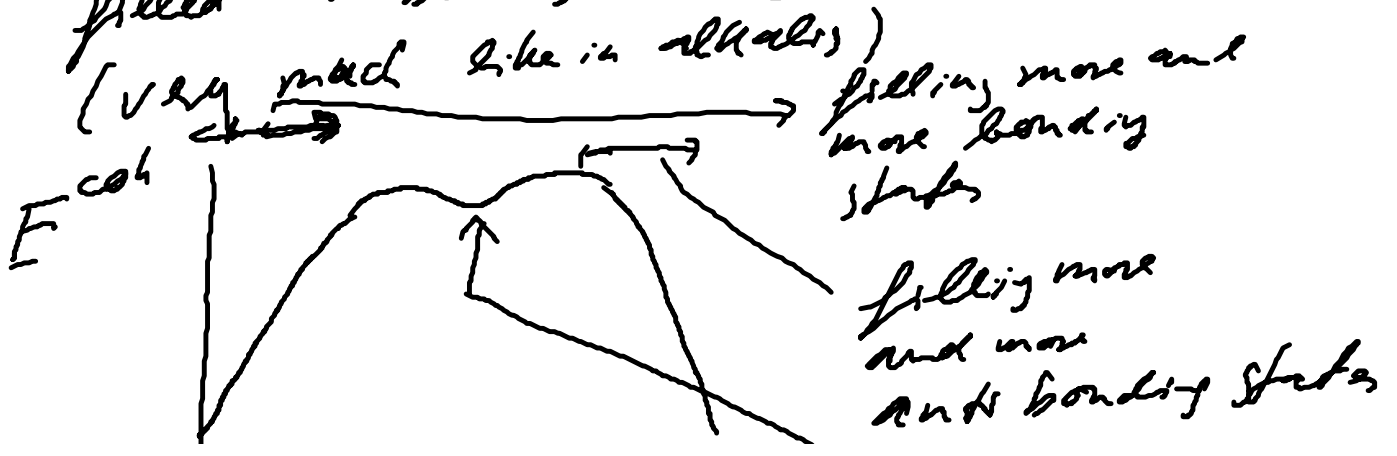
Similar DOS  
 - just the Fermi level is at a different energy.

3d TM are very localized  $\approx$  first d shell, i.e. no d-core;  $\Rightarrow$  no nodes in the radial wavefunctions.  
 d-band width  $\approx 3\text{eV}$



The energetically low bands are bonding.  
 The energetically high bands are antibonding.

for Cu, Ag, Au all d-states are filled  $\Rightarrow$  bonding is only due to s-states (very much like in alkalis)



3d	Sc	-----	Ni	Cu
4d	Y		Pd	Ag

dip due to correlation  
in atoms, e.g.  
stability of d<sup>5</sup>, magnetism

Figure : Moruzzi = 1978

6.6 hydrogen bonding ⇒ Tuesday

d