

TENTATIVE LECTURE SCHEDULE

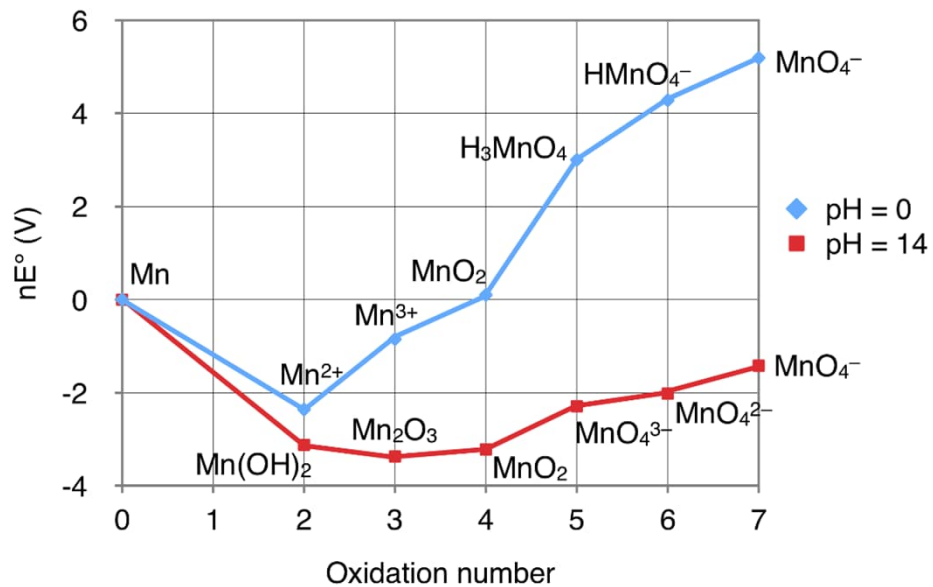
	Date	Topic
1.	Wed 07.09.	Course Introduction & Short Review of the Elements
2.	Fri 09.09.	Periodic Properties & Periodic Table & Main Group Elements (starts)
3.	Mon 12.09.	Short Survey of the Chemistry of Main Group Elements (continues)
4.	Fri 16.09.	Zn + Ti, Zr, Hf & Atomic Layer Deposition (ALD)
5.	Mon 19.09.	Transition Metals: General Aspects & Pigments
6.	Wed 21.09.	Redox Chemistry
7.	Fri 23.09.	Crystal Field Theory (Linda Sederholm)
8.	Mon 26.09.	V, Nb, Ta & Perovskites & Metal Complexes & MOFs & MLD
9.	Wed 28.09.	Cr, Mo, W & 2D materials & Mxenes & Layer-Engineering
10.	Fri 30.09.	Mn, Fe, Co, Ni, Cu & Magnetism & Superconductivity
11.	Mon 03.10.	Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)
12.	Fri 07.10.	Lanthanoids + Actinoids & Luminescence
13.	Mon 10.10.	EXTRA
14.	Wed 12.10.	Resources of Elements & Rare/Critical Elements & Element Substitutions
15.	Fri 14.10.	Inorganic Materials Chemistry Research

EXAM: Oct. 18, 9:00-12:00

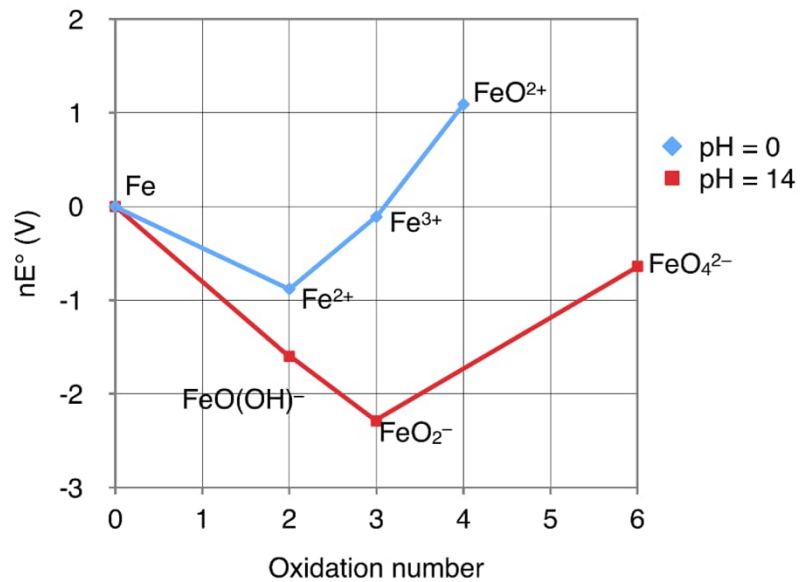
QUESTIONS: Lecture 10

- 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 (simple-minded) reason why Mn is not ferromagnetic.**
- 4. Propose a (simple-minded) reason why Cu is not ferromagnetic.**
- 5. How many unpaired 3d electrons (oct./hs): Fe^{2+} , Fe^{3+} ?**
- 6. Which one(s) of the iron oxides, FeO , Fe_3O_4 and Fe_2O_3 , is/are:**
 - mixed valent**
 - antiferromagnetic**
 - ferrimagnetic**
 - electrically conducting**

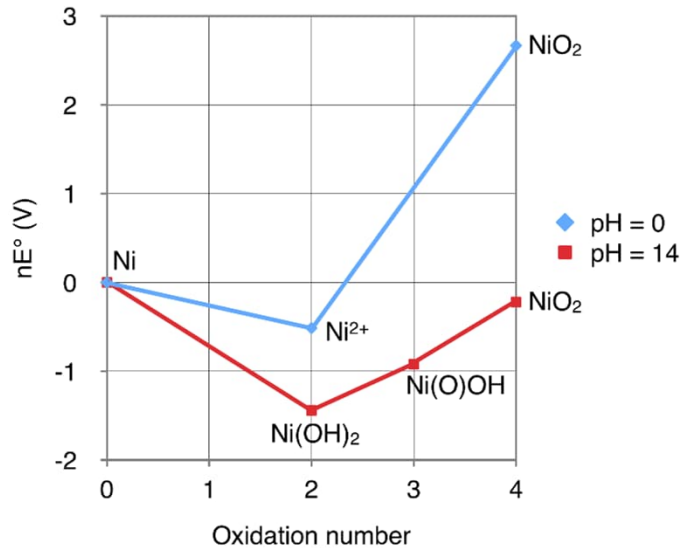
Frost diagram for manganese



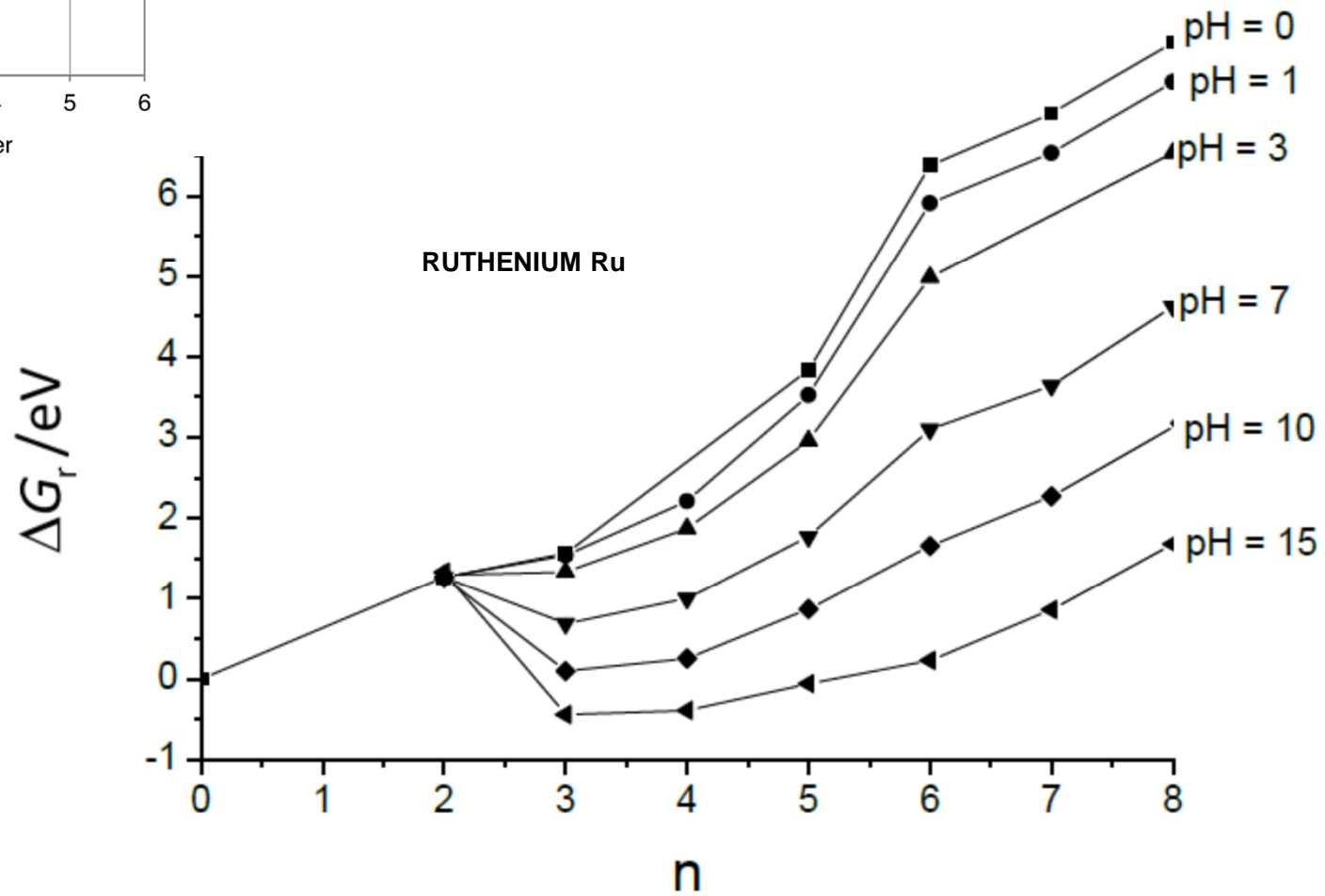
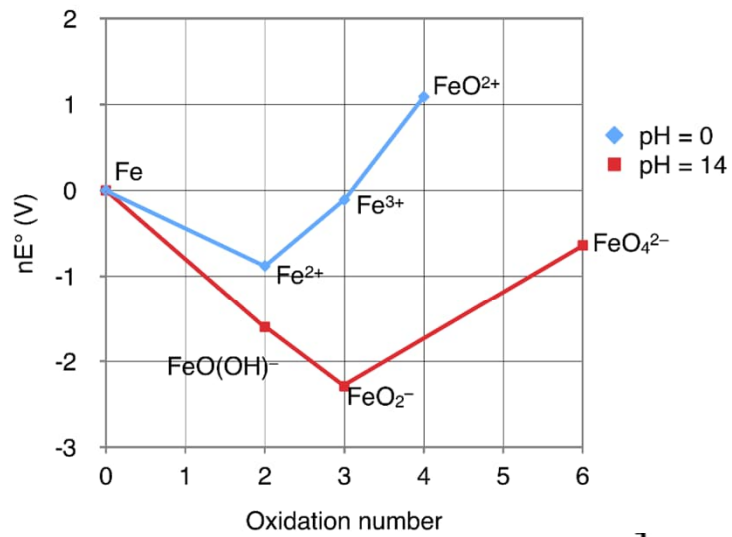
Frost diagram for iron



Frost diagram for nickel



Frost diagram for iron



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)₃O₄
- +III: (Fe,Co,Rh,Ir)₂O₃
- +IV: (Ru,Os,Rh,Ir,Pd,Pt)O₂
- +VIII: (Ru,Os)O₄

26 Fe	27 Co	28 Ni	29 Cu	30 Zn
44 Ru	45 Rh	46 Pd	47 Ag	48 Cd
76 Os	77 Ir	78 Pt	79 Au	80 Hg

OCTAHEDRAL COORDINATION

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

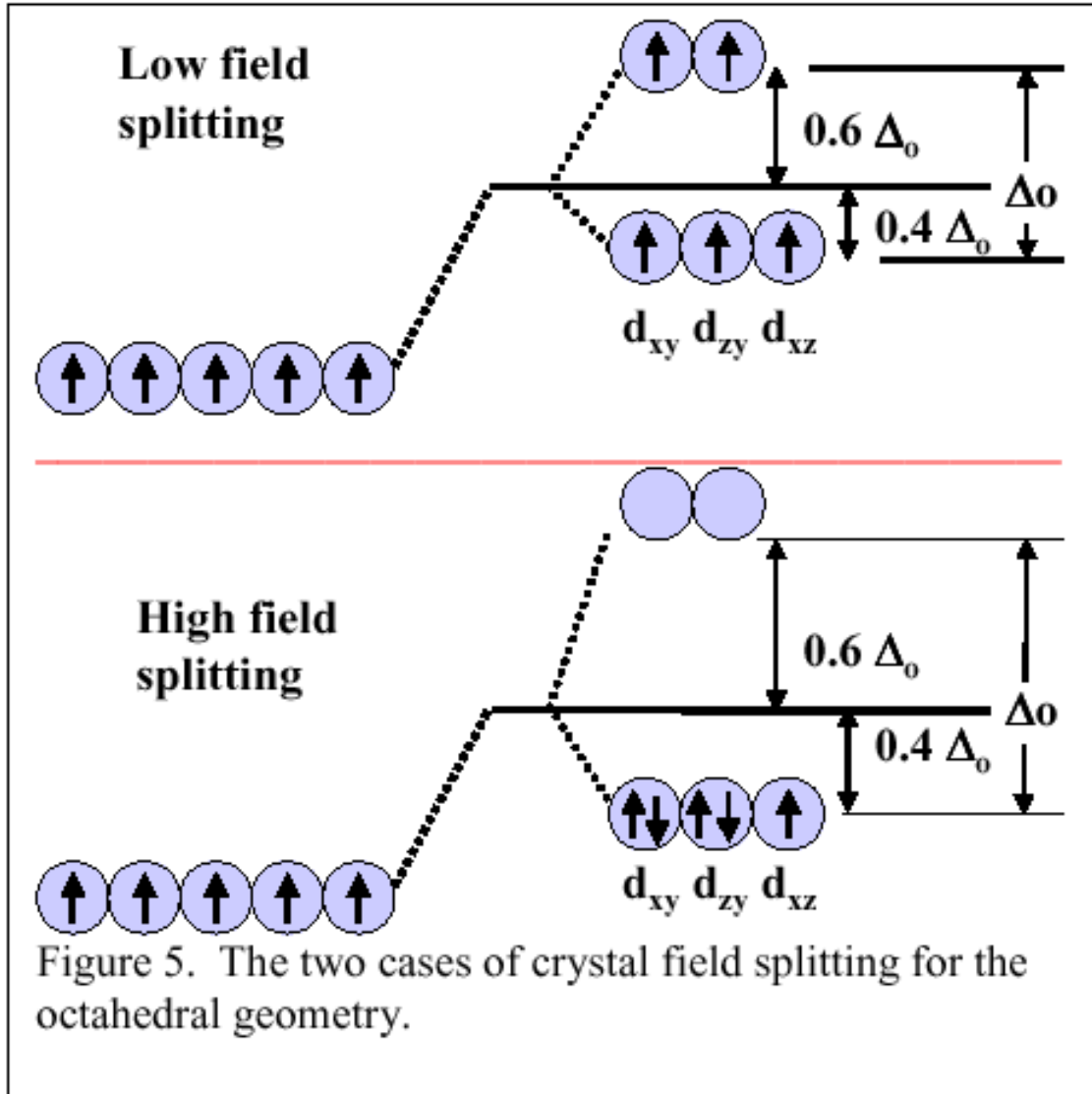
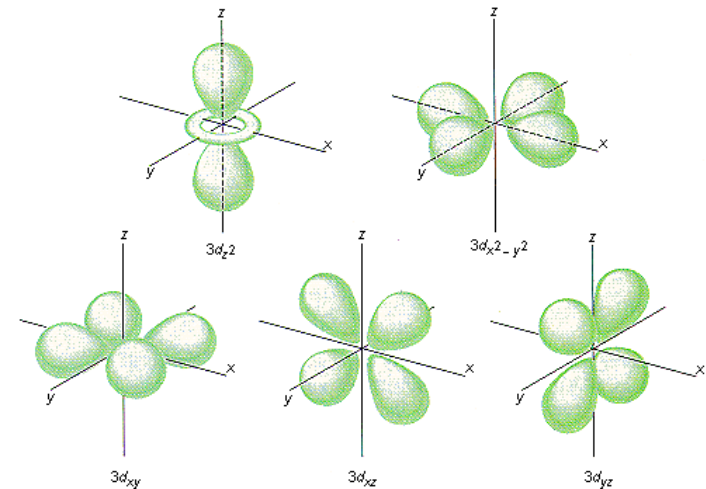


Figure 5. The two cases of crystal field splitting for the octahedral geometry.



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 $[\text{FeO}_4]^{4-}$, $[\text{FeO}_4]^{3-}$ & $[\text{FeO}_4]^{2-}$) !!!
(c.f. sulphite-sulphate, **manganite-manganate**, **supercond. cuprates**)
- Most common oxides: FeO and 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: $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and FeCl_3

COPPER

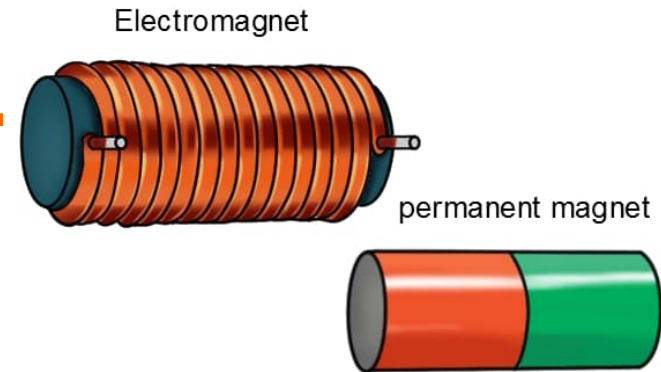
- **Known since 5000 BC:**
lat. *Cuprum* (Cyprus; oldest mining places, 3000 BC)
- **Occurrence:** 68 ppm; mainly as sulphides
- **Electronegativity:** 1.9
- **Similarities with alkali metals:** $d^9s^2 \rightarrow d^{10}s^1$
however, Cu smaller, denser, less reactive, more electronegative, and forms coordination compounds
- **Binary oxides:** Cu_2O , CuO
- **Compounds with higher oxidation states:**
 LaCuO_3 , K_3CuF_6 , KCuO_2 , high- T_c superconducting oxides
- **How to stabilize the high oxidation states for transition metals:**
 - combine with the most electronegative anions
 - combine with the most electropositive cations
 - use highly oxidizing synthesis conditions/high pressures
- **Enzyme reactions:** $\text{Cu(I)} \rightarrow \text{Cu(III)}$

MAGNETISM in BRIEF

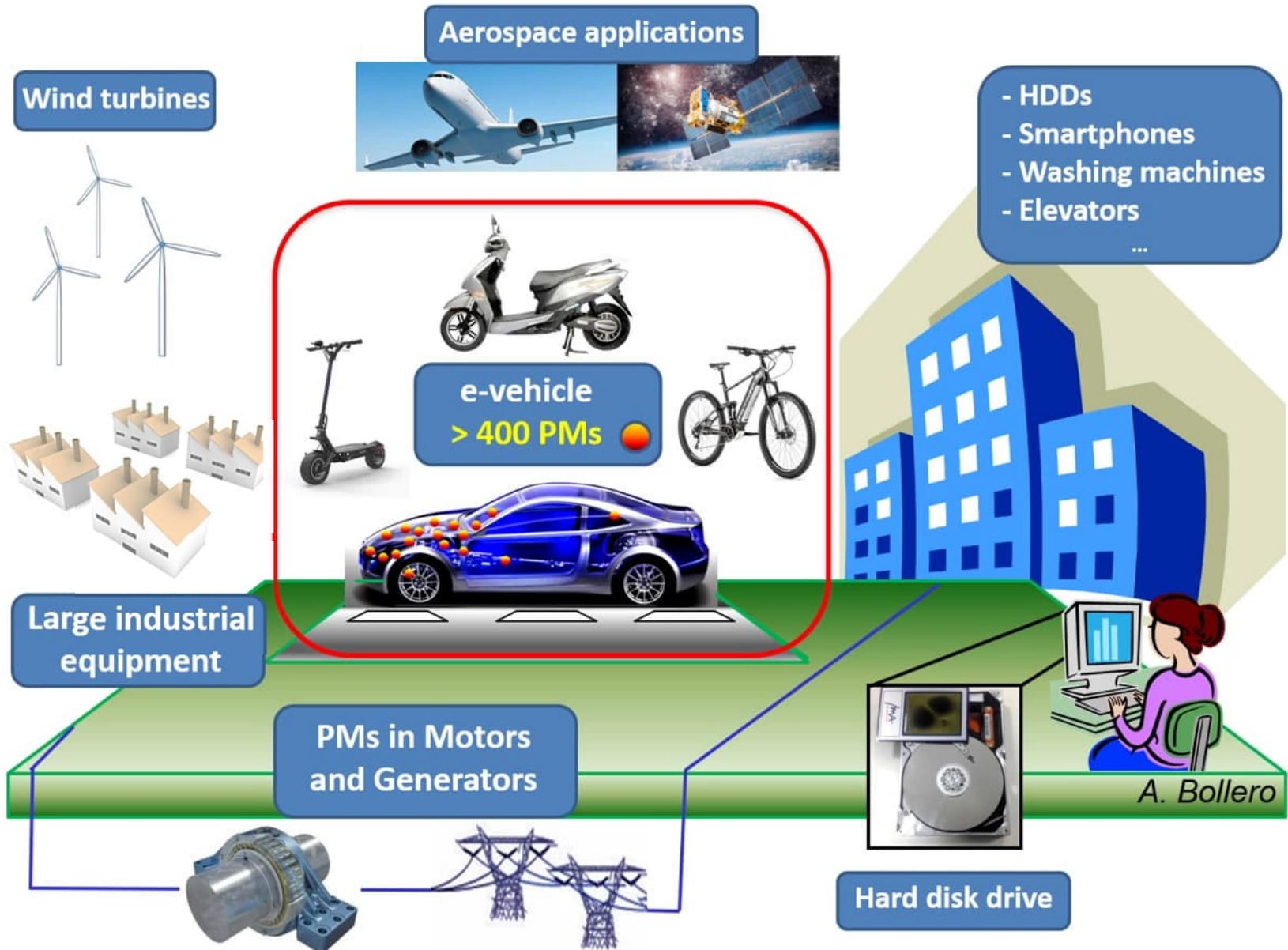
- Magnet: solid that creates a magnetic field
 - (1) Electromagnet: electric current (through a coil)
 - (2) **Permanent magnet: unpaired electrons**

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 PERMANENT MAGNETS



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 $T < T_c$



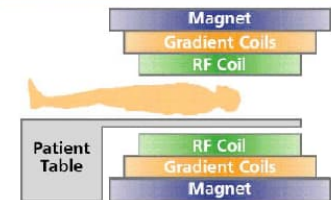
900 MHz NMR (UW Chemistry)



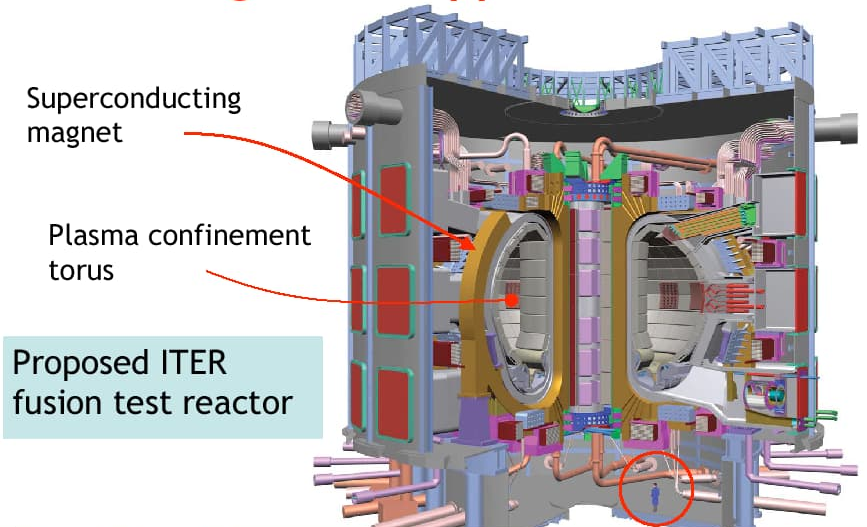
21.7 T field

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.



Large scale applications



MAGNETIC SUSCEPTIBILITY

Magnetization (M):

magnetic field induced in sample in external magnetic field (H)

Magnetic susceptibility: $\chi = M / H$

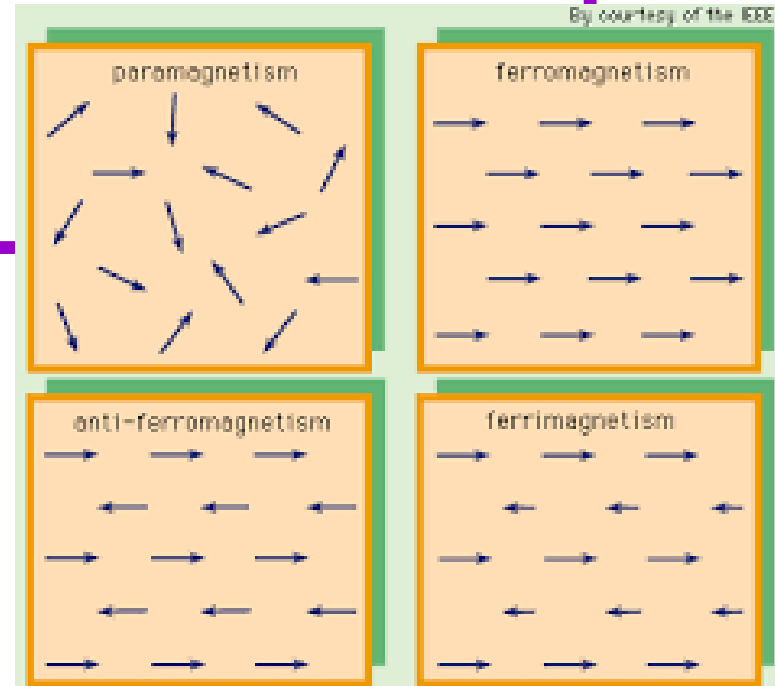
DIAMAGNET: $\chi < 0$ (very small)

PARAMAGNET: $\chi > 0$ (very small)

FERROMAGNET: $\chi > 0$ (very large)

ANTIFERROMAGNET: $\chi > 0$ (small)

FERRIMAGNET: $\chi > 0$ (large)



RoomTemperature MAGNETISM OF PURE ELEMENTS

1 H																	2 He
		<input type="checkbox"/> Paramagnetic <input type="checkbox"/> Diamagnetic															
		<input type="checkbox"/> Ferromagnetic <input type="checkbox"/> Antiferromagnetic															
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
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
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
55 Cs	56 Ba	57 La	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
87 Fr	88 Ra	89 Ac															
			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	

Ferromagnetism in metals

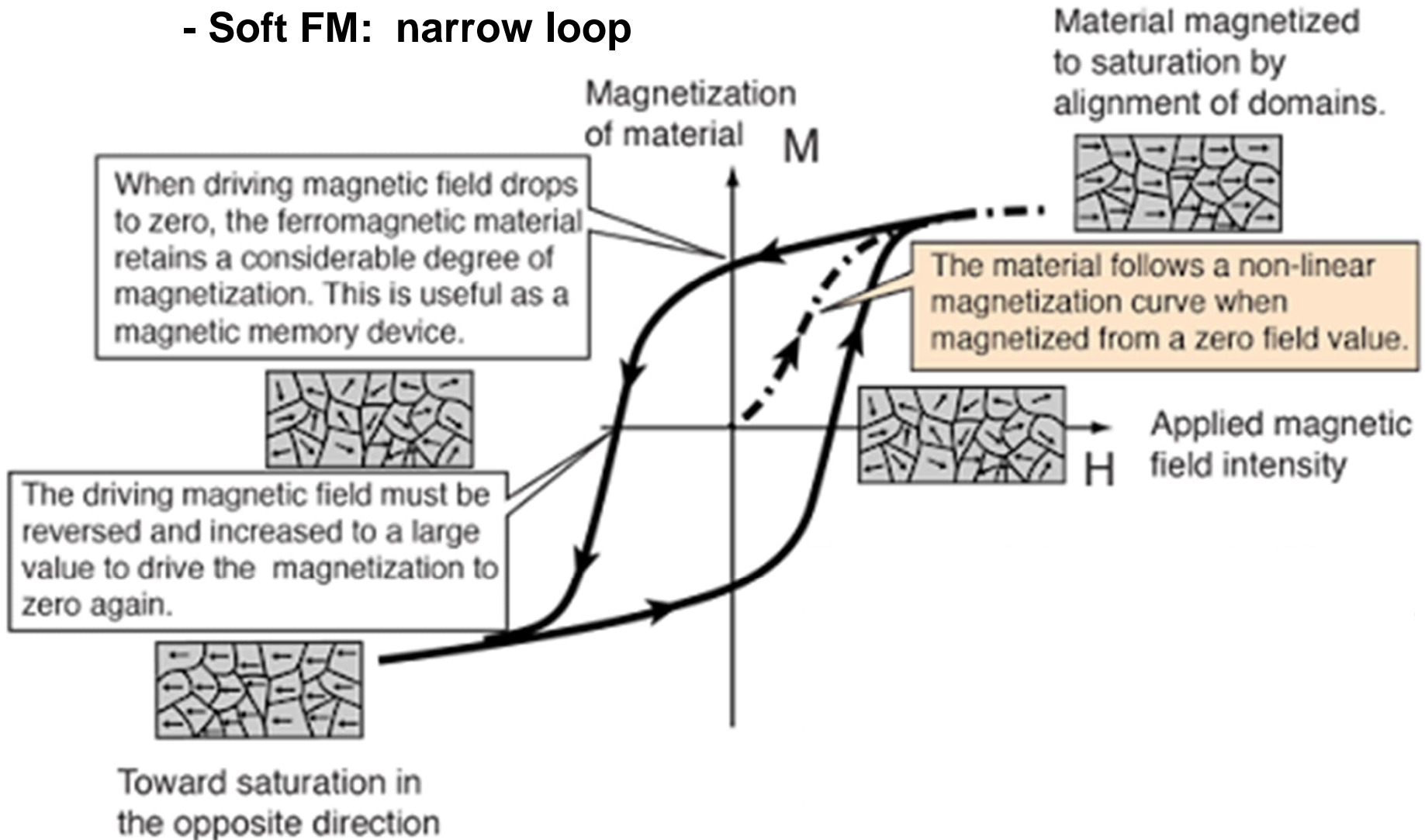
- Only Fe, Co, Ni RT-FM
- Besides unpaired electrons, “exchange interaction” condition should be fulfilled
- This depends on crystal structure/atomic distances:
 - normal Fe FM, but austenite-type Fe not
 - pure Mn not FM (too short Mn-Mn distance), but some Mn alloys are (longer Mn-Mn distance)

Curie temperatures (in K)

■	Co	1388
■	Sm ₂ Co ₁₇	1070
■	Fe	1043
■	SmCo ₅	990
■	Fe ₃ O ₄	858
■	NiFe ₂ O ₄	858
■	CuFe ₂ O ₄	728
■	MgFe ₂ O ₄	713
■	MnBi	630
■	Ni	627
■	MnSb	587
■	Nd ₂ Fe ₁₄ B	580
■	MnFe ₂ O ₄	573
■	Y ₃ Fe ₅ O ₁₂	560
■	CrO ₂	386
■	MnAs	318
■	Gd	292
■	Dy	88
■	Er	32
■	EuO	69

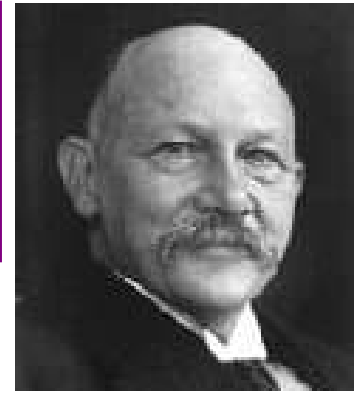
Hysteresis Loop of Ferromagnetic Materials

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

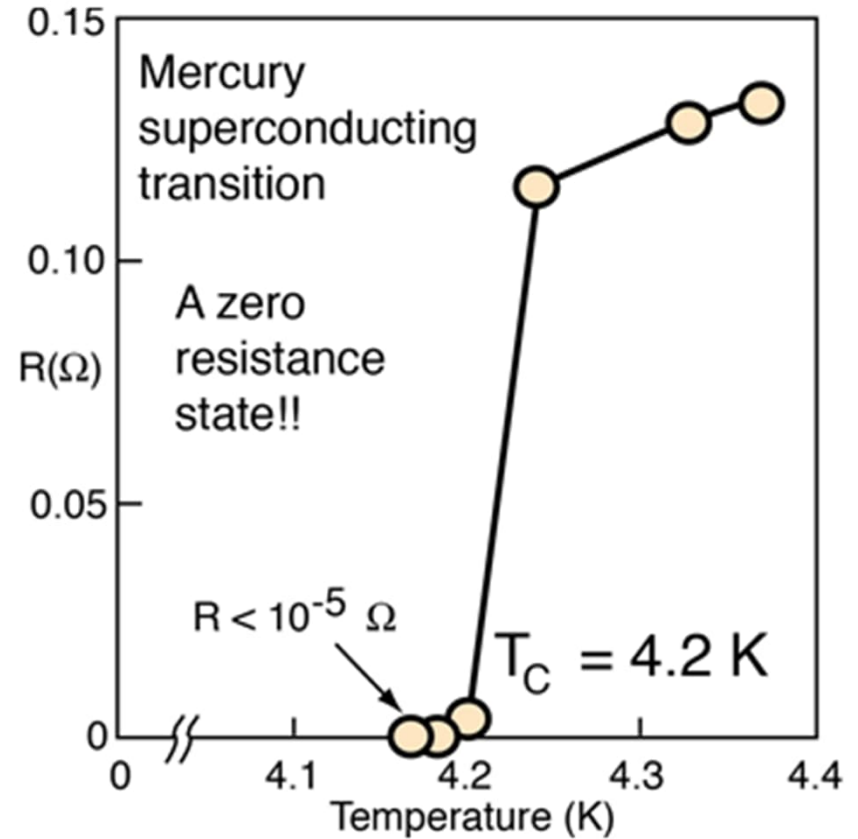
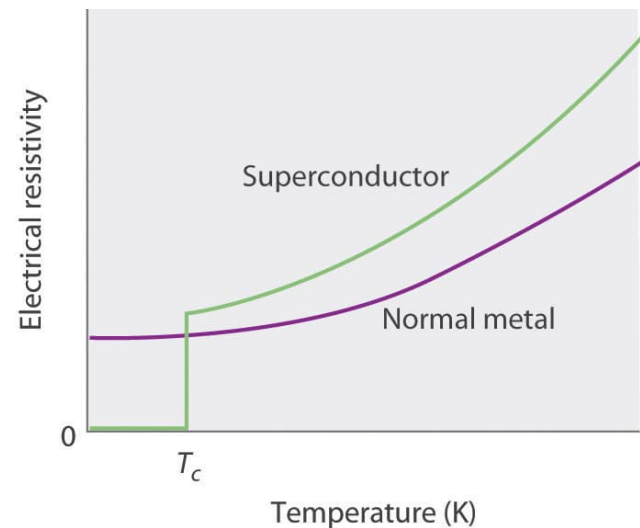
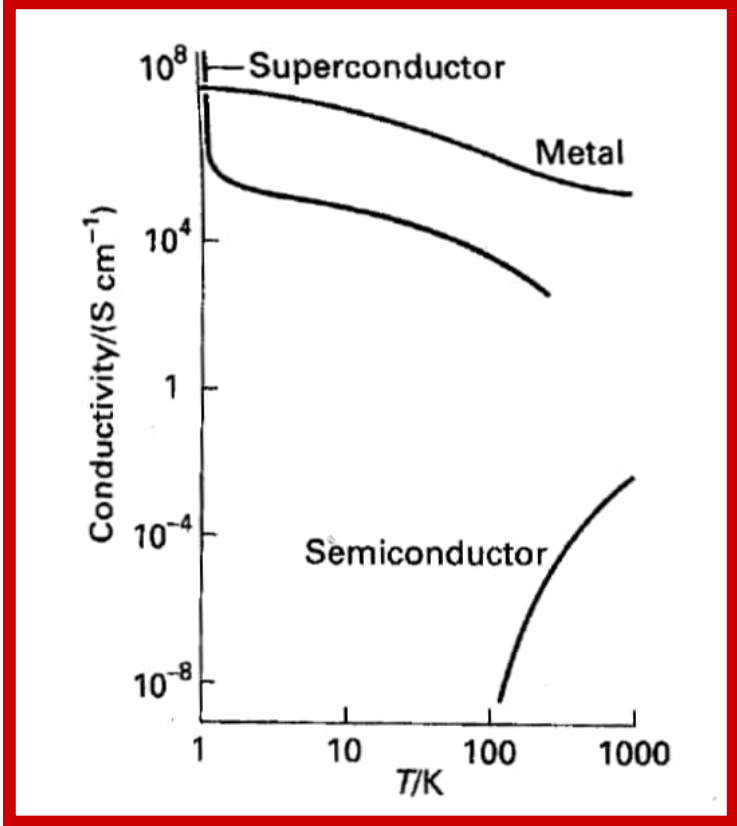


Superconductivity

- 1911 Kamerlingh-Onnes
- $\rho = 0$



Nobel 1913



Superconducting Elements

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	57	La	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	89	Ac	104	Rf	105	Ha	106	Sg	107	Bh	108	Hs	109	Mt	110	Ds	111	Rg	112	Uub												

- In Bulk at Ambient Pressure
- At High Pressure
- In Modified Form

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cr	Es	Fm	Md	No	Lr

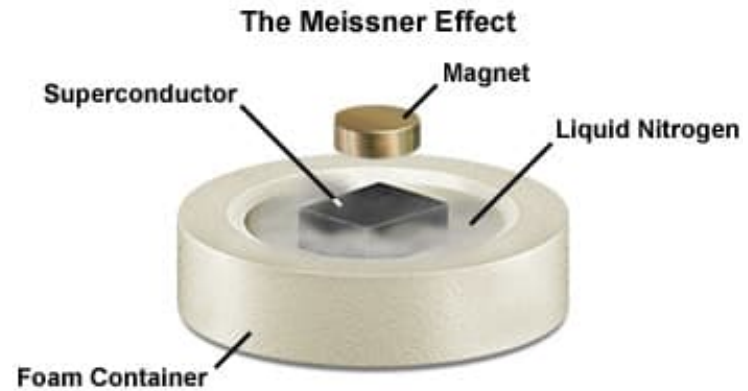
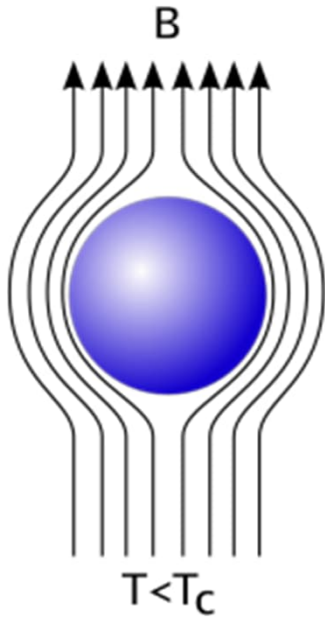
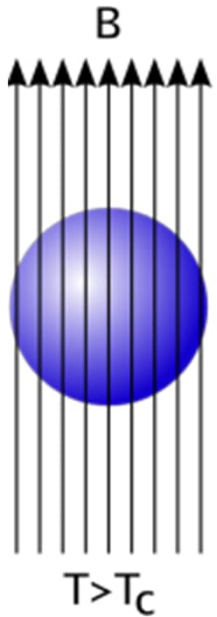
"Meissner effect"

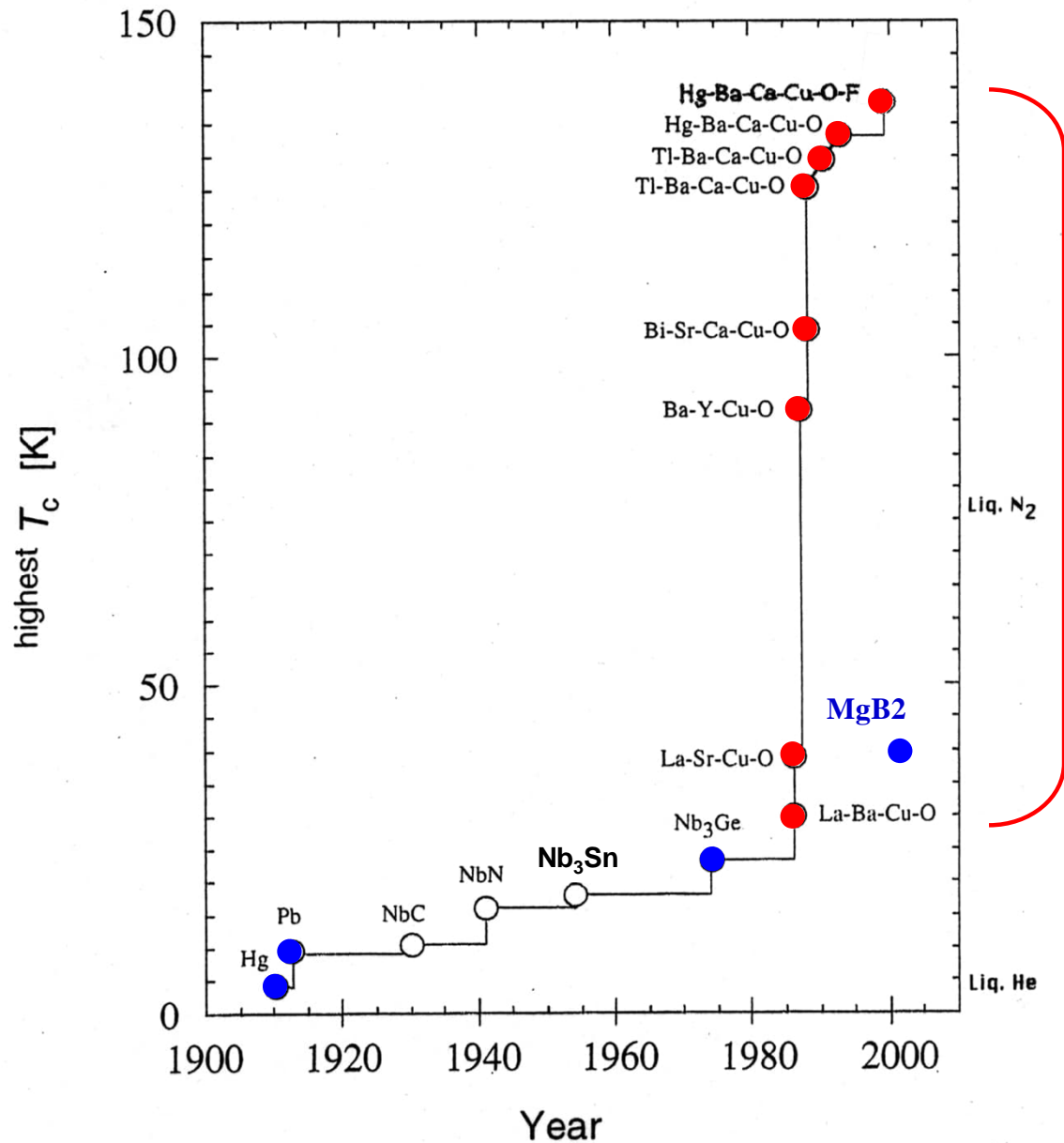
1933 Meissner and Ochenfeld:
 $\chi = B/H < 0 \rightarrow$ levitation



Super-Maglev Train

- 603 km / hour
- Test line 42.8 km





High- T_c superconductivity

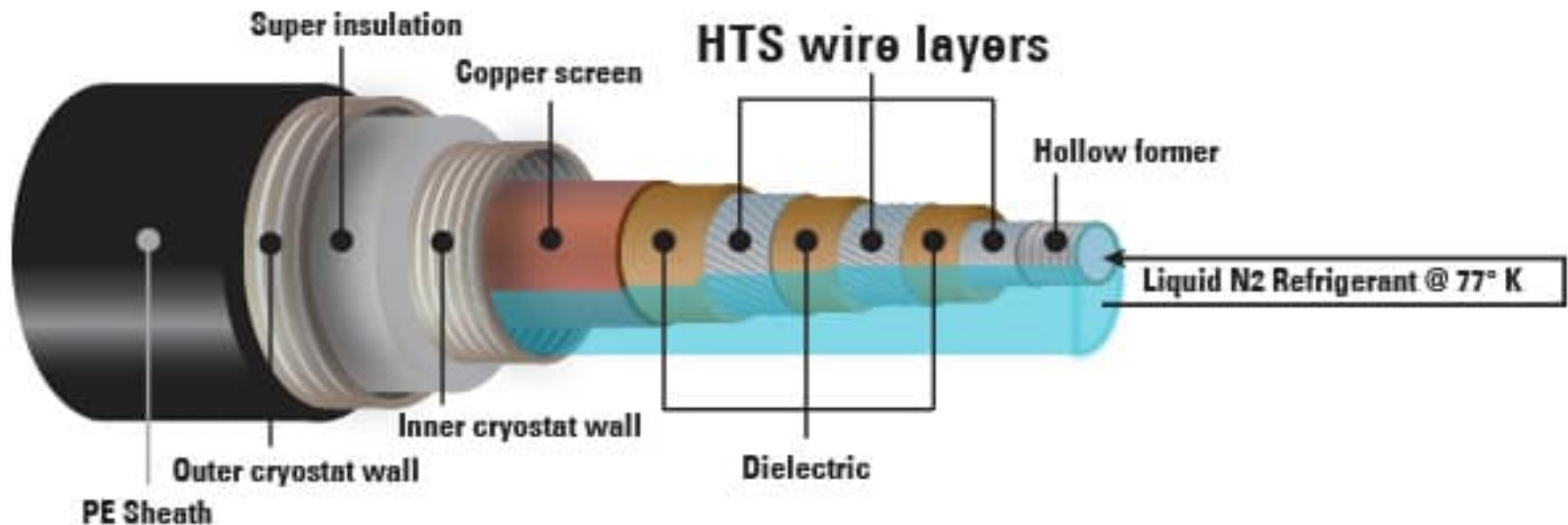
- 1986: Bednorz and Müller
- $(\text{La,Ba})_2\text{CuO}_4$ $T_c = \sim 30$ K
- Nobel 1987



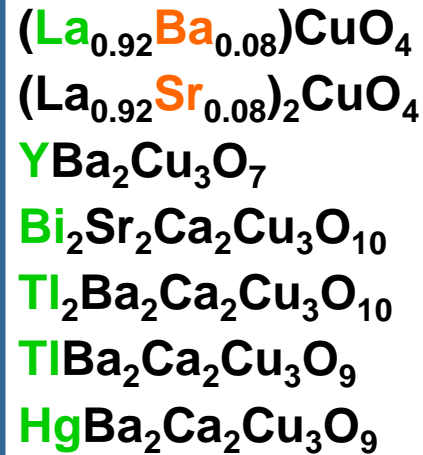
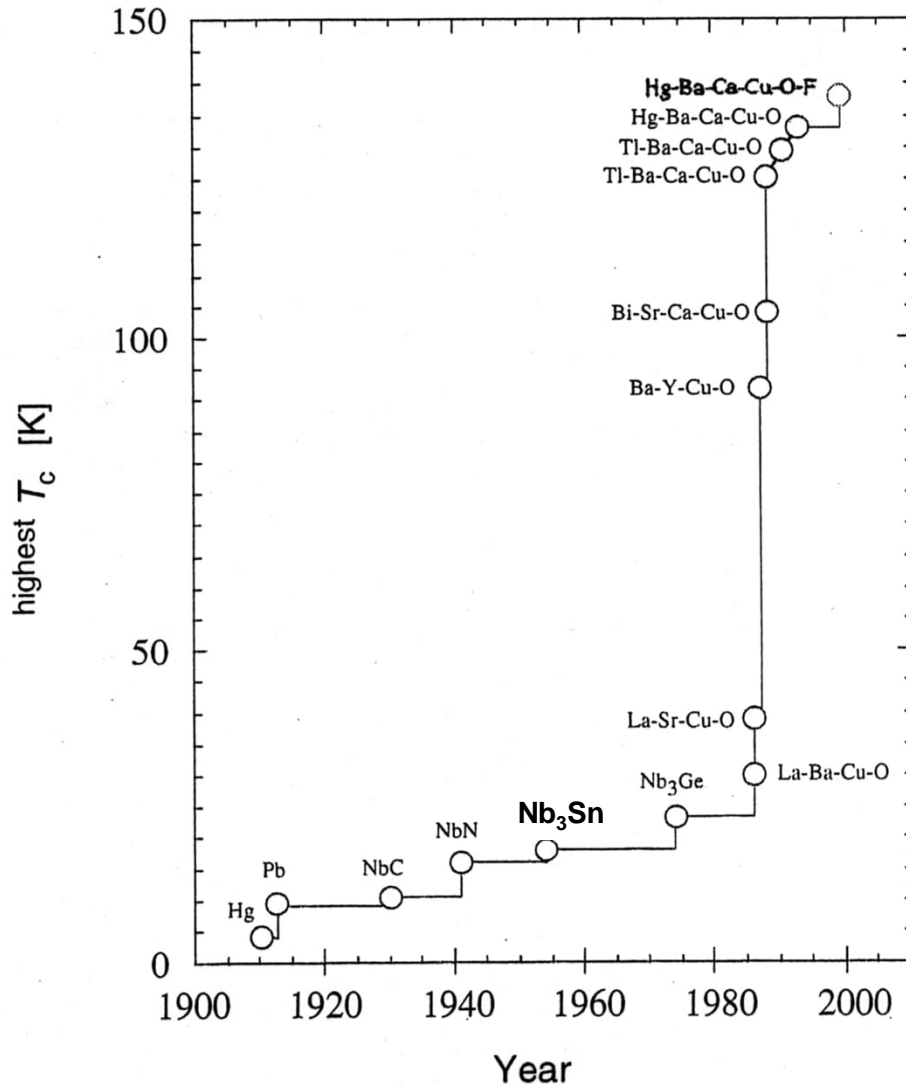
SUPERCONDUCTING POWER CABLES

- Normal Cu wires: 20% energy waste
- High-temperature superconductor cables introduced since 2000s
- In 2008 the longest cable installed in Long Island, New York: transmitting up to 574 megawatts of electricity (enough to power 300,000 homes)

Typical HTS Cable Configuration



Search for new high- T_c superconductors



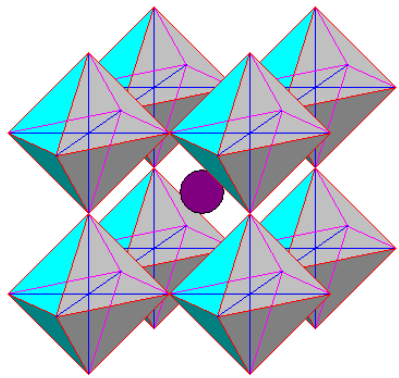
- Chemical pressure
- No. of CuO_2 planes
- Inert-pair effect

Liq. N₂

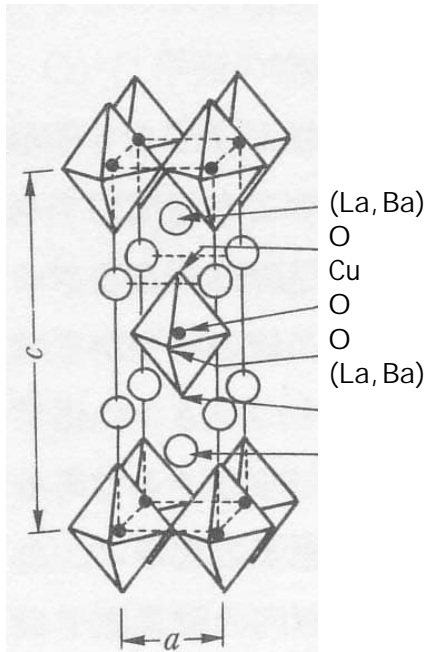
Liq. He

Period 1	IA 1 H																	VIIA or 0 2 He						
Period 2	3 Li	4 Be																	5 B	6 C	7 N	8 O	9 F	10 Ne
Period 3	11 Na	12 Mg	IIIB	IVB	VB	VIB	VIIIB	VIII				IB	IIB	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar					
Period 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						
Period 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						
Period 6	55 Cs	56 Ba	57 to 71 La	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						
Period 7	87 Fr	88 Ra	89 to 103 Ac	104 Rf	105 Ha	106 Sg	107 Ns	108 Hs	109 Mt															
Lanthanide series	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									
Actinide series	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									

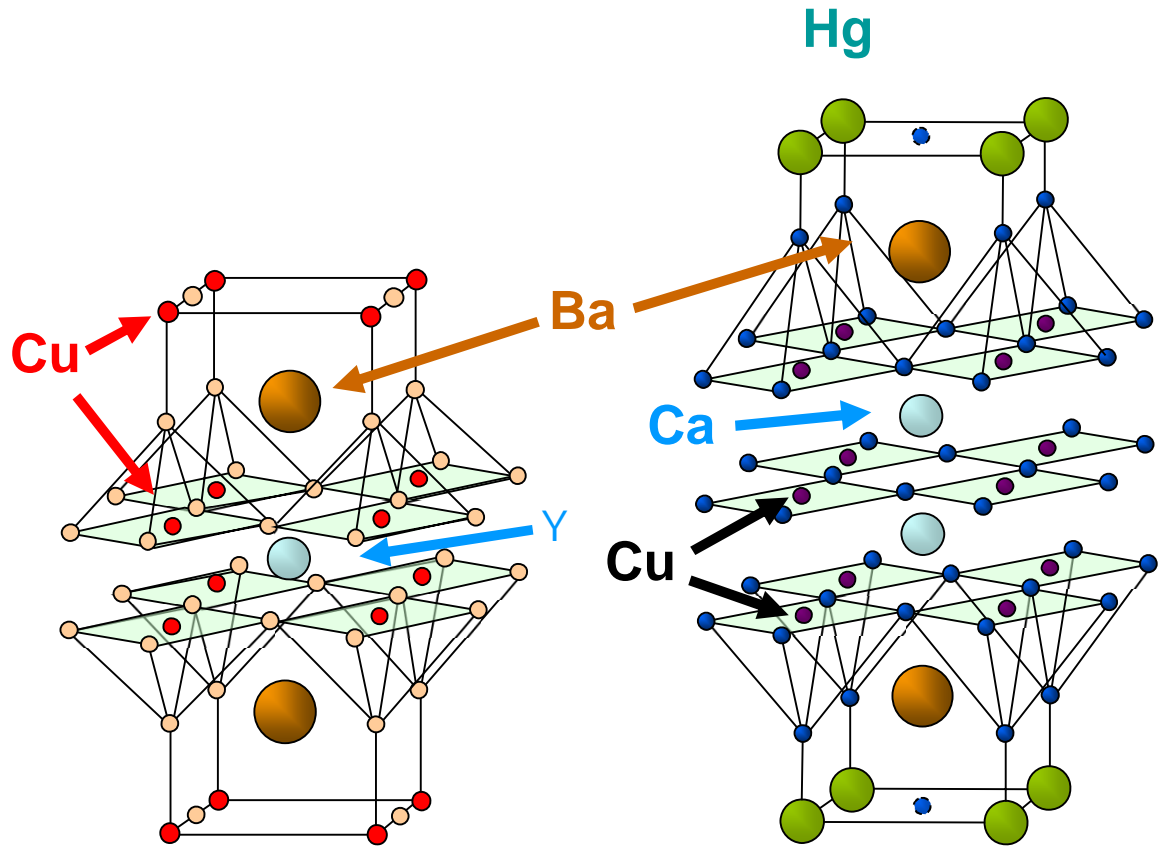
Crystal Structures of High- T_c Superconductive Copper Oxides



Perovskite CaTiO_3



$T_c \approx 35 \text{ K}$

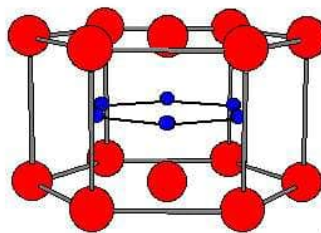


$T_c \approx 92 \text{ K}$



$T_c \approx 135 \text{ K}$

Akimitsu 2001:
MgB₂



Hosono 2006 →
[La(O,F)][FeAs]

