Metals + Alloys: Structure, Bonding, Electronics, Magnetic Properties

Here the octet rule — which worked fine for p-block compounds and ionic s-p block salts — fails miserably.

Molecular elements
$(\text{O}_2, \text{P}_4, \text{S}_8 \ldots)$
(insulators)

Metallic elements
($\approx \frac{2}{3}$ of periodic table)

How can we understand the (covalent) bond in metals, and their other properties (thermal & electrical conductivity, strength & malleability, magnetism)?

To explain these properties, we need to understand something about structure.

All metals (except liquid metals Ge, Hg, Cs) are crystalline solids at room temperature. Crystals are periodic arrays of atoms. The structure repeats like 3D wallpaper.

Possible unit cells
(choice is arbitrary)

In 3D, unit cell is a box which repeats to fill all space.
Crystal Structures of Metals

The bcc structure
(Li, Na, V, W, etc.)

the unit cell in the bcc structure

Close-packed layer
in the hcp and ccp structures of metals
(Zn, Cu, Ag, Au, etc.)
Fig. 12.7. A perspective drawing of a stack of six layers of spheres arranged in accordance with face-centred cubical close-packing. The cubical pattern is shown by the relative positions of spheres 1, 2, 3, 4, 5, 6, 7, 8, which are at the corners of a cube.

Fig. 12.8. The same stack as in Fig. 12.7 canted through 45°. One complete unit of the cubic structure is heavily outlined. A few of the spheres drawn in Fig. 12.7 have been omitted for the sake of clarity. The numbers on the spheres coincide with those in Fig. 12.7. Note that spheres 2, 9, 4, 10, 7, and 14 are all members of the layer D (Fig. 12.7). The spheres at the face centres of the cube are stippled.
Unit cell of a simple cubic array.

How many unit cells does each corner belong to? 1, 2, 4, 8?

Simple cubic arrays do not fill space efficiently (only 52%), so structure is rare.

Each atom has 8 nearest neighbors.

Bcc structure packs more efficiently, is fairly common for metals (Na, Mo, Fe, ...).

Best packing has 12 nearest neighbors.

$\Rightarrow$ cubic + hexagonal close packing

ccp = fcc (face-centered cubic)

hcp = hexagonal close packed

stacking direction is along body diagonal of fcc cell

How many atoms per cell? 1, 2, 4, 8, 12?
Non-metals: p-block elements (upper right of periodic table)

Down a group, properties change gradually

nonmetal ——> metalloid ——> metal
(insulator) (semiconductor) (conductor)

<table>
<thead>
<tr>
<th>Element</th>
<th>Structure</th>
<th>Coord. No.</th>
<th>Conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>graphite</td>
<td>3</td>
<td>semimetal</td>
</tr>
<tr>
<td></td>
<td>diamond</td>
<td>4</td>
<td>insulator</td>
</tr>
<tr>
<td>Si</td>
<td>diamond</td>
<td>4</td>
<td>semiconductor</td>
</tr>
<tr>
<td>Ge</td>
<td>diamond</td>
<td>4</td>
<td>semiconductor</td>
</tr>
<tr>
<td>Sn</td>
<td>diamond</td>
<td>4</td>
<td>semiconductor</td>
</tr>
<tr>
<td></td>
<td>distorted bcc</td>
<td>8</td>
<td>metal</td>
</tr>
<tr>
<td>Pb</td>
<td>ccp</td>
<td>12</td>
<td>metal</td>
</tr>
</tbody>
</table>
Semiconductors, insulators: just the right number of electrons for bonds to all nearest neighbors (e.g., Si has 4 n.n. 
P " 3 " 
S " 2 " )

Metallic elements have too few valence electrons to make electron pair bonds to all neighbors

Valence electrons are delocalized over entire crystal

"sea" of valence electrons

positively charged "cores"

Delocalized electrons can move in electric field

=> electrical conductivity, thermal conductivity
Bonding in metals

Too few valence electrons to make "conventional" 2-electron bonds.

E.g. Na metal, \( \text{Na} = [\text{Ar}] 3s^1 \) 1e\(^-\)/atom

Unit cell contains 2 Na atoms \( \Rightarrow \) 2e\(^-\).

But there are 8 Na...Na "bands" in the cell \( \Rightarrow \) bond order \( = \frac{1}{8} \).

MO theory - gives a more accurate picture (band model)

Start by recalling the picture for two atoms:

\[ E \]

\[ v_N \]

\[ v_N-Na \]

\[ 2 \] isolated atoms

This is the same picture we drew for \( \text{He}_2 \) molecule.

We can put 2e\(^-\) in each orbital, so in \( \text{Na}_2 \) we would put them both in the bonding orbital.
Now consider a chain of 6 Na atoms:

| \( \Psi_6 \) | 5 |
| \( \Psi_5 \) | 4 |
| \( \Psi_4 \) | 3 |
| \( \Psi_3 \) | 2 |
| \( \Psi_2 \) | 1 |
| \( \Psi_1 \) | 0 |

We fill the lowest 3 orbitals with 6 electrons.
(Still \( \frac{1}{2} \) bond per Na atom)

Extrapolate to Avogadro number.

There are allowed levels between \( E_1 \) and \( E_2 \):

- \( E_1 \), bonding, long wavelength (\( \lambda = \infty \))
- \( E_2 \), antibonding, short wavelength (\( \lambda = 2\alpha \))

All electrons are delocalized over the whole crystal (valence).
Density of states (DOS)

=> Number of orbitals per unit energy

1D crystal (chain of Na atoms, carbon nanotube, nanowire) has highest DOS at band edges.

3D crystal has highest DOS in center of band

How does this picture explain conductivity of metals?

All N.o.'s extend over entire crystal (e^- is "traveling wave")

Imagine 2 bands — e^- traveling to right and left

In zero E field, there are equal numbers of electrons in the "left" and "right" bands.

Apply E field: (lowers energy of one band, raises the other)

Now, more electrons are traveling with the field than in the opposite direction.
Conduction in metals

Valence electrons are in MO's that extend over the entire crystal

Band (in Na, Ag, ...) is typically half-filled

Classically, we would expect the electronic specific heat of a metal to be 3R per mole of free electrons

Experimentally, \( C_p, \text{electrons} \approx 0.02 R \) per mole of metal

\( \Rightarrow \) only about \( 1/2 \) of valence electrons can be thermally excited at room temp, but essentially all of them are free to move & conduct electricity. Why?

Fermi-Dirac distribution implies that the Fermi energy \( E_F \) is \( \gg \) thermal energy \( kT \).

How fast are electrons traveling in the metal?

Most electrons have \( E \approx E_F \)

At halfway point in band, MO's have one node for every 2 atoms

\( \Rightarrow \lambda \approx 4a \) (\( a = \) interatomic distance) \( \approx 8a \) for typical metal

De Broglie relation: \( \lambda = \frac{h}{p} = \frac{h}{m E_F} = \frac{6.62 \times 10^{-34} \text{J s}}{(9.1 \times 10^{-31} \text{kg})(V)} = 8 \times 10^{-10} \text{m} \)

\( \Rightarrow \) Solving for \( V_F \), we get the Fermi velocity \( \approx 1.0 \times 10^6 \text{ m/s} \)

(Exact values: Na: \( 1 \times 10^6 \), Ag: \( 1.39 \times 10^6 \text{ m/s} \))
Electrons are moving very fast in a metal!

\[ V_F \approx 10^6 \text{ m/s} \]  
\[ \text{speed of light} = 3 \times 10^8 \text{ m/s} \]
\[ \text{speed of sound} = 3 \times 10^2 \text{ m/s} \]

But the drift velocity of electrons is slow, \( \approx 0.01 \text{ m/s} \).

Why?

**Physical picture**

\[ F = ma \]
\[ V_{drift} = \frac{eE}{m_e} \]

Here, \( \tau \) is the scattering time, which is related to the mean free path, \( \lambda \):

\[ \lambda = \frac{1}{\tau} \approx V_F \tau \]

In Cu metal at 300K, \( \lambda \approx 40 \text{ nm} \)

\[ \tau \approx 2 \times 10^{-14} \text{ s (0.2 ps)} \]

Note that \( V_{drift} \) (and current) increase linearly with \( E \) <

\[ \Rightarrow \text{Ohm's law, } V = \ell R \]

\[ R = \frac{L}{A} = \rho \frac{1}{\lambda} \]

The resistivity of a metal is inversely related to \( \tau \) (\( \propto \lambda \))

\[ \rho = \frac{m_e}{n e^2 \tau} \]

For Cu, \( \rho = \frac{(9.1 \times 10^{-31} \text{ kg})}{(8.5 \times 10^{-8} \text{ e/m}^3)(1.6 \times 10^{-19} \text{ Coul})[(2 \times 10^{-14})]} \]

\[ = 1.4 \times 10^{-8} \Omega \cdot \text{m} = 1.4 \times 10^{-6} \Omega \cdot \text{cm} \]

Conductivity of Cu metal: \( \sigma = \frac{1}{\rho} = \frac{7 \times 10^5}{\Omega^{-1} \text{ cm}^{-1}} \)
Picture for a semiconductor or insulator (filled band)

1 bond to each nearest neighbor

\[ \text{Many orders of magnitude lower conductivity than metal} \]

This explains conductivity of Na \((3s^1)\), but what about Mg \((3s^2)\) ?

\[ \begin{align*}
\text{Mg} & \xrightarrow{+146 \text{kJ}} \text{Mg} (\text{metal}) \\
\text{Mg} (3s^2) & \xrightarrow{+264 \text{kJ}} \text{Mg} (3s^1 3p^1) \\
\text{The promotion energy (+264 kJ) is more than offset by the bonding energy (-410 kJ)}
\end{align*} \]

Cohesive energy of metals = bonding energy - promotion energy \((\Delta E_{\text{Evap}})\)

\[ \begin{array}{cccccccc}
\text{Cs} & \text{Ba} & \text{La} & \text{Hf} & \text{Ta} & \text{W} \\
\text{e}^-/\text{atom} & 1 & 2 & 3 & 4 & 5 & 6 \\
\Delta H_{fs} & 75 & 180 & 431 & 623 & 782 & 862 \text{ kJ/mol} \\
M_p & 29 & 704 & 920 & 2300 & 2997 & 3380 \text{ °C}
\end{array} \]

- the highest cohesive energy is in the middle of the periodic table, e.g., W \((6s^1 5d^5)\) \(\Rightarrow 6\) bonding e\(^-\)/atom
The situation is more complex for Re, Os, Ir, Pt

e.g. Pt 6s^2 5d^8 \rightarrow 6s^1 6p^2 5d^7 \rightarrow 6e^-/atom

\Delta H_f = 565 \text{ kJ/mol}, \text{ MP} = 1769^\circ C

less than W because of promotion energy

d-"acid/base" alloys:

\begin{align*}
\text{Hf} 6s^25d^2 &+ \text{Pt} 6s^15d^9 \\
\text{"acid"} &+ \text{"base"} \rightarrow \text{"salt"}
\end{align*}

\begin{align*}
2\text{R} + 3\text{Pt} &\rightarrow \text{ZrPt}_3 + \text{C} \\
\text{very stable carbide} &\text{more stable alloy}
\end{align*}

Some d-"acid/base" alloys are of special interest for catalysis. Eg, Sc-Pt alloys are good catalysts for oxygen reduction in fuel cells

\[ \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \xrightarrow{\text{cat}} 2\text{H}_2\text{O} \]

Even though Sc is an active metal, it is stabilized in the aqueous acid environment of the fuel cell by alloying with Pt. (Gready et al., Nature Chem. 1, 552 (2009))
Atomic Orbitals & Magnetism

Trends in atomic orbital sizes:

Sc Ti V Cr Fe → orbitals contract (increasing nuclear charge)
Y Zr Nb ↓ orbitals expand
La Hf Ta ↓ (increasing principal quantum number)

Lanthanide series (La → Lu) → contraction

Key trends:
- 3d orbitals are small (contracted)
- 4d, 5d are similar in size to each other.

4d, 5d elements in the same triad have very similar chemical properties.
E.g. Mn group

\[ \text{Mn} \quad \text{Tc} \quad \text{Re} \]

99 Tc is radioactive, so we work out the chemistry using Re as a surrogate (similar reactivity, redox behavior, etc). Mn is not a good model for Tc.

Orbital sizes

\[ \text{Cr} \quad \text{core} \quad 3s^2 \quad 3p^6 \quad 4s^1 \quad 3d^3 \]

\[ \text{W} \quad \text{core} \quad 5s^2 \quad 4d^6 \quad 6s^2 \quad 5d^3 \]

5s electrons feel increased nuclear charge more than d-electrons.

3d is contracted, not very effective in bonding.

Compare atomization energies:
- Cr 397 kJ/mol, MP = 1900°
- W 862 kJ/mol, MP = 3380°
**Bonding in the 5d vs. 3d metals**

**Heat of atomization at MP (kJ/mol)**

<table>
<thead>
<tr>
<th>Number of Valence Electrons</th>
<th>K</th>
<th>Ca</th>
<th>Ba</th>
<th>Sc</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc, Ti, V, Cr, Mn, Fe</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Co</td>
<td>Ni</td>
<td>Cu</td>
<td>Zn</td>
</tr>
<tr>
<td>Alt eup</td>
<td>378</td>
<td>470</td>
<td>515</td>
<td>397</td>
<td>283</td>
<td>415</td>
<td>426</td>
<td>431</td>
<td>338</td>
<td>131</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>bcc</td>
<td>hcp</td>
<td>bcc</td>
<td>bcc</td>
<td>bcc</td>
<td>bcc</td>
<td>hcp</td>
<td>fcc</td>
<td>fcc</td>
<td>hcp</td>
<td>hcp</td>
<td>hcp</td>
<td></td>
<td></td>
</tr>
<tr>
<td>binding</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>4-8</td>
<td>5</td>
<td>6</td>
<td>5</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>e⁻/atom</td>
<td>spd</td>
<td>spd²</td>
<td>sd⁴</td>
<td>sd⁵</td>
<td>spd⁵</td>
<td>sd⁷</td>
<td>spd⁷</td>
<td>spd⁸</td>
<td>spd⁹</td>
<td>spd¹⁰</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Past V, d-orbital contraction makes the 3d electrons much less effective in bonding.

At the same point, we see the onset of magnetic behavior. Spins unpair + exchange interaction causes ordering of spins.

Fe, Co, Ni = ferromagnetic metals
Recall MO picture for H\(_2\) atom:

Hund's rule says that spins do not need to pair at long distances.

"Narrow" band in infinite crystal.

\[ \Rightarrow \text{poor overlap of 3d-orbitals gives narrow d-bands} \]

\[ \Rightarrow \text{good } \quad 4s, 4p \quad \text{for wide } s,p \text{-bands} \]

\[ \begin{align*}
\text{Ti} & \quad 4s, 4p \\
\text{Fe, Co, Ni} & \quad \text{Ferromagnetic} \\
\text{Cu, Zn, Ge} & \quad \text{Pauli paramagnetic}
\end{align*} \]

Pauli paramagnetic

Most e\(^{-}\) paired

A few at EF are unpaired

Diamagnetic \(\Rightarrow\) All e\(^{-}\) spin paired (core + valence)

Substance is weakly repelled by inhomogeneous magnetic field \(\Rightarrow\) negative susceptibility

Paramagnetic \(\Rightarrow\) Valence e\(^{-}\) are unpaired (some or all)

Substance is attracted to region of higher field \(\Rightarrow\) positive susceptibility
Ferrimagnetic

Individual Fe atom in bcc iron is \( d^7 \)

\[ 4t + 4t + 4t \]

\( S = \) total spin angular momentum

\( = 3(\frac{1}{2}) = \frac{3}{2} \) (in units of \( \hbar \))

(Localized picture -

extreme case of narrow
d-band)

We can think of each Fe atom as a little bar magnet.

\( \uparrow S = \frac{3}{2} \) Neighbours can align \( \uparrow \) or \( \downarrow \) (or randomly)

How are these magnetic dipoles arranged in the crystal?

<table>
<thead>
<tr>
<th>Susceptibility</th>
<th>( \uparrow \uparrow \uparrow \uparrow \uparrow )</th>
<th>( \uparrow \uparrow \uparrow \uparrow \uparrow )</th>
<th>( \uparrow \uparrow \uparrow \uparrow \uparrow )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \chi &gt; 0 )</td>
<td>ferromagnet (Fe, CrO, ...)</td>
<td>antiferromagnet (MnO, Mn_3O_4, ...)</td>
<td>ferrimagnet (Fe_3O_4)</td>
</tr>
<tr>
<td></td>
<td>micron-size domains have all spins aligned (spontaneous magnetization)</td>
<td>zero net magnetic moment at ( 0 ) K</td>
<td>same as ferro ( Fe^{2+} + Fe^{3+} ) moments do not cancel</td>
</tr>
<tr>
<td>( \chi &lt; 0 )</td>
<td>( \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \chi &gt; 0 )</td>
<td>( \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \downarrow )</td>
<td>paramagnetic</td>
<td></td>
</tr>
<tr>
<td>(random)</td>
<td>(any of the above at high ( T ))</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

paramagnetic
We see these kinds of magnetic ordering primarily among the 3d and 4f elements (and their compounds).

Sm, Nd alloys with Co, Fe, Ni make powerful magnets,

e.g. $\text{Nd}_2\text{Fe}_{14}\text{B}$ : permanent magnets, used in motors, hard disk drives, fasteners, ferrofluids

$\text{SmCo}_5$, $\text{YCo}_5$ : strong permanent magnets, high magnetic anisotropy

**Magnetization and Susceptibility**

Definitions:

- $H$ = applied magnetic field (units: Henry (H))

- $B$ = induced magnetic field in a material (units = Tesla (T))

- $M$ = magnetization : represents the magnetic moments within a material in the presence of an external field $H$

Magnetic susceptibility $\chi = \frac{M}{H}$

Usually $\chi$ is given in molar units in the CGS system

$\chi_m$ = molar susceptibility (units: $\text{cm}^3/\text{mol}$)

Typical values:

- $-3 \times 10^{-4}$ $\text{SiO}_2$ (diamagnet)
- $+2 \times 10^{-4}$ $\text{Pt}$ (paramagnetic)
- $+5 \times 10^{-2}$ $\text{Gd}_2(\text{Si}_2)\text{O}_3\cdot8\text{H}_2\text{O}$ (paramagnet)
- $+10^{-6}$ to $10^{-12}$ $\text{Nd-Fe}$ alloy (ferromagnet below $T_C$)
To correlate $X$ with the number of unpaired electrons in a compound, we typically correct for the diamagnetic core electrons:

$$X_{\text{corr}} = X_{\text{obs}} - X_{\text{diamagnetic cores}}$$

For a paramagnet,

$$X_M = \frac{N_A \mu^2}{3k_B t} = \frac{C}{t} \quad (C = \text{Curie constant} = \frac{N_A \mu^2}{3k_B})$$

In CGS units, $\frac{N_A \mu^2}{3k_B} = 0.125$, so $X_M = \frac{0.125}{t} \left( \frac{\mu}{\mu_B} \right)^2$

Here $\mu_B = \text{Bohr magneton} = \frac{e \hbar}{2m_e} = 9.274 \times 10^{-24} \text{erg/ gauss}$ (in CGS units)

$\mu = \text{magnetic moment of the atom}$

$$\mu = 2 \sqrt{S(S+1)} \mu_B$$

Since $S = \frac{n}{2}$, where $n$ = number of unpaired electrons

$$\mu = \sqrt{n(n+2)} \mu_B$$

e.g. for a Fe atom with 3 unpaired $e^-$, $\mu = \sqrt{(3)(5)} \mu_B = 3.87 \mu_B$

and $X_M = \frac{0.125}{1} (3.87)^2 \approx 6 \times 10^{-3} \text{ cm}^3/\text{mol at 300 K}$
Curie constant $C \Rightarrow \mu^2 \Rightarrow \#\text{unpaired } e^-/\text{atom}$

When spins order cooperatively, the $\chi$ vs $T$ behavior is more complex:

$T_c = \text{Curie temperature}$ \hspace{1cm} $\Theta > 0$ for antiferromagnet
$T_n = \text{Néel temperature}$ \hspace{1cm} $\Theta < 0$ for ferro, ferrimagnet

At high temp ($T \geq 3T_c$ or $3T_n$), both systems follow the Curie-Weiss law

$$\chi = \frac{C}{1+\Theta}$$
Ferromagnetic domain structure

Below $T_c$:

- **Micron-size domains** in a ferromagnet point in random dimensions so that their magnetic dipoles cancel. Individual domains have aligned spins.
- Domain walls are not sharp.
- Coercive field ($H_c$) is needed to bring $B$ to zero.
- Remanent magnetization at zero applied field ($B_r$).
- Saturation magnetization ($B_{sat}$).

Hysteresis loop

$m/T$ vs. $T$

- antiferromagnets (Co, MnO...)
- ferro, ferrimagnets (Fe, Fe$_3$O$_4$)
Hard magnet

\[ B \]
\[ \frac{\text{large } B_r}{H} \]
\[ \text{large } H_c \]

Useful for permanent magnets, e.g. \( \text{Nd}_2\text{Fe}_{14}\text{B} \)

Soft magnet

\[ B \]
\[ \frac{\text{small } B_r}{H} \]
\[ \text{small } H_c \]

Useful for transformer cores, e.g. permalloy Fe-Ni

\[ \text{Fe can make hard or soft magnets, depending on } \]
\[ \text{crystal grain size. Small grains pin magnetic domains } \Rightarrow \text{hard. } \]
\[ \text{Annealed Fe } \Rightarrow \text{large grains, soft magnet (easy to move domain walls). } \]