LECTURE SCHEDULE

Mon (Ke3) 12.15 – 14.00
Wed (Ke2) 10.15 – 12.00
Fri (Ke5) 10.15 – 12.00

		Date	Topic
1.	Wed	06.09.	Course Introduction & Short Review on Elements & Periodic Table
2.	Fri	08.09.	Short Survey of Main Group Elements
3.	Mon	11.09.	Zn + Ti, Zr, Hf & Atomic Layer Deposition (ALD)
4.	Wed	13.09.	Transition Metals: General Aspects & Pigments
5.	Fri	15.09.	Redox Chemistry
6.	Mon	18.09.	Crystal Field Theory (Linda Sederholm)
7.	Wed	20.09.	V, Nb, Ta & Perovskites & Metal Complexes & MOFs & MLD
8.	Mon	25.09.	Cr, Mo, W & 2D materials & Mxenes & Layer-Engineering
9.	Wed	27.09.	Mn, Fe, Co, Ni, (Cu) & Magnetism
10.	Fri	29.09.	Cu & Superconductivity
11.	Mon	02.10.	Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)
12.	Wed	04.10.	Lanthanoids + Actinoids & Luminescence
13.	Fri	06.10.	Resources of Elements & Rare/Critical Elements & Element Substitutions
14.	Fri	13.10.	Inorganic Materials Chemistry Research

EXAM: Tuesday Oct. 17, 9:00-12:00 in Ke2

PRESENTATION TOPICS/SCHEDULE

Mon	25.09.	Mo:	Maryam Jafarishiad & Saara Siekkinen
Wed	27.09.	Mn:	Naomi Lyle & Sanni Ilmaranta
		Ru:	Miklos Nemeszeghy & Timo de Jonge
Fri	29.09.	Cu:	Koshila Hiruni & Kaushalya Poonanoo
Wed	04.10.	Eu:	Binglu Wang & Mari
		Nd:	Patrich Wiesenfeldt & Tomoki Nakayama
		U:	Miikka Viirto & Ashish Singh
Fri	06.10.	Co:	Gabrielle Laurent & Yan Zheng
		In:	Sonja Alasaukko-oja & Katri Haapalinna
		Te:	Sofia Rantala & Roger Peltonen

QUESTIONS: Lecture 9

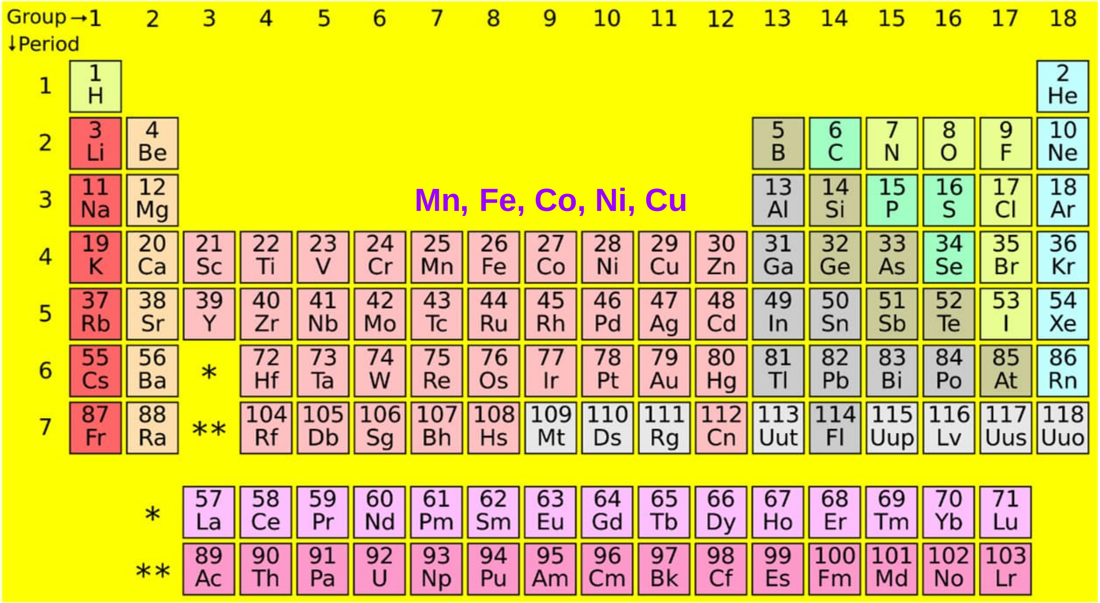
1. How many unpaired 3d electrons in metals: Mn, Fe, Co, Ni, Cu ?

2. Propose a (simple-minded) reason why Mn is not ferromagnetic.

3. Propose a (simple-minded) reason why Cu is not ferromagnetic.

4. How many unpaired 3d electrons (oct./hs): Fe^{2+}, Fe^{3+} ?

5. Which one(s) of the iron oxides, FeO, Fe_3O_4 and Fe_2O_3, is/are:
   - mixed valent
   - antiferromagnetic
   - ferrimagnetic
   - electrically conducting

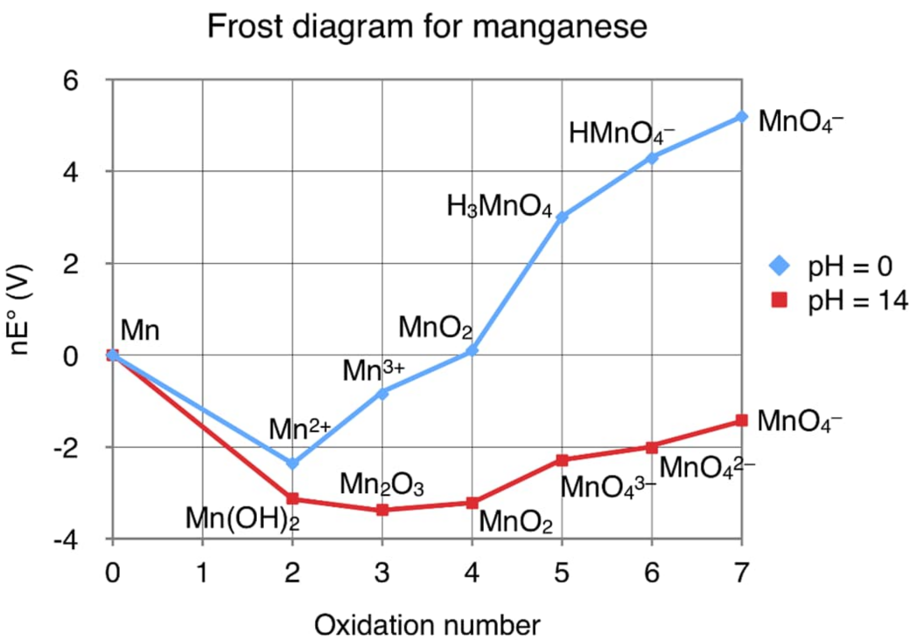


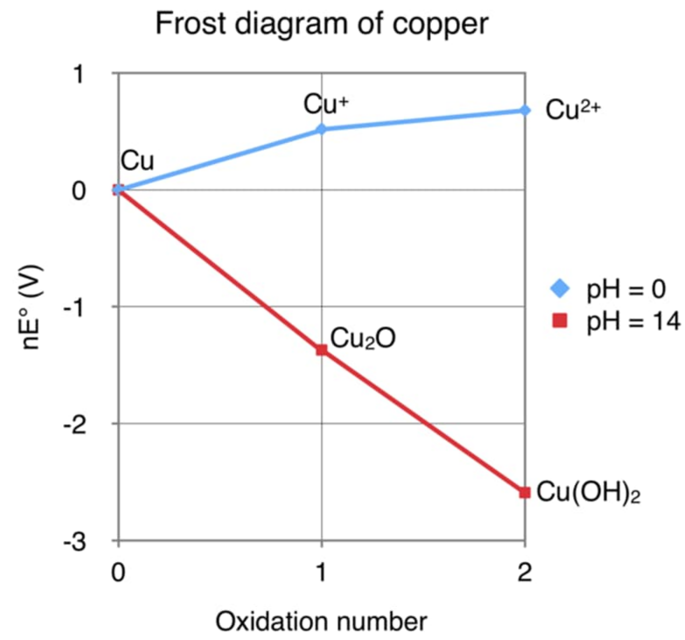
Melt. points (°C)

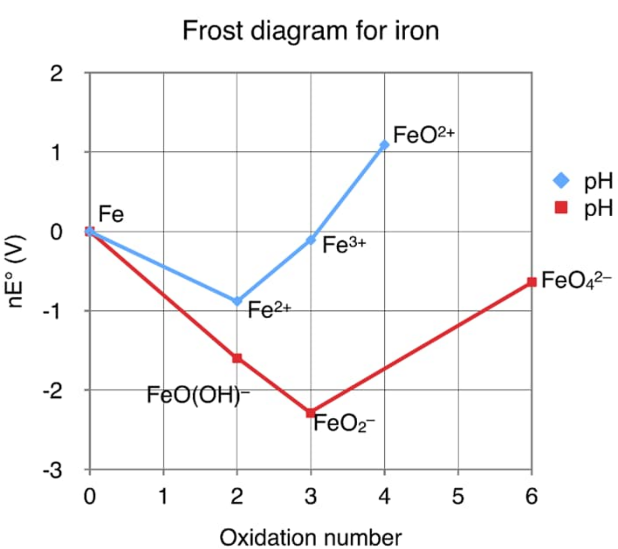
Ti	**1668**
V	**1890**
Cr	**1860**
Mn	**1245**
Fe	**1535**
Co	**1492**
Ni	**1452**
Cu	**1083**

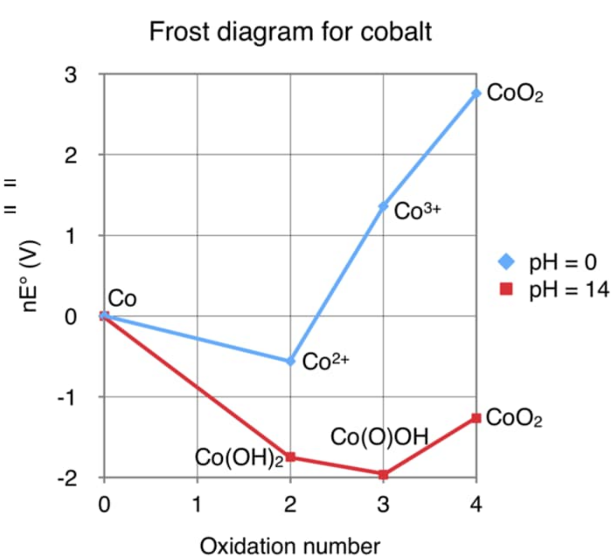
Element	**Symbol**	**Electronic Configuration**
Scandium	Sc	$[Ar]3d^1 4s^2$
Titanium	Ti	$[Ar]3d^2 4s^2$
Vanadium	V	$[Ar]3d^3 4s^2$
Chromium	Cr	$[Ar]3d^5 4s^1$
Manganese	Mn	$[Ar]3d^5 4s^2$
Iron	Fe	$[Ar]3d^6 4s^2$
Cobalt	Co	$[Ar]3d^7 4s^2$
Nickel	Ni	$[Ar]3d^8 4s^2$
Copper	Cu	$[Ar]3d^{10} 4s^1$
Zinc	Zn	$[Ar]3d^{10} 4s^2$

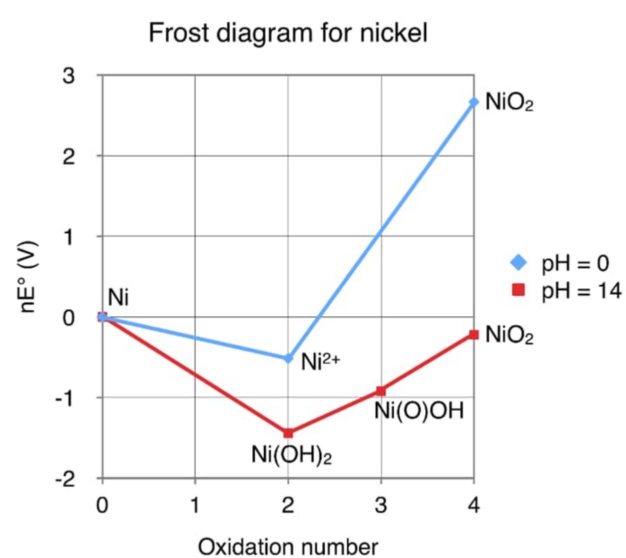
Element							
Sc			+3				
Ti		+2	+3	+4			
V		+2	+3	+4	+5		
Cr		+2	+3	+4	+5	+6	
Mn		+2	+3	+4	+5	+6	+7
Fe		+2	+3	+4	+5	+6	
Co		+2	+3	+4	+5		
Ni		+2	+3	+4			
Cu	+1	+2	+3				
Zn		+2					


Frost diagram for manganese
nE° (V)
Oxidation number
pH = 0
pH = 14
Mn
Mn2+
Mn3+
MnO2
H3MnO4
HMnO4−
MnO4−
Mn(OH)2
Mn2O3
MnO2
MnO43−
MnO42−
MnO4−


Frost diagram of copper
nE° (V)
Oxidation number
pH = 0
pH = 14
Cu
Cu+
Cu2+
Cu2O
Cu(OH)2


Frost diagram for iron
nE° (V)
Oxidation number
pH =
pH =
Fe
Fe2+
Fe3+
FeO2+
FeO(OH)−
FeO2−
FeO42−


Frost diagram for cobalt
nE° (V)
Oxidation number
pH = 0
pH = 14
Co
Co2+
Co3+
CoO2
Co(OH)2
Co(O)OH
CoO2


Frost diagram for nickel
nE° (V)
Oxidation number
pH = 0
pH = 14
Ni
Ni2+
NiO2
Ni(OH)2
Ni(O)OH
NiO2

Fe, Co, Ni & Platinum Metals (Ru, Os, Rh, Ir, Pd, Pt)

- **Horizontal relationships:**

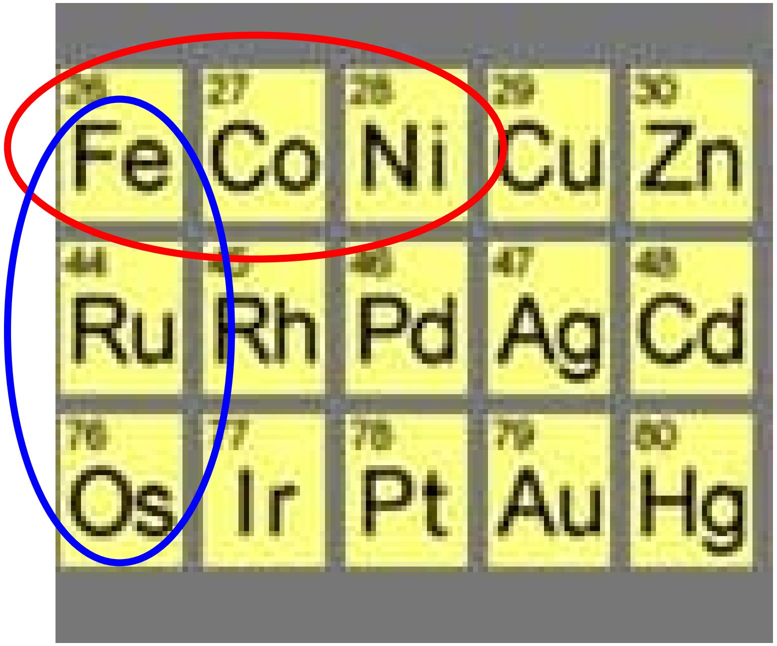
  (1) Fe, Co, Ni, (2) light Pt metals, (3) heavy Pt metals

- **Vertical relationships:**

  (1) Fe, Ru, Os, (2) Co, Rh, Ir, (3) Ni, Pd, Pt

- **Electronegativities: Fe 1.8, Co 1.9, Ni 1.9, all Pt metals 2.2**

- **Oxides:**
  - **+II: (Fe,Co,Ni,Pd)O**
  - **+II/III: $(Fe,Co)_3O_4$**
  - **+III: $(Fe,Co,Rh,Ir)_2O_3$**
  - **+IV: $(Ru,Os,Rh,Ir,Pd,Pt)O_2$**
  - **+VIII: $(Ru,Os)O_4$**



IRON COMPOUNDS

- Iron compounds mainly at the oxidation states +II and +III
- Fe(II) compounds tend to be oxidized to Fe(III) compounds in air
- **Ferrous Fe(II)** compounds & **Ferric Fe(III)** compounds
- **Ferrite** (magnetic spinel Fe(II/III) oxides) &
  Ferrate (highest oxidation state $[FeO_4]^{4-}$, $[FeO_4]^{3-}$ & $[FeO_4]^{2-}$) **!!!**
  (c.f. sulphite-sulphate, **manganite-manganate**, **supercond. cuprates**)
- Most common oxides: FeO
  Fe_2O_3 (hematite) antiferromagnetic
  Fe_3O_4 ferrimagnetic & electrically conducting,
  mixed-valence Fe(II)/Fe(III)
- In rare compounds Fe occurs also at higher oxidation states, e.g. K_2FeO_4
- **Fe(IV) is common intermediate in biochemical oxidation reactions**
- ^{57}Fe Mössbauer spectroscopy is a powerful tool to investigate oxidation states and other bonding properties of Fe in its compounds
- Main **industrial-scale** products/intermediates: $FeSO_4 \cdot 7H_2O$ and $FeCl_3$

OCTAHEDRAL COORDINATION

- Common for Mn, Fe, Co, Ni, Cu

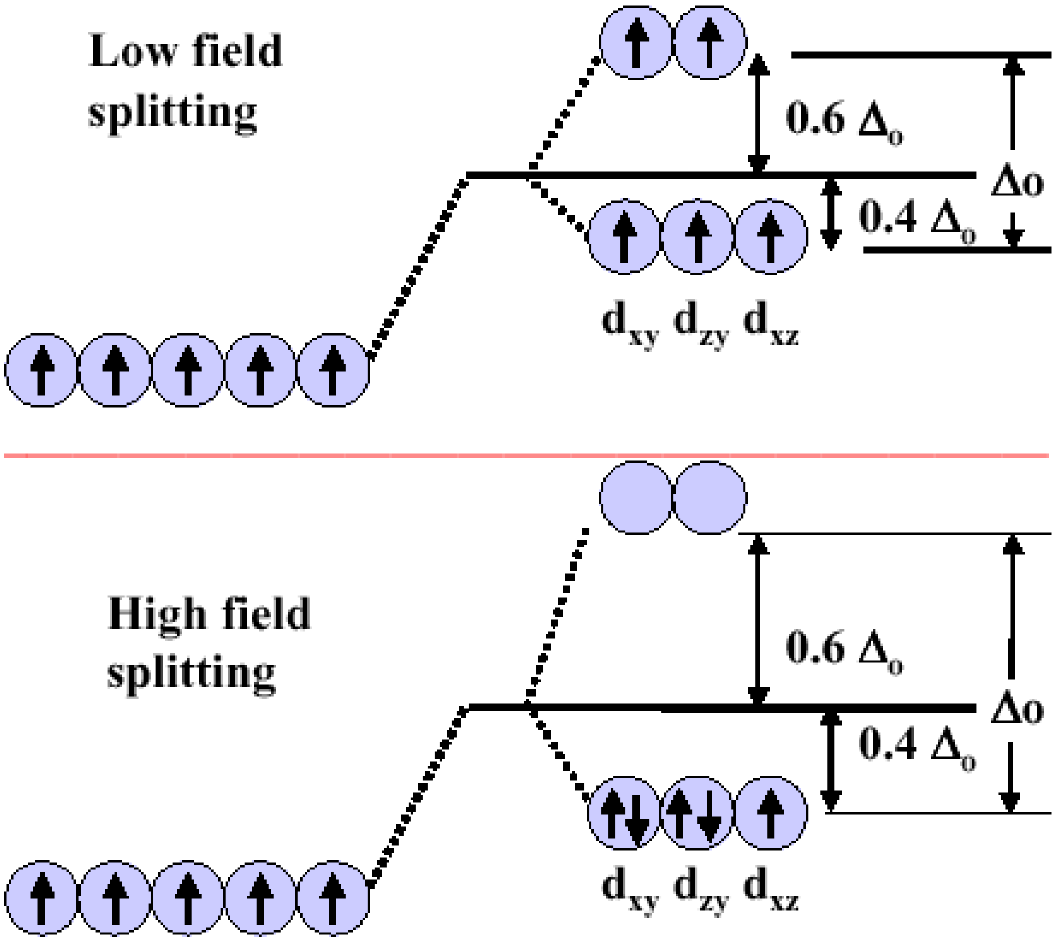
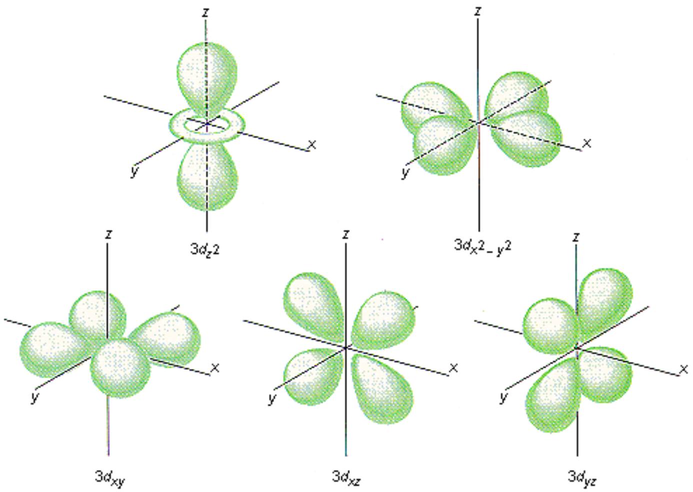
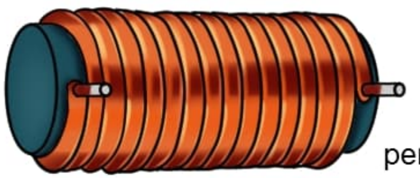


Figure 5. The two cases of crystal field splitting for the octahedral geometry.



MAGNETISM in BRIEF



- **Magnet: solid that creates a magnetic field**

  (1) Electromagnet: electric current (through a coil)

  (2) Permanent magnet: unpaired electrons

PERMANENT MAGNETS

- **Each electron is a small magnet due to its spin**
- **In most materials, the countless electrons have randomly oriented spins, leaving no magnetic effect on average**
- **In some rare magnetic materials, many of the electron spins are aligned in the same direction, such that they create a net magnetic field**
- **There is also an additional (minor) magnetic field that results from the electron's orbital motion (cf. electromagnets)**
- **Magnetic properties of solids depend on:**

  - electron configuration

  - crystal structure

APPLICATIONS of ELECTROMAGNETS

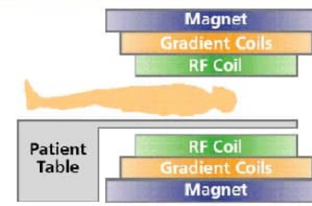
Superconducting Magnets

- Solenoid as in conventional electromagnet.
- But once current is injected, power supply turned off, current and magnetic field stays forever...

...as long as $T < T_c$

Magnets for MRI

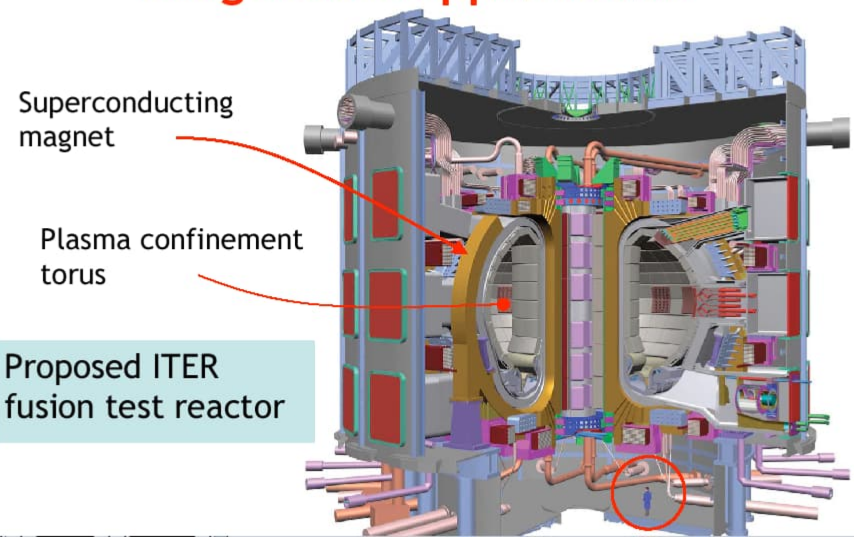
- Magnetic Resonance Imaging typically done at 1.5 T
- Superconducting magnet to provides static magnetic field
- Spatial resolution of positions of tracer atomic nuclei.



900 MHz NMR (UW Chemistry)

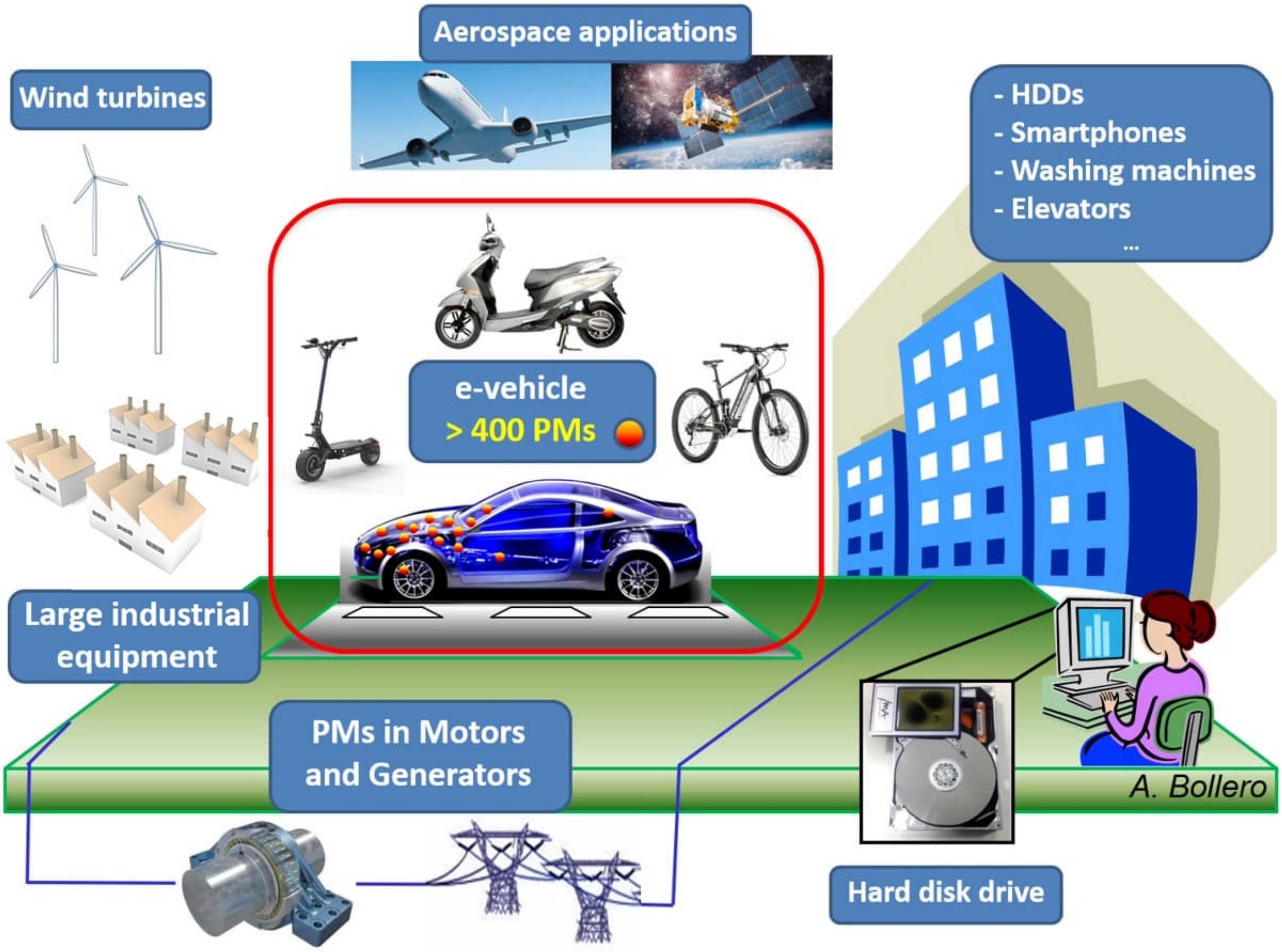
21.7 T field

Large scale applications



Proposed ITER fusion test reactor

APPLICATIONS of PERMANENT MAGNETS

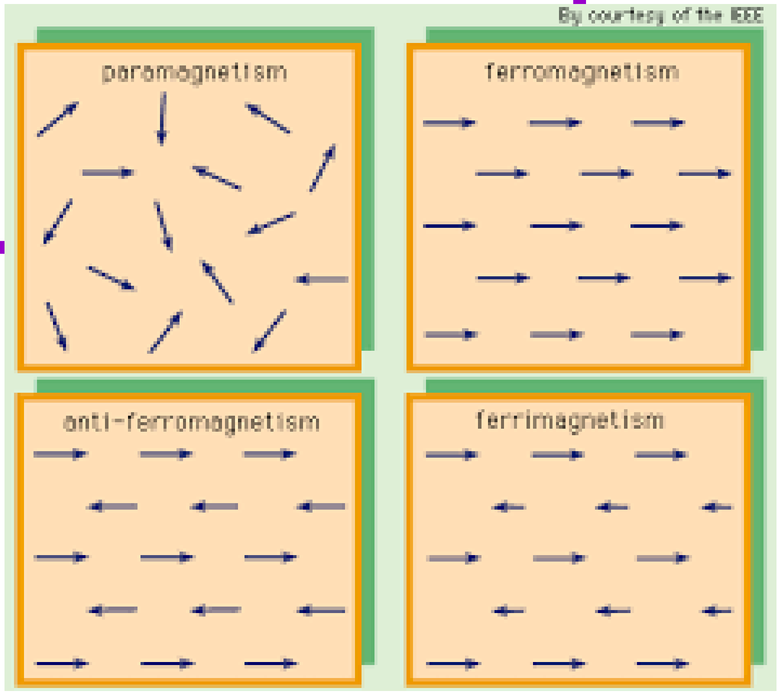


MAGNETIC SUSCEPTIBILITY

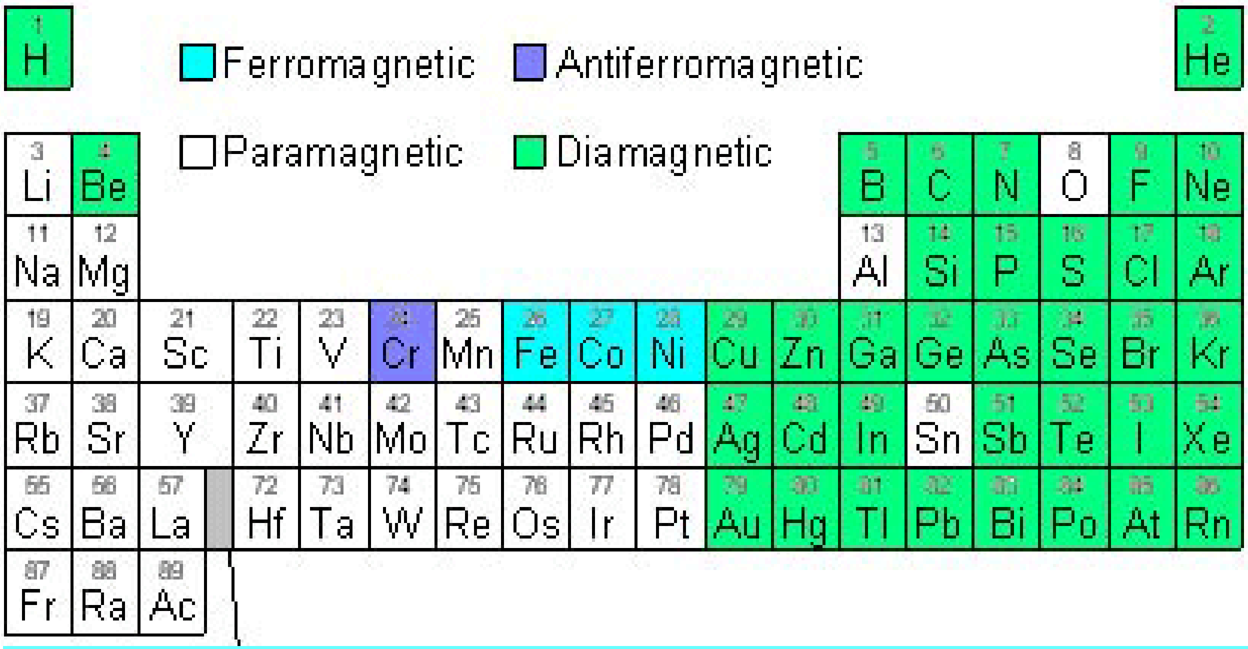
Magnetization (M):
magnetic field induced in sample in external magnetic field (H)

Magnetic susceptibility: $\chi = M / H$

DIAMAGNET: $\chi < 0$ **(very small)**
PARAMAGNET: $\chi > 0$ **(very small)**
FERROMAGNET: $\chi > 0$ **(very large)**
ANTIFERROMAGNET: $\chi > 0$ **(small)**
FERRIMAGNET: $\chi > 0$ **(large)**



RoomTemperature MAGNETISM OF PURE ELEMENTS



Ferromagnetism in metals

- Only Fe, Co and Ni are ferromagnetic at/above RT
- **Unpaired electrons & "Exchange interaction"** condition fulfilled
- Depends on crystal structure, e.g. atomic distances:

  - normal Fe FM, but austenite-type Fe not (too long Fe-Fe distance)

  - pure Mn not FM (too short Mn-Mn distance), but some Mn alloys are (longer Mn-Mn distance)

Curie temperatures (in K)

Co	1388
Sm_2Co_{17}	1070
Fe	1043
$SmCo_5$	990
Fe_3O_4	858
$NiFe_2O_4$	858
$CuFe_2O_4$	728
$MgFe_2O_4$	713
MnBi	630
Ni	627
MnSb	587
$Nd_2Fe_{14}B$	580
$MnFe_2O_4$	573
$Y_3Fe_5O_{12}$	560
CrO_2	386
MnAs	318
Gd	292
Dy	88
Er	32
EuO	69

Hystersis Loop of Ferromagnetic Materials

- Coersivity field & Remanent magnetization
- Hard FM: wide loop
- Soft FM: narrow loop