TENTATIVE LECTURE SCHEDULE

		Date	Topic
1.	Mon	13.09.	Course Introduction & Short Review of the Elements
2.	Wed	15.09.	Periodic Properties & Periodic Table & Main Group Elements (starts)
3.	Fri	17.09.	Short Survey of the Chemistry of Main Group Elements (continues)
4.	Mon	20.09.	Zn + Ti, Zr, Hf & Atomic Layer Deposition (ALD)
5.	Wed	22.09.	Transition Metals: General Aspects & Pigments
6.	Mon	27.09.	Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)
7.	Wed	29.09.	Redox Chemistry
8.	Mon	04.10.	Crystal Field Theory
9.	Wed	06.10.	V, Nb, Ta & Metal Complex & POM, MOF, MLD
10.	Fri	08.10.	Cr, Mo, W & 2D materials
11.	Mon	11.10.	Mn, Fe, Ni, Pt metals & Magnetism
12.	Wed	13.10.	Co, Cu & Superconductivity
13.	Fri	15.10.	Resources of Elements & Rare/Critical Elements & Element Substitutions
14.	Mon	18.10.	Lanthanoids + Actinoids & Luminescence (Down/Upconversion)
15.	Wed	20.10.	Inorganic Materials Chemistry Research

EXAM: Thu Oct. 28, 2021 (in ZOOM)

PRESENTATION TOPICS/SCHEDULE

Wed	06.10.	Nb:	Toivonen
Fri	08.10.	Mo:	Ahmed, Shamshad
Mon	11.10.	Mn:	Majaniemi, Thakur, Ahkiola
		Ru:	Ichanson, Locqueville, Olsio
Wed	13.10.	Co:	Ekholm, Olander, Syväniemi
		Cu:	Kolawole, Nguyen, Munib
Fri	15.10.	In:	Kovanen, Ogunyemi, Svinhufvud
		Te:	Huhtakangas, Wallin, Kaarne
Mon	18.10.	Eu:	Sonphasit, Tuisku
		Nd:	Jussila, Siuro, Perttu
		U:	Sinkkonen, Wennberg, Partanen

QUESTIONS: Lecture 11

1. Most stable oxidation state(s) for: Mn, Fe, Co, Ni, Cu ?

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

3. Propose a reason why Mn is not ferromagnetic.

4. Propose a reason why Cu is not ferromagnetic.

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

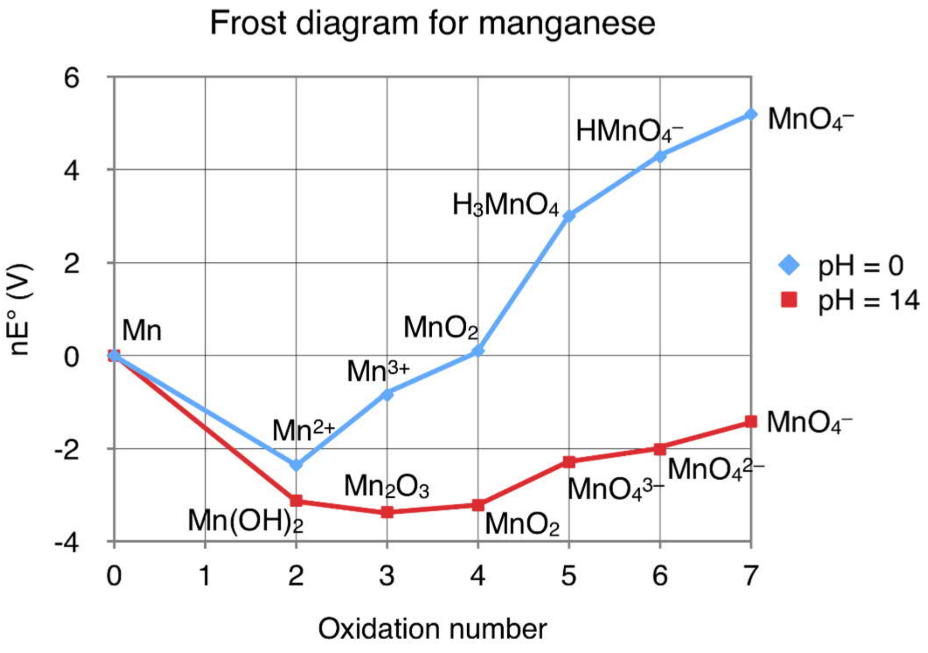
6. Which one of the iron oxides, FeO, Fe_3O_4 and Fe_2O_3, is:
   - mixed valent
   - antiferromagnetic
   - ferrimagnetic
   - electrically conducting

Group → / ↓Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo
		*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
		**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

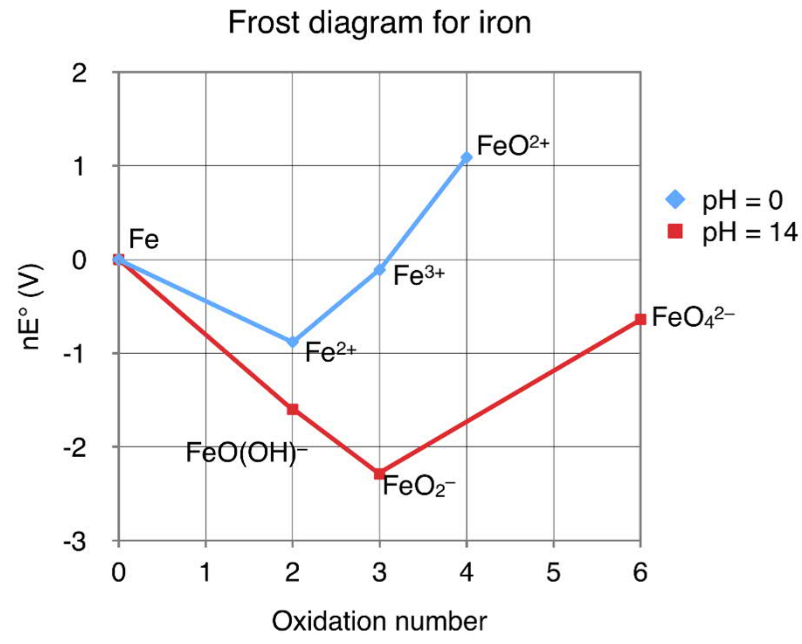
Element	Symbol	Electronic Configuration
Scandium	Sc	$[Ar]3d^1 4s^2$
Titanium	Ti	$[Ar]3d^2 4s^2$
Vanadium	V	$[Ar]3d^3 4s^2$
Chromium	Cr	$[Ar]3d^5 4s^1$
Manganese	Mn	$[Ar]3d^5 4s^2$
Iron	Fe	$[Ar]3d^6 4s^2$
Cobalt	Co	$[Ar]3d^7 4s^2$
Nickel	Ni	$[Ar]3d^8 4s^2$
Copper	Cu	$[Ar]3d^{10} 4s^1$
Zinc	Zn	$[Ar]3d^{10}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

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**					

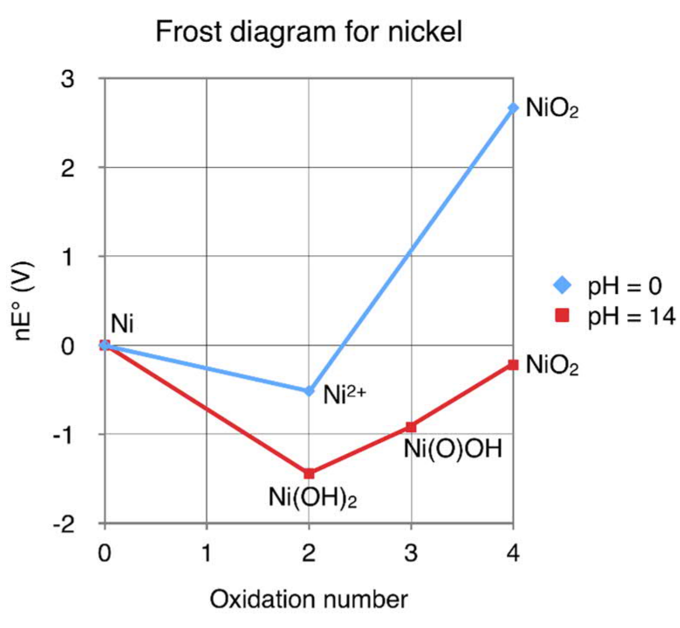
Mn, Fe, Co, Ni, Cu



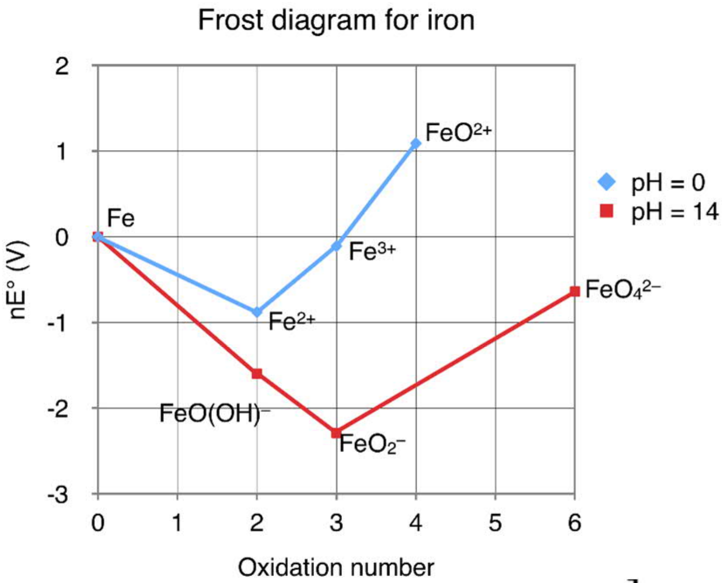
Frost diagram for manganese
nE° (V)
Oxidation number
pH = 0
pH = 14
Mn
Mn²⁺
Mn³⁺
MnO₂
H₃MnO₄
HMnO₄⁻
MnO₄⁻
Mn(OH)₂
Mn₂O₃
MnO₂
MnO₄³⁻
MnO₄²⁻
MnO₄⁻



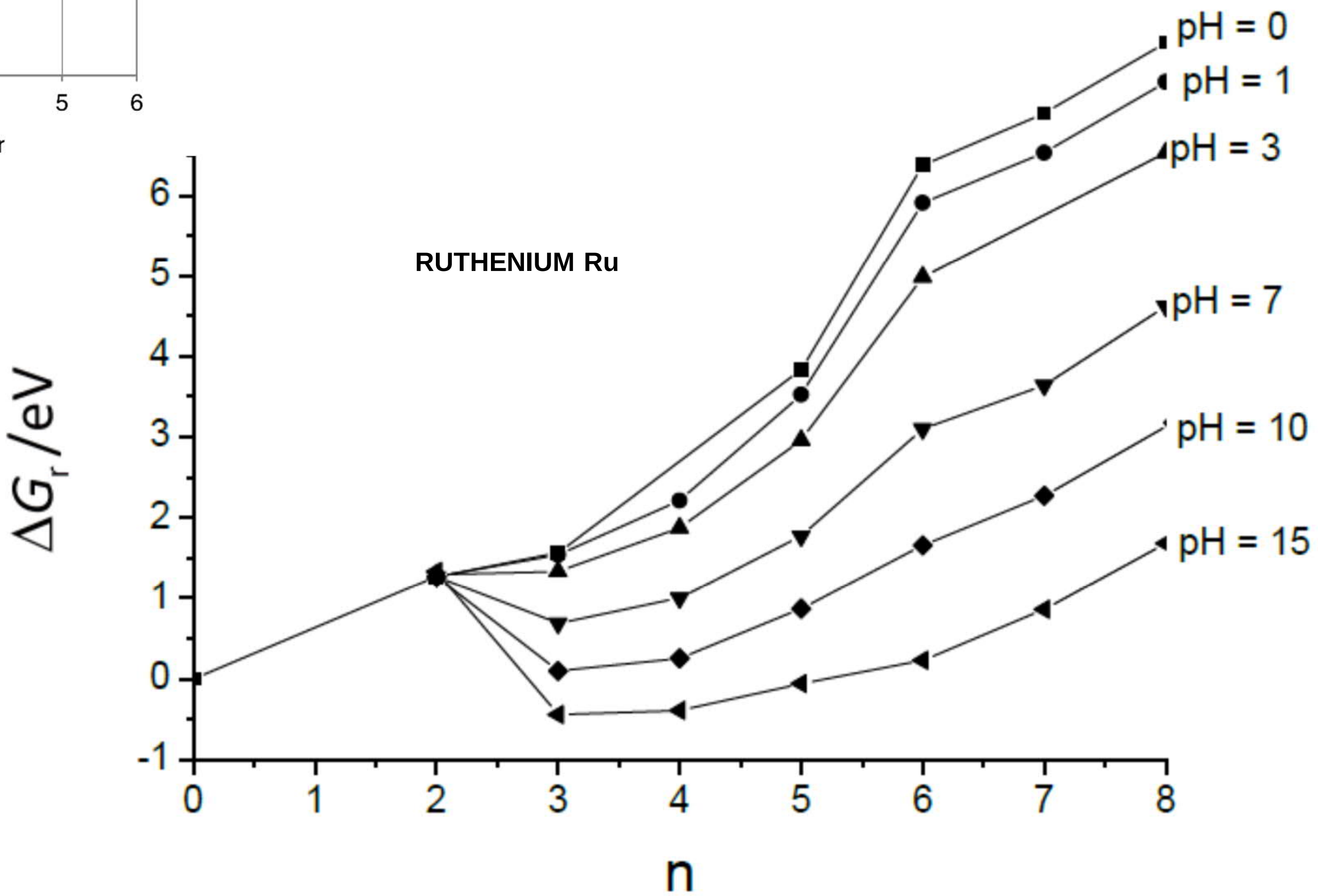
Frost diagram for iron
nE° (V)
Oxidation number
pH = 0
pH = 14
Fe
Fe²⁺
Fe³⁺
FeO²⁺
FeO(OH)⁻
FeO₂⁻
FeO₄²⁻



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



Frost diagram for iron
nE° (V)
Oxidation number
Fe
Fe2+
Fe3+
FeO2+
FeO(OH)−
FeO2−
FeO42−
pH = 0
pH = 14



RUTHENIUM Ru
ΔGr /eV
n
pH = 0
pH = 1
pH = 3
pH = 7
pH = 10
pH = 15

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

- **Horizontal relationships:**

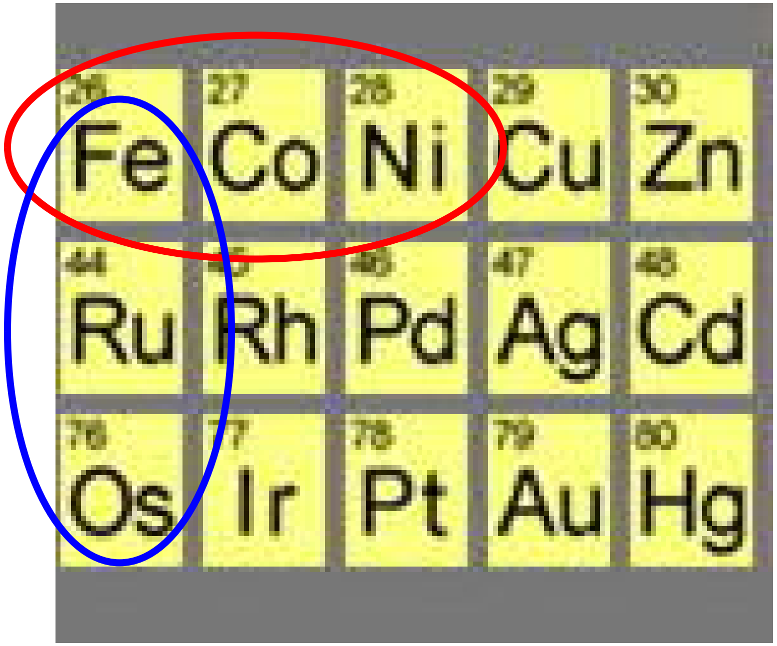
  (1) Fe, Co, Ni, (2) light Pt metals, (3) heavy Pt metals

- **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: $(Ru,Os)O_4$**



OCTAHEDRAL COORDINATION

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

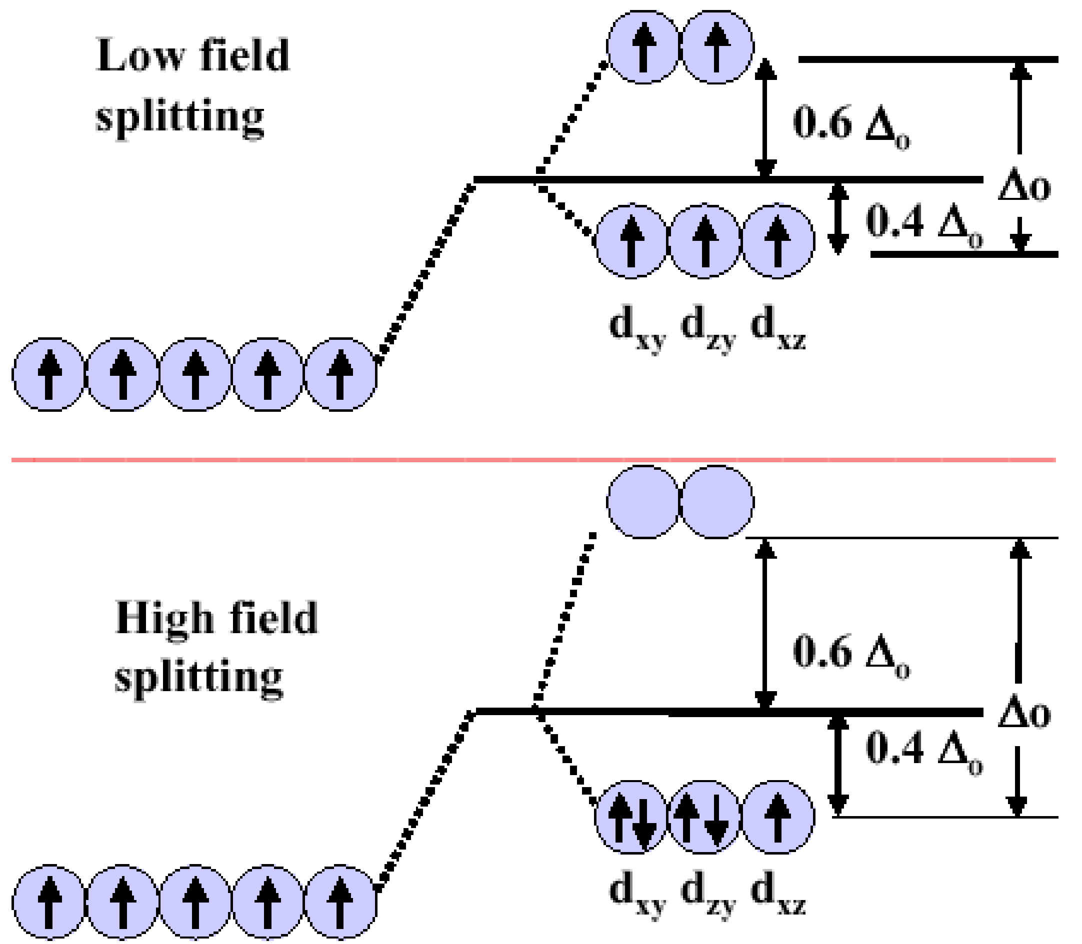
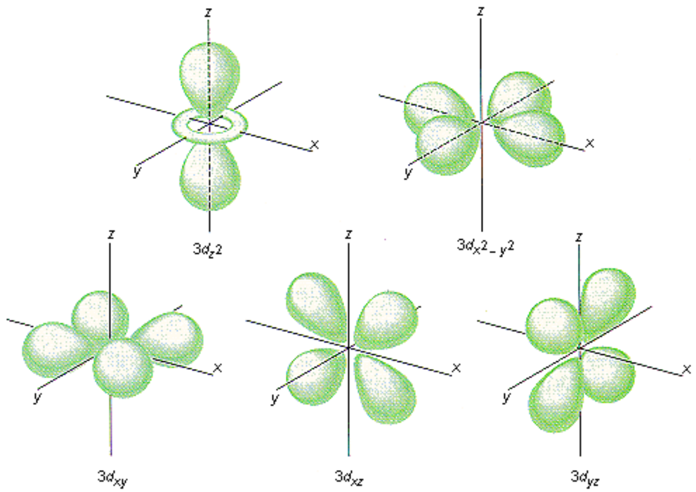
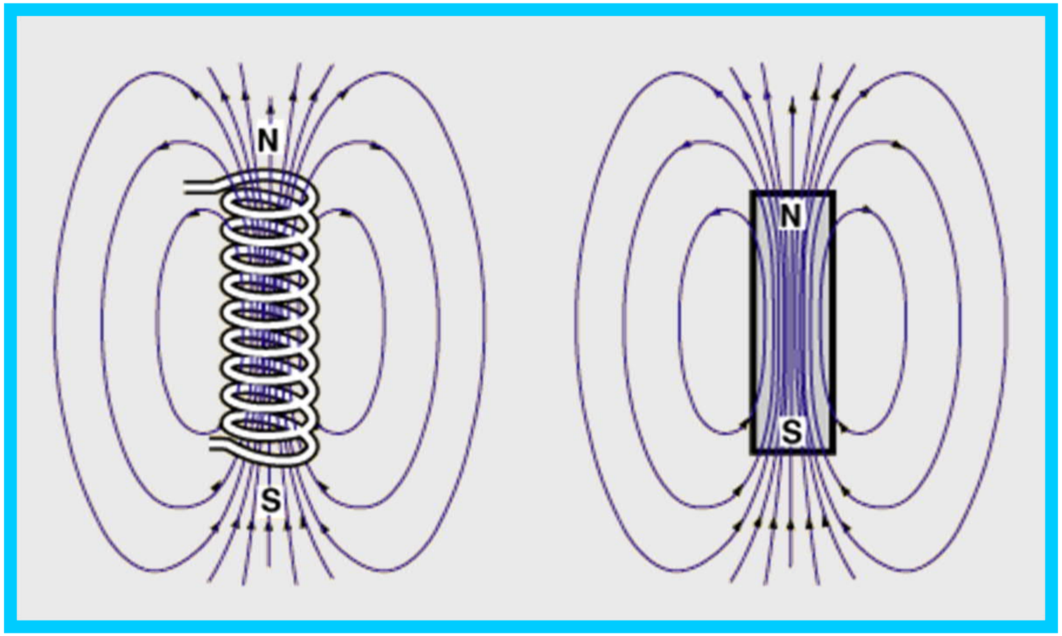


Figure 5. The two cases of crystal field splitting for the octahedral geometry.



IRON COMPOUNDS

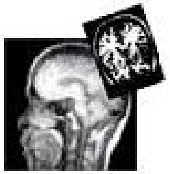
- Iron compounds mainly at the oxidation states +II and +III
- Fe(II) compounds tend to be oxidized to Fe(III) compounds in air
- **Ferrous Fe(II)** compounds & **Ferric Fe(III)** compounds
- **Ferrite** (magnetic spinel Fe(II/III) oxides) &
  Ferrate (highest oxidation state $[FeO_4]^{4-}$, $[FeO_4]^{3-}$ & $[FeO_4]^{2-}$) **!!!**
  (c.f. sulphite-sulphate, **manganite-manganate**, **cuprates !!!**)
- Many important **mixed-valence Fe(II)/Fe(III) compounds**, such as magnetite Fe_3O_4
- 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 $FeCl_3$

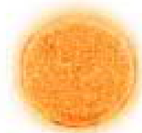
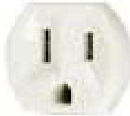
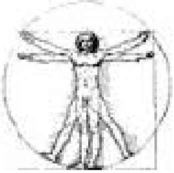


MAGNET

- **Magnet: solid/bar/coil that creates a magnetic field**
- **Electromagnet: electric current**
- **Permanent magnet: unpaired electrons**
- **Magnets have two poles: *S* (*south*) and *N* (*north*)**
- **Same-type poles repel each other and opposite-type poles attract each other**

Magnetic Field Ranges

Field Size		Example
850T		the strongest Destructive Pulsed magnet
60T		60 T long Pulse magnet
33T		33T continuous field magnet
2T		MRI machine
4×10^{-1}T		Stereo Speaker Magnets

Field Size		Example
4×10^{-1}T		lodestone Mineral magnetite
3×10^{-1}T		Household refrigerator magnet
10^{-2} T		Surface of Sun
10^{-4} T		Near Household Wiring
3×10^{-5} T		Surface of Earth
3×10^{-10}T		Produced by Human Body

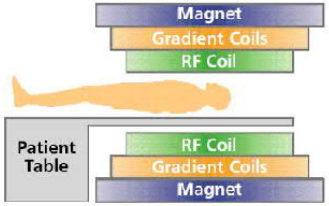
Superconducting Magnets

- 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

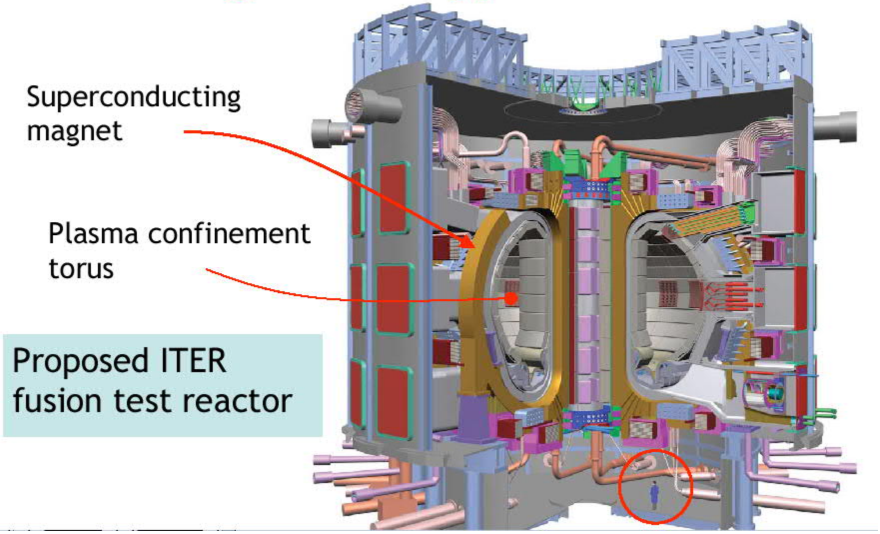
- Magnetic Resonance Imaging typically done at 1.5 T
- Superconducting magnet to provides static magnetic field
- Spatial resolution of positions of tracer atomic nuclei.



900 MHz NMR (UW Chemistry)

21.7 T field

Large scale applications



MAGNETIC SUSCEPTIBILITY

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

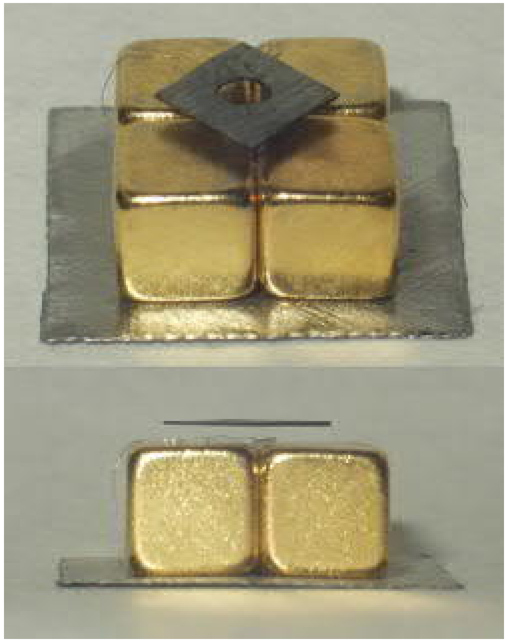
Magnetic susceptibility: $\chi = M / H$

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

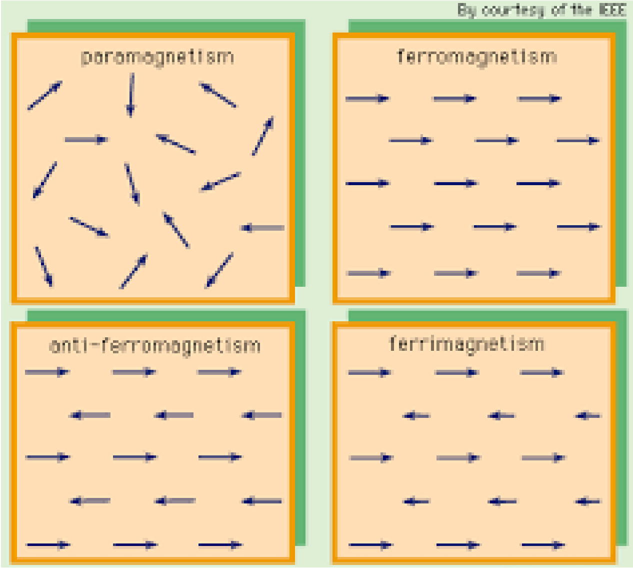
DIAMAGNETISM ("NON-MAGNETISM")

- **All materials are diamagnetic**
- **Due to the movement of all electrons in atoms**
- **Diamagnetic material repels external field ($\chi < 0$)**
- **Diamagnetism is of several orders of magnitude weaker phenomenon compared to other phenomena of magnetism**

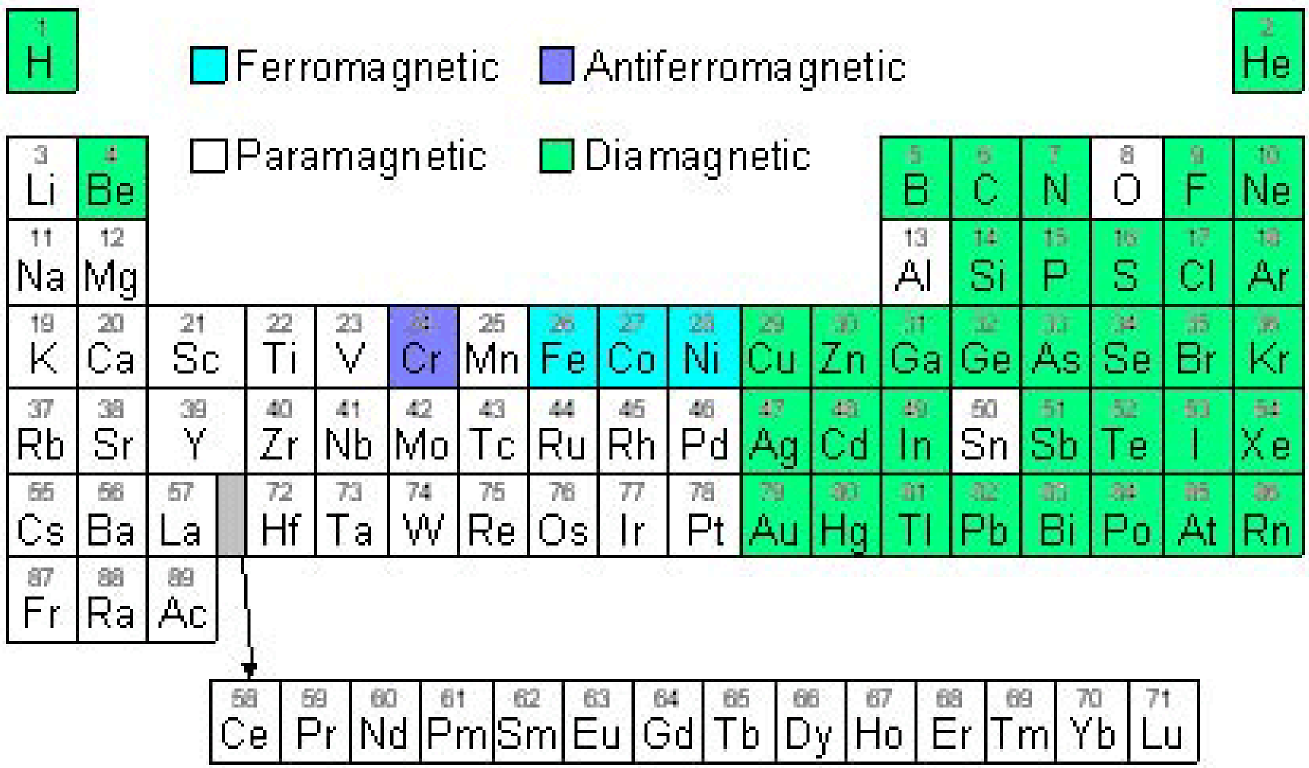
  (material is said to be diamagnetic only if it does not show other forms of magnetism)
- **e.g. water: $\chi = -9.05\times10^{-6}$**
- **So-called pyrolytic carbon is a particularly strong diamagnet (χ up to -400×10^{-6})**
- **Superconductors are perfect diamagnets and repel perfectly external magnetic field (Meissner) in their superconducting state: $\chi = -1$**



Pyrolitic carbon bar levitates above permanent magnet



RT MAGNETISM OF PURE ELEMENTS



Ferromagnetism (in pure metals)

- Unpaired electrons needed (but this is not the only requirement)
- There are other factors as well: exchange interaction
- Fine balance between the different factors/interactions define whether the metal/material is FM, AFM, or paramagnetic
- Crystal structure/atomic distances affect:
  - normal metallic iron FM, but austenite-type iron not
  - pure Mn metal not FM (Mn-Mn distance too short), but some Mn alloys are FM (Mn-Mn distance longer)

Ferromagnets: T_C [K]		Antiferromagnets: T_N [K]	
iron	1043	$CoCl_2$	25
cobalt	1404	CoF_2	38
nickel	628	CoO	291
gadolinium	289	chromium	475
erbium	32	Cr_2O_3	307
dysprosium	155	erbium	80
		$FeCl_2$	70
barium ferrite	720	FeF_2	79 - 90
strontium ferrite	720	FeO	198
Alnico	1160	FeMn	490
Alumel	436	α-Fe_2O_3	953
Mutamel	659	MnF_2	72 - 75
Permalloy	869	MnO	122
Trafoperm	1027	MnSe	173
NdFeB	580	MnTe	310 - 323
$SmCo_5$	990	$NiCl_2$	50
Sm_2Co_{17}	1070	NiF_2	78 - 83
		NiFeO	180
CrO_2	390	NiO	533 - 650
$CuAlMn_3$	???	$TiCl_3$	100
$La_xCa_{1-x}B_6$	900	UCu_5	15
MnAs	318	V_2O_3	170
MnBi	633		
polymerized C_{60}	~500		

Hystersis Loop of Ferromagnetic Materials

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