Functional Inorganic Materials
Fall 2022

Tuesdays: 12.15 - 14.00 (U8)
Thursdays: 10.15 - 12.00 (Ke1)

#	Date	Who	Topic
1	Mon 5.9.	Maarit	Introduction + Materials design consepts
2	Thu 8.9.	Antti	Introduction + Computational materials design
3	Tue 13.9.	Maarit	Superconductivity: High-T_c superconducting Cu oxides
4	**Thu 15.9.**	**Maarit**	**Magnetic (oxide) materials**
5	Tue 20.9.	Maarit	Ionic conductivity (Oxygen): Oxygen storage and SOFC
6	Thu 22.9.	Maarit	Ionic conductivity (Lithium): Li-ion battery
7	Tue 27.9.	Antti	Thermal conductivity
8	Thu 29.9.	Antti	Thermoelectricity
9	Tue 4.10.	Antti	Piezoelectricity
10	Thu 6.10.	Antti	Pyroelectricity and ferroelectricity
11	Tue 11.10.	Maarit	Hybrid materials
12	Thu 13.10.	Antti	Luminescent and optically active materials

LECTURE 4: Magnetic (Oxide) Materials

- Electromagnets and **Permanent magnets**
- Magnetic field strength, Magnetization, Magnetic susceptibility
- Dia-, Para-, Ferro-, Ferri- & Antiferromagnetic
- Type of ordering: unpaired electrons & crystal structure
- Curie-Weiss Law
- Magnetic moment → Chemistry
- Superexchange & Double exchange interactions
- (Double) Perovskite & (Inverse) Spinel structures
- Hard versus Soft Magnets: Coercivity field

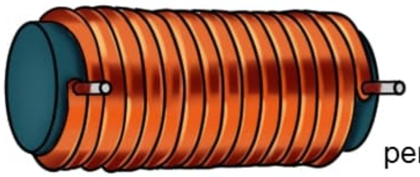
LECTURE EXERCISE 4

1. Please, rationalize the ferrimagnetism of magnetite Fe_3O_4 based on its crystal structure.

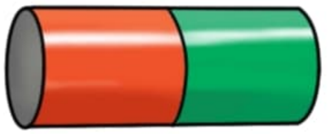
2. Sr_2FeMoO_6 is one of the rare halfmetallic materials (simultaneously metallic and ferro/ferrimagnetic). Give a rational explanation for the fact that its T_C is higher than those of the related Ca_2FeMoO_6 and Ba_2FeMoO_6 compounds.

3. Make a quick search (lecture slides and/or literature) for few representative soft and hard magnetic materials.

   EXTRA: Did you find/can you propose any specific applications for the materials of your choice?



Electromagnet



permanent magnet

MAGNETISM in BRIEF

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

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

  (2) Permanent magnet: unpaired electrons

PERMANENT MAGNETS

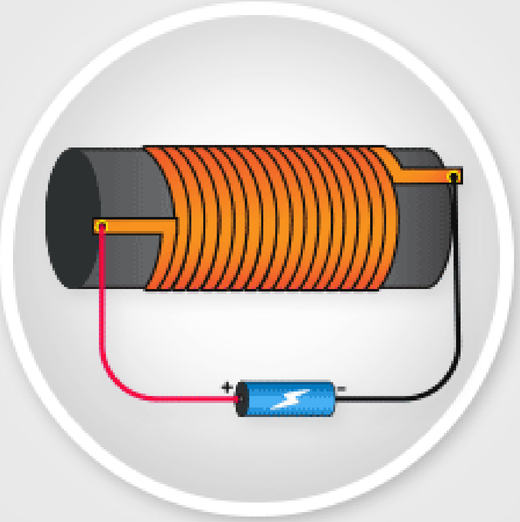
- **Each electron is a small magnet due to its spin**
- **In most materials, the countless electrons have randomly oriented spins, leaving no magnetic effect on average**
- **In some rare magnetic materials, many of the electron spins are aligned in the same direction, such that they create a net magnetic 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:**

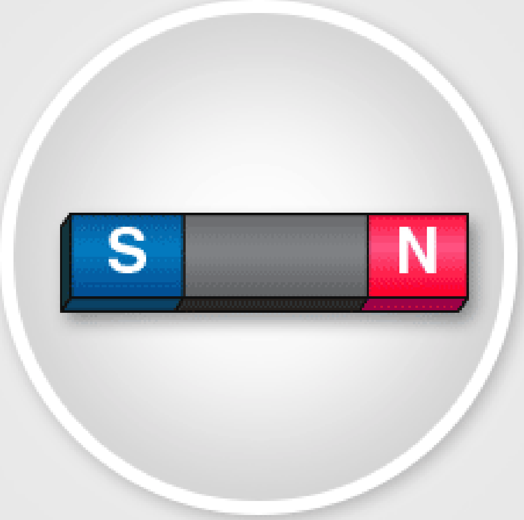
  - electron configuration

  - crystal structure

DIFFERENCE BETWEEN ELECTROMAGNET AND PERMANENT MAGNET

BYJU'S The Learning App





ELECTROMAGNET

AN ELECTROMAGNET IS A TYPE OF MAGNET IN WHICH THE MAGNETIC FIELD IS PRODUCED BY AN ELECTRIC CURRENT. THE MAGNETIC FIELD DISAPPEARS WHEN THE CURRENT IS TURNED OFF. ELECTROMAGNETS USUALLY CONSIST OF WIRE WOUND INTO A COIL.

PERMANENT MAGNET

A PERMANENT MAGNET IS AN OBJECT MADE FROM A MATERIAL THAT IS MAGNETIZED AND CREATES ITS OWN PERSISTENT MAGNETIC FIELD. AN EVERYDAY EXAMPLE IS A REFRIGERATOR MAGNET USED TO HOLD NOTES ON A REFRIGERATOR DOOR.

HOW STRONG THE MAGNET IS ?

- Magnetic field strength (H): magnetic field produced by the flow of current in a wire (A/m) → **Örsted (Oe)**
- Magnetic flux density (B): total magnetic field including the contribution (magnetization M) of the magnetic material in the field (Nm/A) → **Tesla (T)**
- **$H = B/\mu - M$**
- **Human body: 3×10^{-10} T**
- **Earth surface: 3×10^{-5} T**
- **Near household wiring: 10^{-4} T**
- **Household ("refrigerator") magnet: 0.3 T**
- **Mineral magnetite (Fe_3O_4): 0.4 T**
- **Strongest permanent magnet ($Nd_2Fe_{14}B$; General Motors & Sumitomo 1984): 1.5 T**
- **Magnet in MRI device: 2 T**
- **Electromagnet with Cu wires: 2 T**
- **Electromagnet with (high-T_c) superconducting wires: 33 T**
- **Record achieved with the strongest destructive pulsed magnet: 850 T**

APPLICATIONS of ELECTROMAGNETS

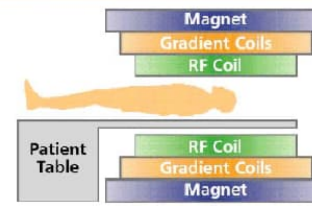
Superconducting Magnets

- 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)

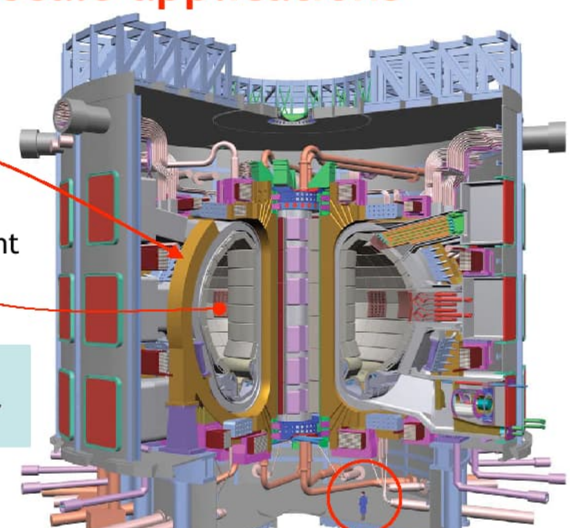
21.7 T field

Large scale applications

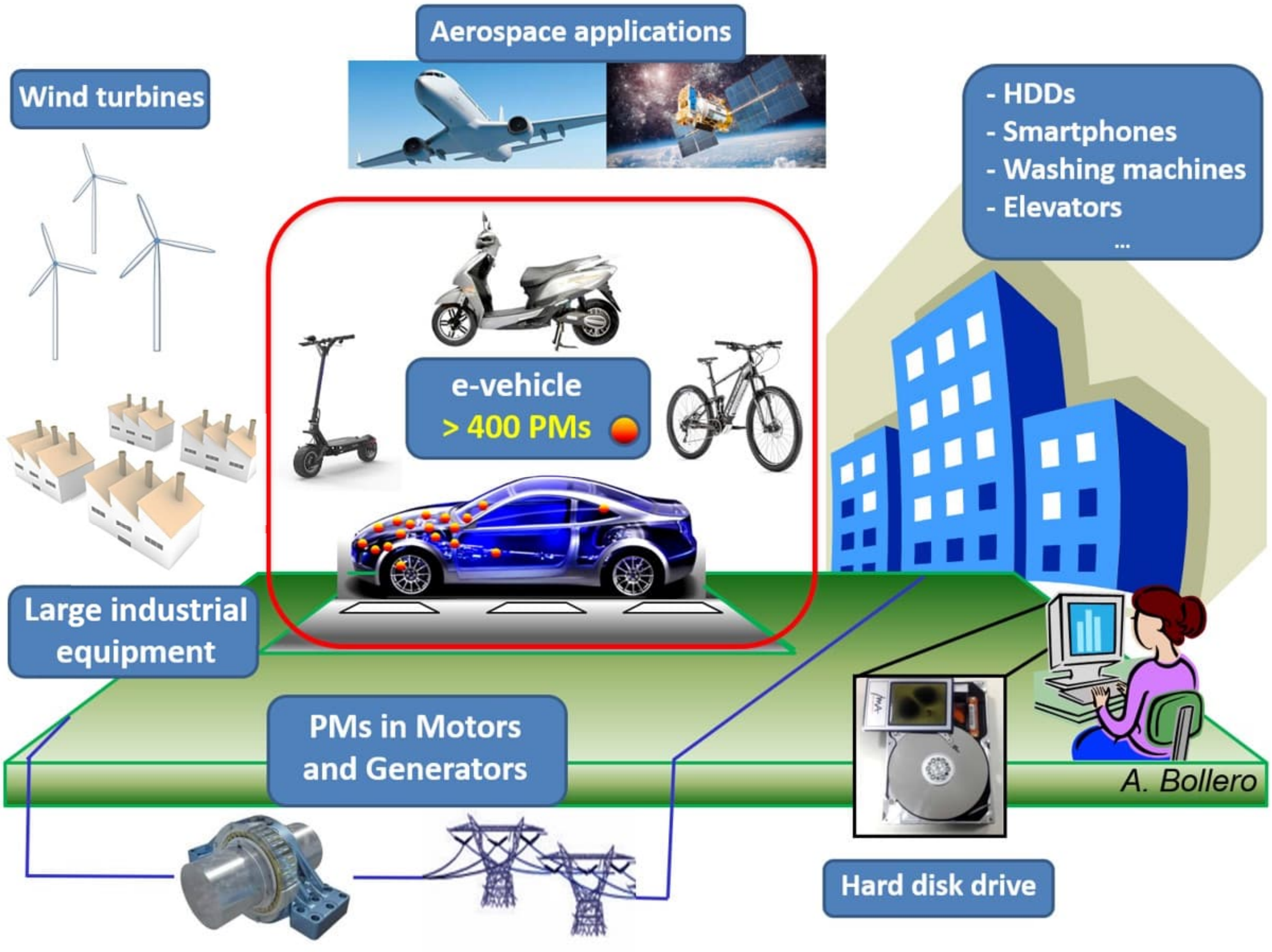
Superconducting magnet

Plasma confinement torus

Proposed ITER fusion test reactor



APPLICATIONS of PERMANENT MAGNETS



MAGNETIC MATERIALS: with unpaired electrons

Ferromagnetic ↑ ↑ ↑ ↑ ↑ ↑ ↑	Below T_C, spins are aligned parallel in magnetic domains
Antiferromagnetic ↑ ↓ ↑ ↓ ↑ ↓ ↑	Below T_N, spins are aligned antiparallel in magnetic domains
Ferrimagnetic ↑ ↓ ↑ ↓ ↑ ↓ ↑	Below T_C, spins are aligned antiparallel but do not cancel
Paramagnetic ↑ ↓ ↑ ↑ ↓ ↑ ↓	Spins are randomly oriented

T_C: Curie temperature

T_N: Neel temperature

Diamagnet:

- Electron motion in orbitals

Pauli paramagnet:

- Delocalized electrons in metal

MAGNETIC SUSCEPTIBILITY (χ)

- Magnetization (M):

The strength of the magnetic field induced in the material in an external magnetic field (H)

- Magnetic susceptibility: $\chi = M / H$

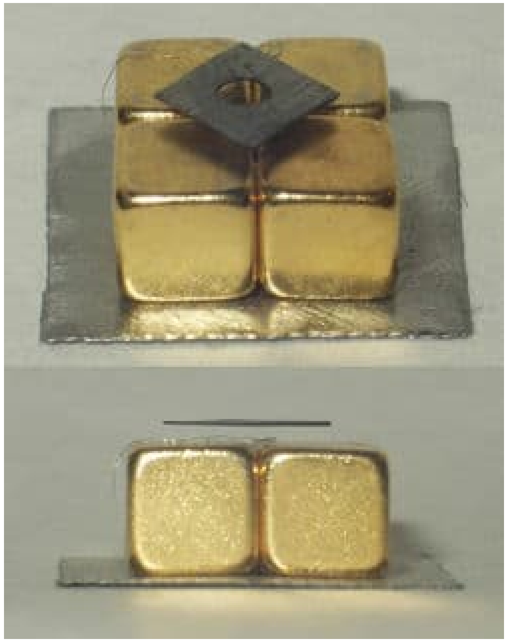
- χ Can be positive or negative

Usually measured using a so-called SQUID (superconducting quantum interference device) magnetometer operating up to ~9 T

DIAMAGNETISM (“NON-MAGNETIC”)

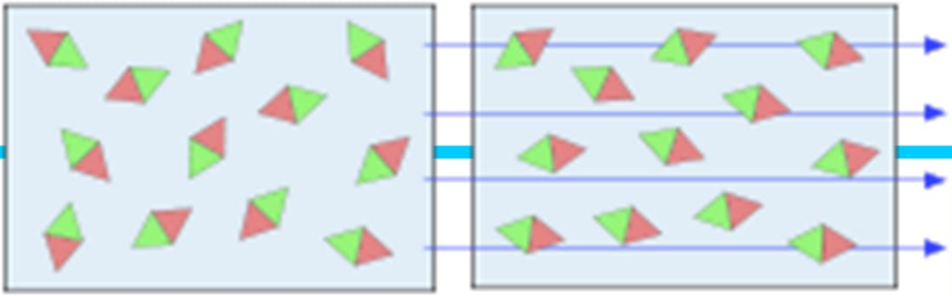
- **All materials are diamagnetic**
- **Due to motion of all electrons in atoms**
- **Diamagnetic material repels external field ($\chi < 0$)**
- **Diamagnetism is of several orders of magnitude weaker phenomenon compared to other phenomena of magnetism**

  (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: $\chi = -1$**

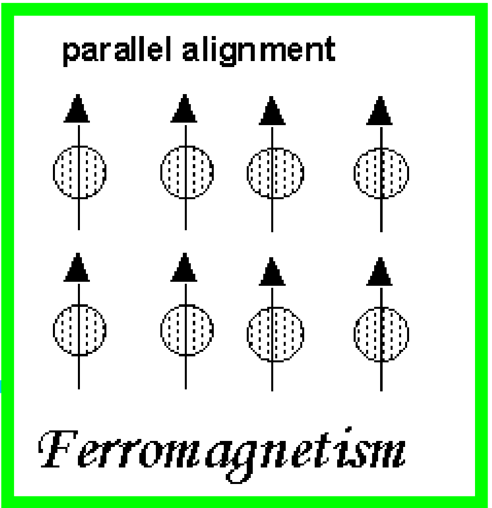


Pyrolitic carbon bar levitates above permanent magnet

PARAMAGNETISM



- Due to unpaired electrons (stronger effect than diamagnetism)
- In the absence of external magnetic field the magnetic moments of the spins of unpaired electrons are randomly oriented due to thermal agitation, but in an external magnetic field the moments tend to align with the field
- Positive magnetization effect ($\chi > 0$)
- Magnetization disappears as soon as the external magnetic field is removed
- Examples
  - many transition metal complexes/compounds
  - some salts
  - some molecules (*e.g*. NO_2)
  - some metals (*e.g*. Al, Pt)

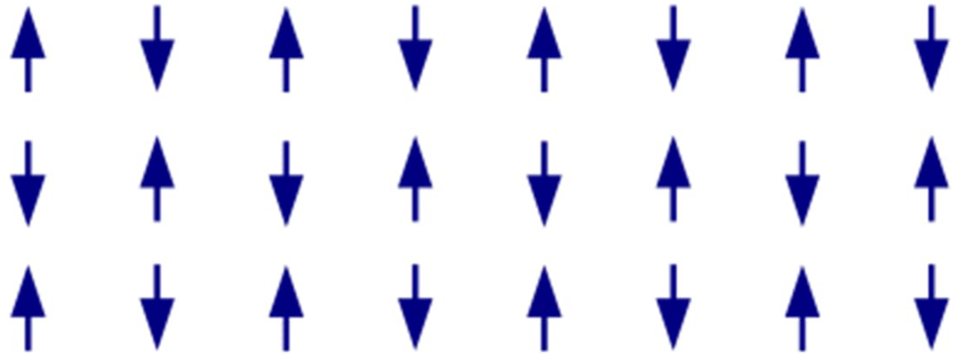


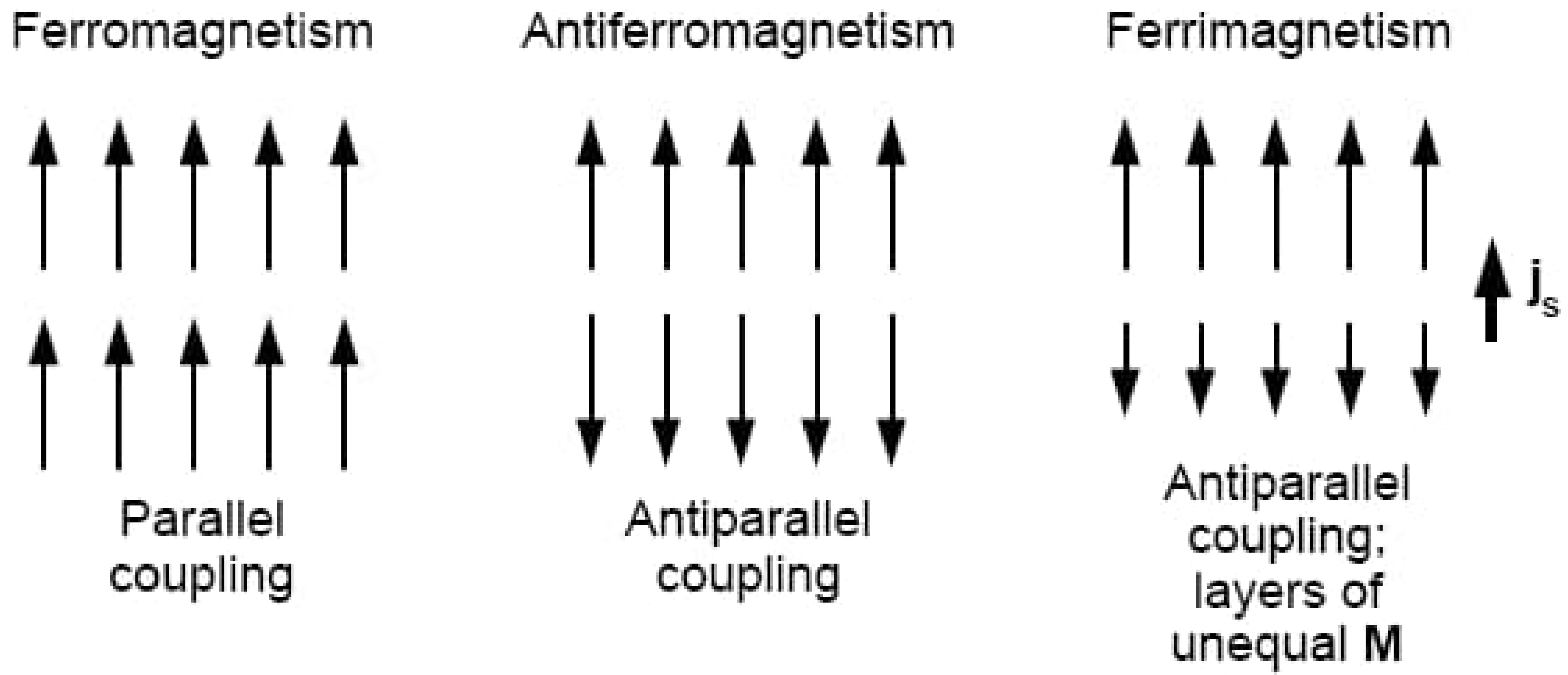
FERROMAGNETISM

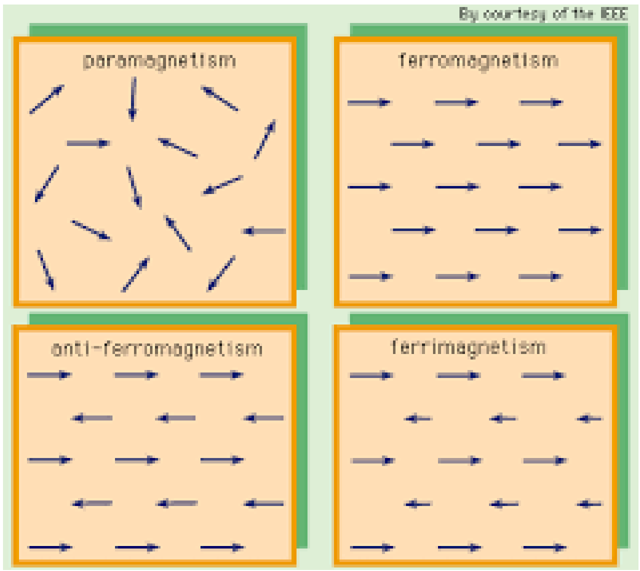
- **Below a certain temperature (Curie temperature T_C) magnetic moments of individual electrons align spontaneously (in a parallel way) → PERMANENT MAGNET**
- **Very strong magnetic effect**
- **Curie-Weiss Law: $\chi = C / (T - \theta)$; θ = Weiss temperature**
- **Ferromagnetic metals: Fe, Co, Ni, Gd, Tb**
- **Ferromagnetic intermetallic compounds, e.g. $SmCo_5$, $Nd_2Fe_{14}B$**
- **Ferromagnetic oxides, e.g. CrO_2 (T_C=392 K)**
- **Heusler-metal alloys, e.g. Cu_2MnSn**
  (individual metals are not ferromagnetic)

ANTIFERROMAGNETISM

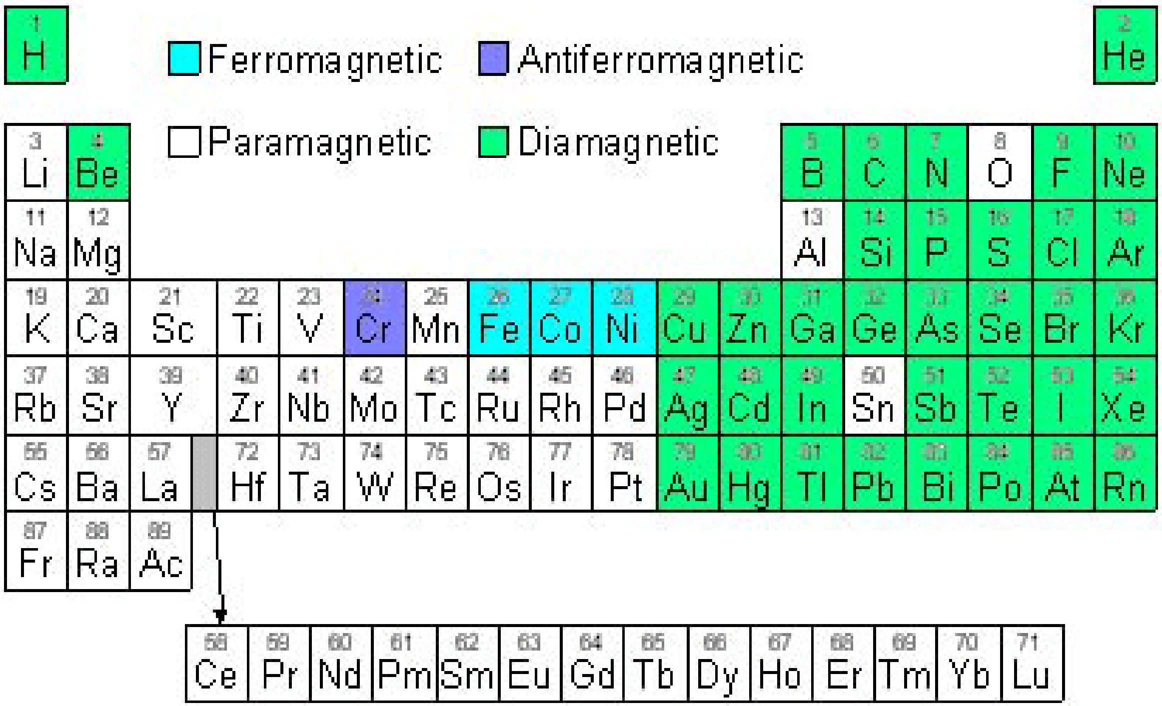
- **Below a certain temperature (Neel temperature T_N) magnetic moments of individual electrons align spontaneously (in an antiparallel way)**
- $\chi = C / (T + \theta)$
- **e.g. NiO**




Ferromagnetism
Antiferromagnetism
Ferrimagnetism
j_s
Parallel coupling
Antiparallel coupling
Antiparallel coupling; layers of unequal **M**


By courtesy of the IEEE
paramagnetism
ferromagnetism
anti-ferromagnetism
ferrimagnetism

RoomTemperature MAGNETISM OF PURE ELEMENTS



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_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

MAGNETIC SUSCEPTIBILITY

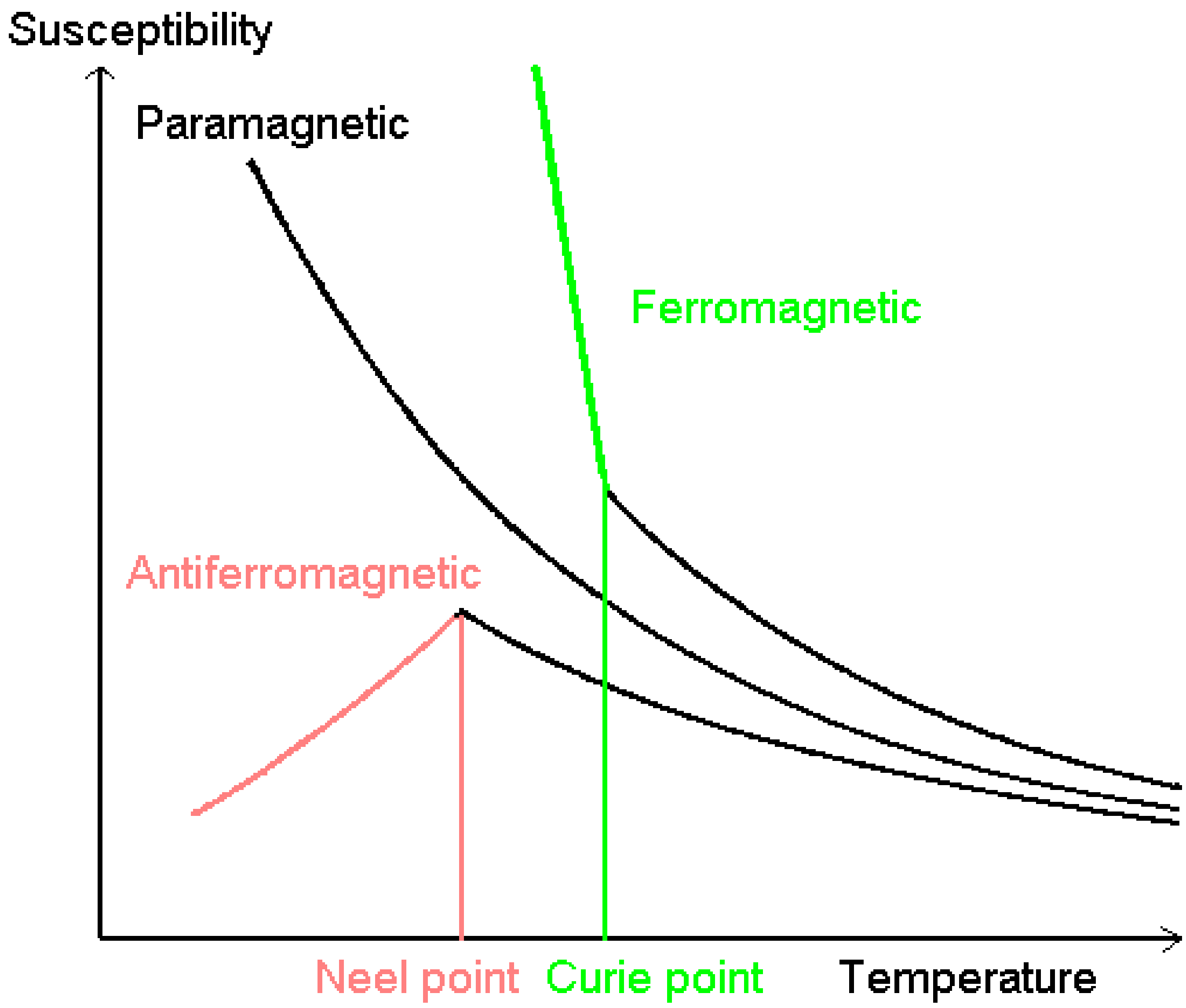
Magnetization (M):
magnetic field induced in sample in external magnetic field (H)

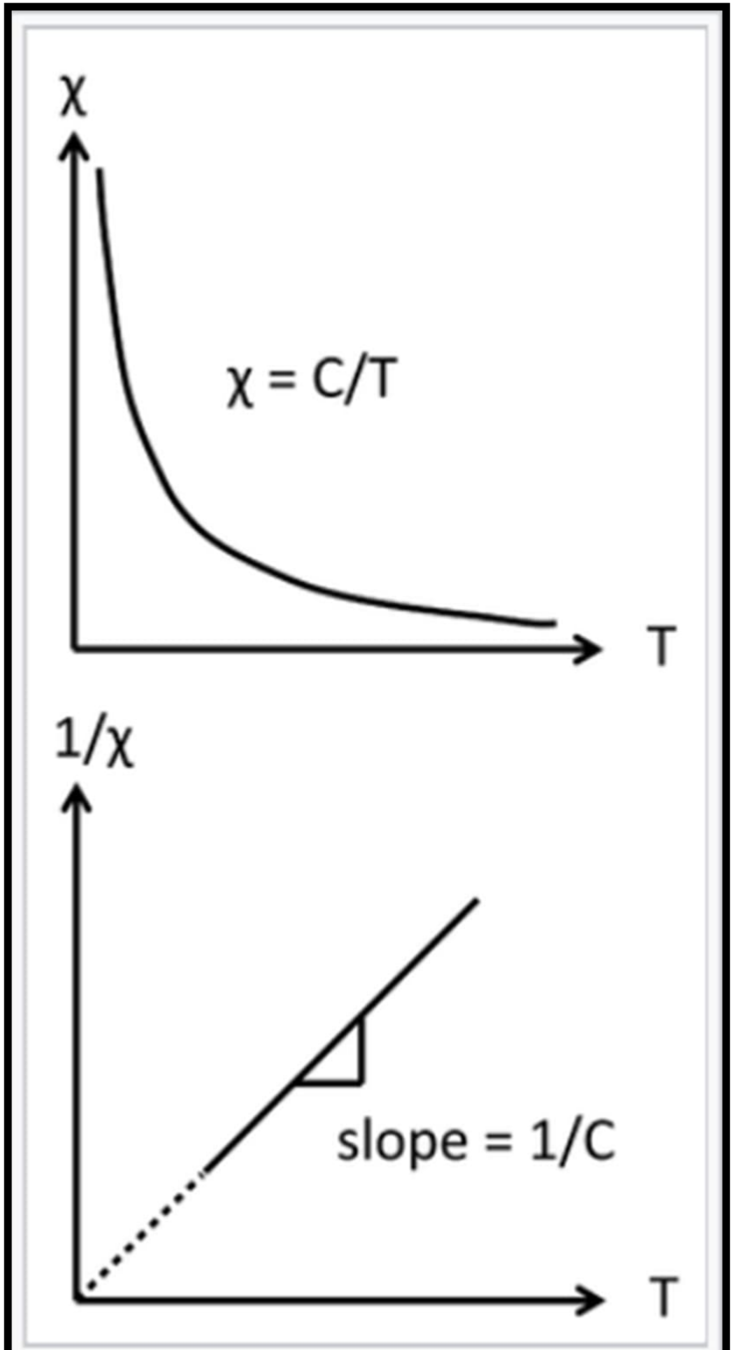
Magnetic susceptibility: $\chi = M / H$

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

Compound	Type of Magnetism	χ at 300K (cm^3/mol)
SiO_2	Diamagnetic	$- 3 \times 10^{-4}$
Pt metal	Pauli paramagnetic	$+ 2 \times 10^{-4}$
$Gd_2(SO_4)_3 \cdot 8H_2O$	Paramagnetic	$+ 5 \times 10^{-2}$
Ni-Fe alloy	Ferromagnetic	$+ 10^4 - 10^6$

MAGNETIZATION in DIFFERENT MAGNETIC MATERIALS





CURIE LAW

- **Temperature dependence of magnetization of paramagnetic materials**
- **External field tends to align magnetic moments, while thermal energy works to the opposite direction**

Curie law: $\chi = C/T$

$C = N_A^2 \mu^2 / 3R$

N_A = Avogadro constant

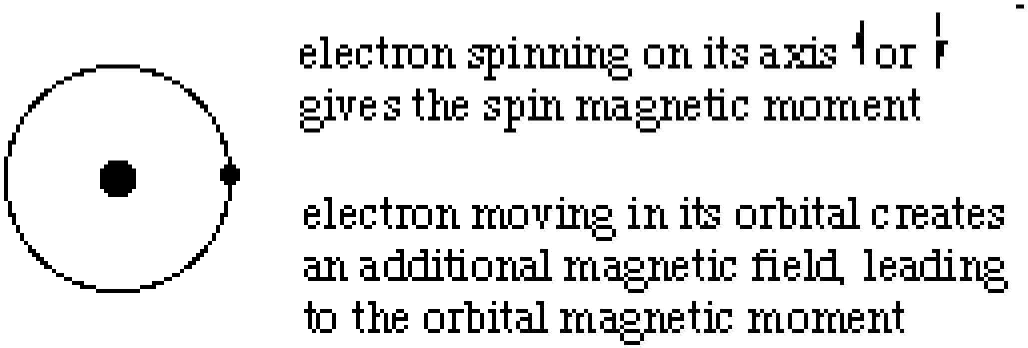
R = gas constant

μ = magnetic moment

MAGNETIC MOMENT (μ)

- $\mu \neq f(T)$
- $\mu_{eff} = \mu / \mu_B$ (μ_B = Bohr magneton = $eh/4\pi m_e c$)
- Magnetic moment consists of terms due to spin (*S*) and orbital motion (*L*)
- For 3*d* transition metals *L* is meaningless:

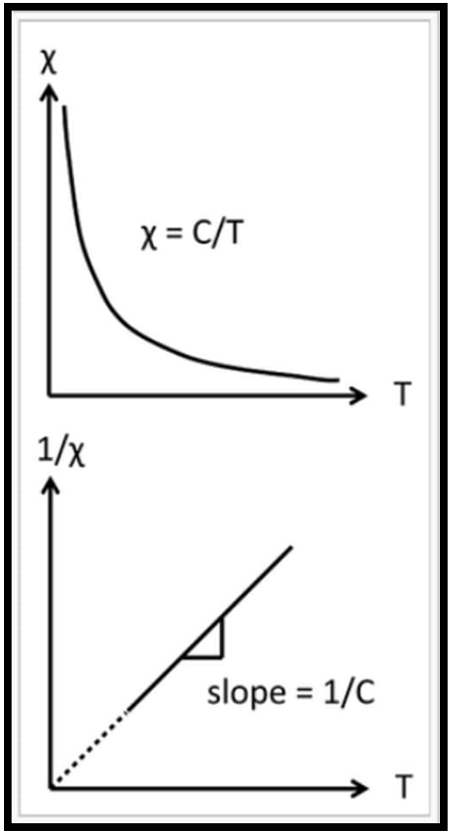
$\mu_{eff} \approx g\sqrt{S(S+1)}$ (free electron: g = 2.00023)



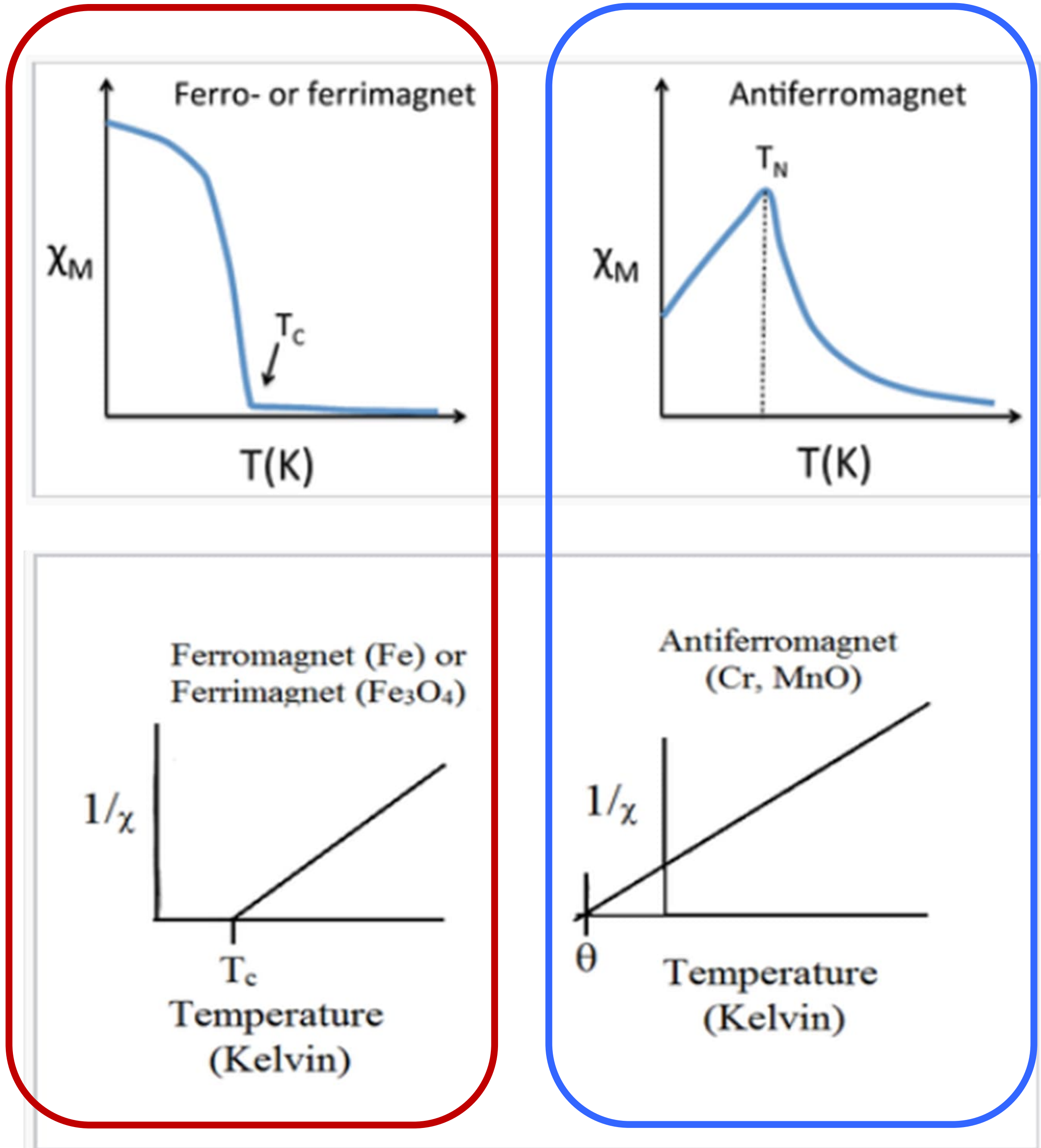
Number of unpaired electrons	Spin-only moment /μ_B
1	1.73
2	2.83
3	3.87
4	4.90
5	5.92

Ion	Number of unpaired electrons	Spin-only moment /μ_B	observed moment /μ_B
Ti^{3+}	1	1.73	1.73
V^{4+}	1		1.68–1.78
Cu^{2+}	1		1.70–2.20
V^{3+}	2	2.83	2.75–2.85
Ni^{2+}	2		2.8–3.5
V^{2+}	3	3.87	3.80–3.90
Cr^{3+}	3		3.70–3.90
Co^{2+}	3		4.3–5.0
Mn^{4+}	3		3.80–4.0
Cr^{2+}	4	4.90	4.75–4.90
Fe^{2+}	4		5.1–5.7
Mn^{2+}	5	5.92	5.65–6.10
Fe^{3+}	5		5.7–6.0

PARAMAGNETIC



FERROMAGNETIC **ANTIFERROMAGNETIC**



CURIE-WEISS LAW

$$\chi = C/T - \theta\ (\approx T_C)$$

$$\chi = C/T + \theta\ (\approx T_N)$$

Curie temperatures (in K)

Co	1388
Sm_2Co_{17}	1070
Fe	1043
$SmCo_5$	990
Fe_3O_4	858
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CrO_2	386
MnAs	318
Gd	292
Dy	88
Er	32
EuO	69

Ferromagnets: T_C [K]

iron	1043
cobalt	1404
nickel	628
gadolinium	289
erbium	32
dysprosium	155
barium ferrite	720
strontium ferrite	720
Alnico	1160
Alumel	436
Mutamel	659
Permalloy	869
Trafoperm	1027
NdFeB	580
$SmCo_5$	990
Sm_2Co_{17}	1070
CrO_2	390
$CuAlMn_3$	???
$La_xCa_{1-x}B_6$	900
MnAs	318
MnBi	633
polymerized C_{60}	~500

Antiferromagnets: T_N [K]

$CoCl_2$	25
CoF_2	38
CoO	291
chromium	475
Cr_2O_3	307
erbium	80
$FeCl_2$	70
FeF_2	79 - 90
FeO	198
FeMn	490
α-Fe_2O_3	953
MnF_2	72 - 75
MnO	122
MnSe	173
MnTe	310 - 323
$NiCl_2$	50
NiF_2	78 - 83
NiFeO	180
NiO	533 - 650
$TiCl_3$	100
UCu_5	15
V_2O_3	170

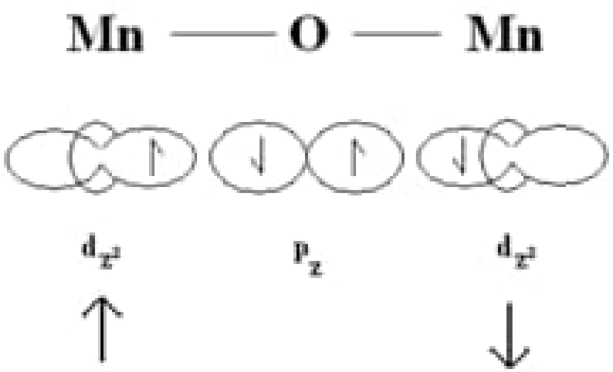
There are many FM and AFM metal oxides (based on Earth-abundant elements !)

SUPEREXCHANGE INTERACTION

- Hendrik Kramers in 1934:

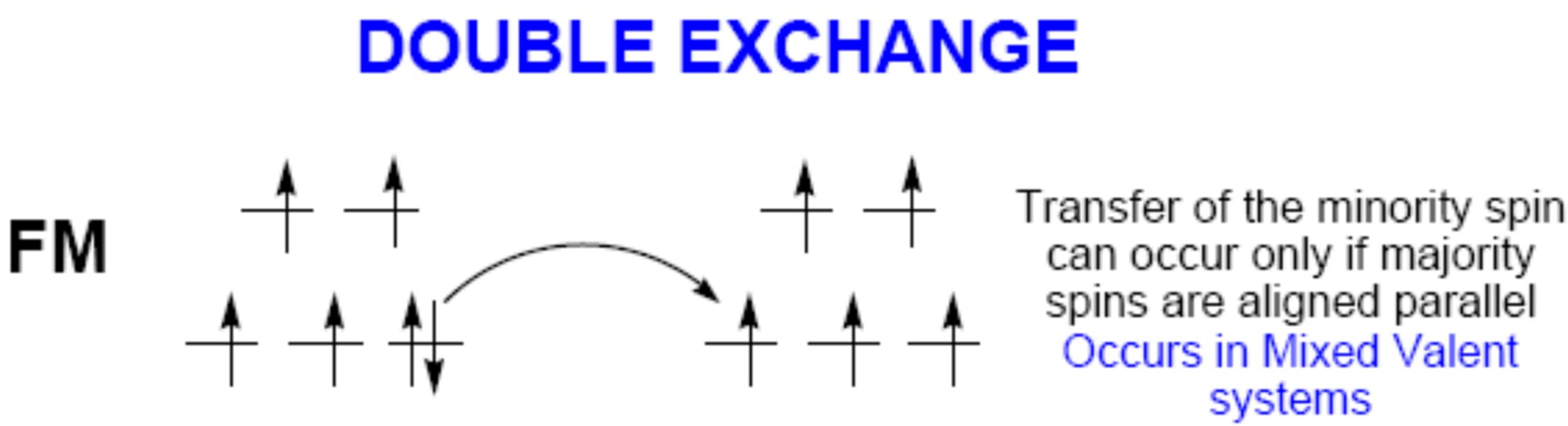
  MnO: interaction of magnetic Mn atoms with each other through nonmagnetic O atoms between them
- Philip Anderson refined the model in 1950
- Explains the strong (usually) antiferromagnetic coupling between two next-to-nearest neighbour positive ions (which are too far apart to have a direct exchange inter-action) through a nonmagnetic anion (such as O^{2-})
- **GOODENOUGH-KANAMORI RULES (1950s):**

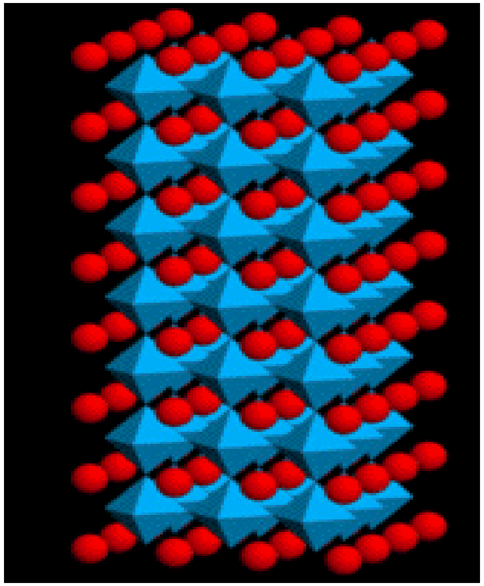
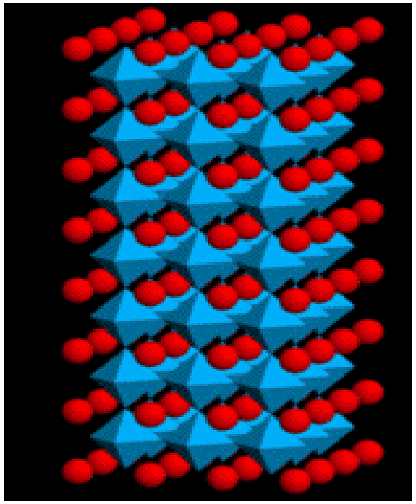
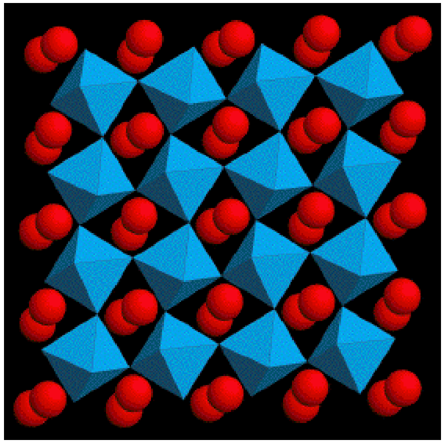
  Semi-empirical rules to predict the type of interaction based on the interact. angle (magn. cation – anion – magn. cation): AFM for180º, FM for 90º



DOUBLE EXCHANGE INTERACTION

- **Proposed by Clarence Zener in 1951**
- **Superexchange considers magnetic (AFM or FM) alignment between two atoms with the same valence, while double-exchange considers the cases when one atom has an extra electron compared to the other**
- **Predicts the relative ease with which an electron may be exchanged between two species, and whether the material is FM, AFM, or neither**
- **Double-exchange: electron movement from one species to another occurs more easily if the electrons do not have to change spin direction**



PEROVSKITE OXIDES A*M*O_3

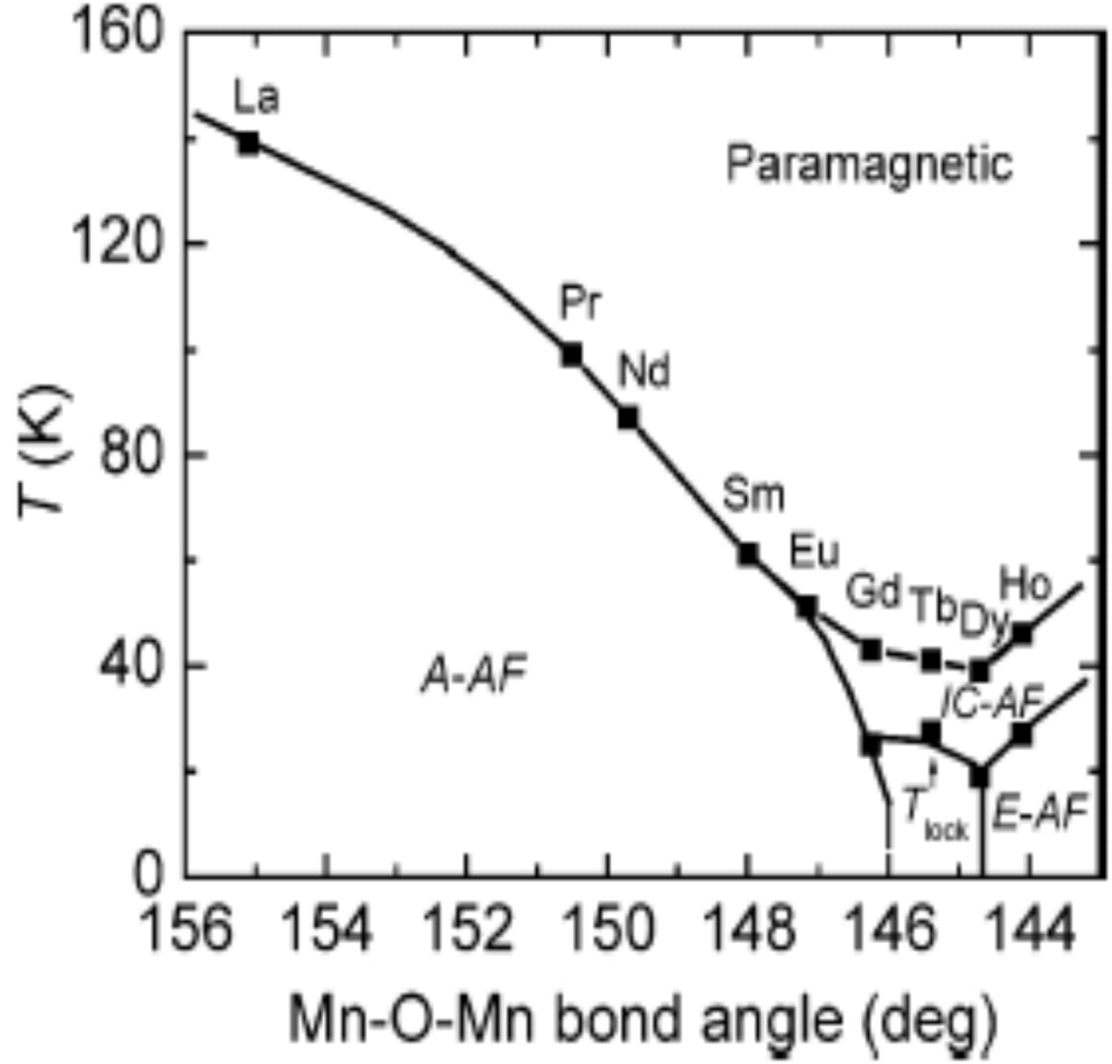
- **Magnetic interactions are maximized and transition temperature increased by:**

  - decreasing *M*-O-*M* bond length

  - increasing *M*-O-*M* bond angle (closer to 180°)

  - these two requirements are often contradictory

$LnMnO_3$



Y.H. Huang, H. Fjellvåg, M. Karppinen, B.C. Hauback, H. Yamauchi & J.B. Goodenough, Crystal and magnetic structure of the orthorhombic perovskite $YbMnO_3$, *Chemistry of Materials* **18**, 2130 (2006).

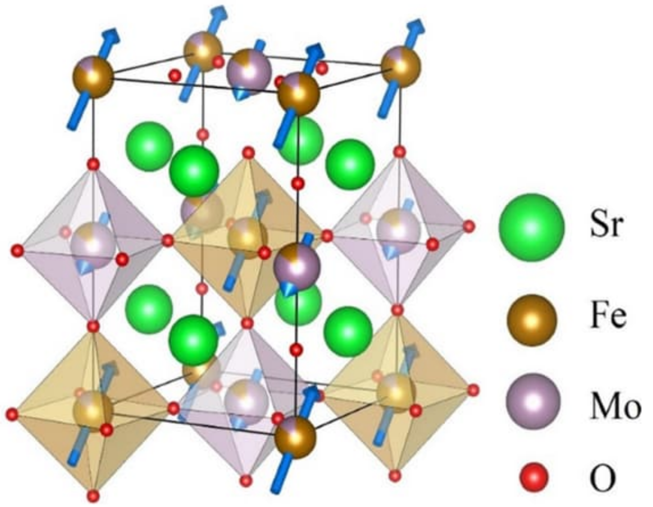
FERROMAGNETIC A_2FeMoO_6 Double Perovskite (Halfmetal)

- **With decreasing $r(A^{II})$ the crystal symmetry is lowered:**

  - cubic (*Fm*3*m*) for *A* = Ba

  - tetragonal (*I*4/*m*) for *A* = Sr

  - monoclinic (*P*21/*n*) for *A* = Ca



- **T_C shows a bell-shaped behaviour:**

  - 330 K for *A* = Ba

  - 410 K for *A* = Sr

  - 320 K for *A* = Ca

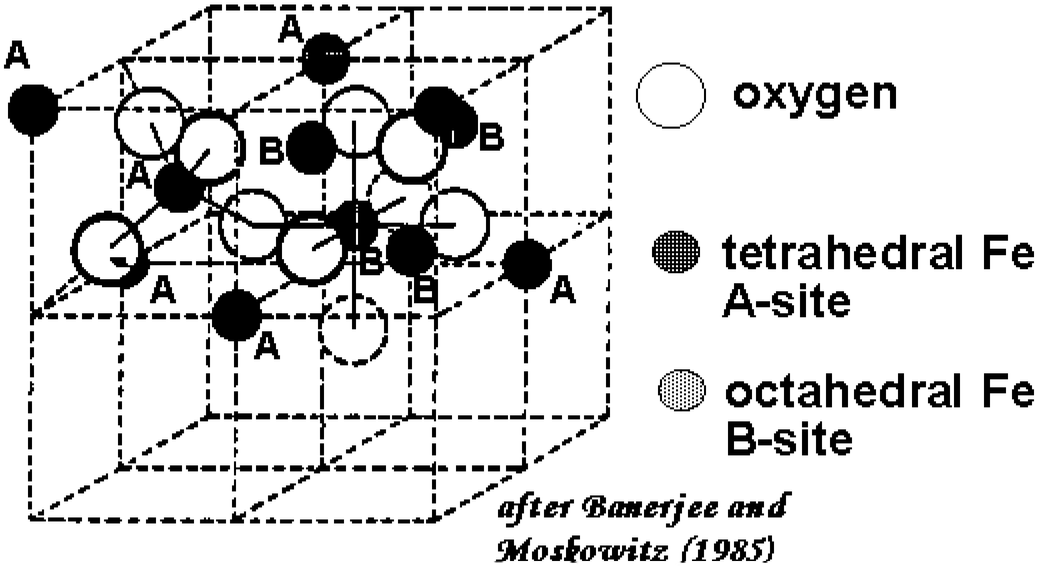
- **T_C increases with decreasing Fe-O-Mo bond distance and increasing Fe-O-Mo bond angle:**

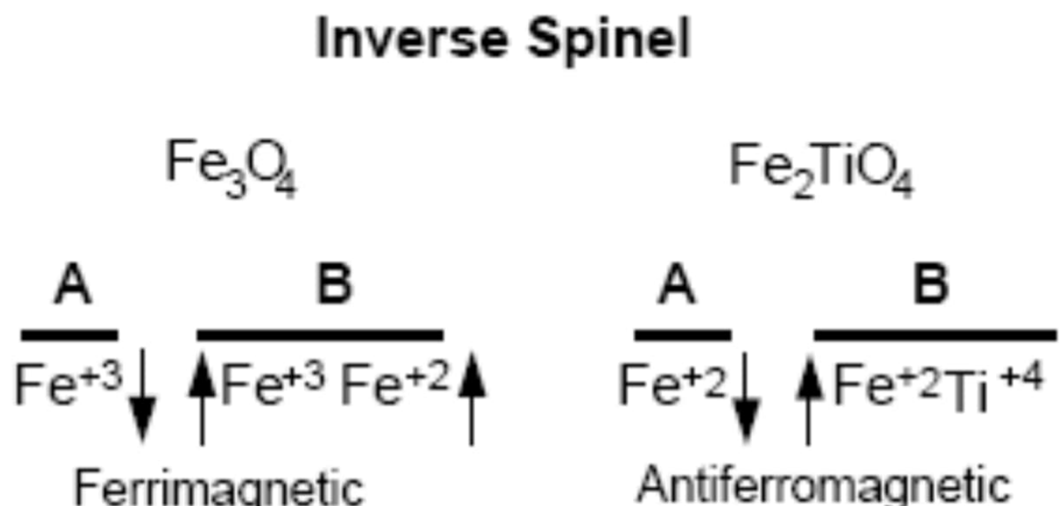
  - when going from Ba to Sr, T_C increases as a concequence of the decreasing bond distance

  - when going from Sr to Ca the effect of the decreased bond distance is less influential than the decrease in the Fe-O-Mo bond angle

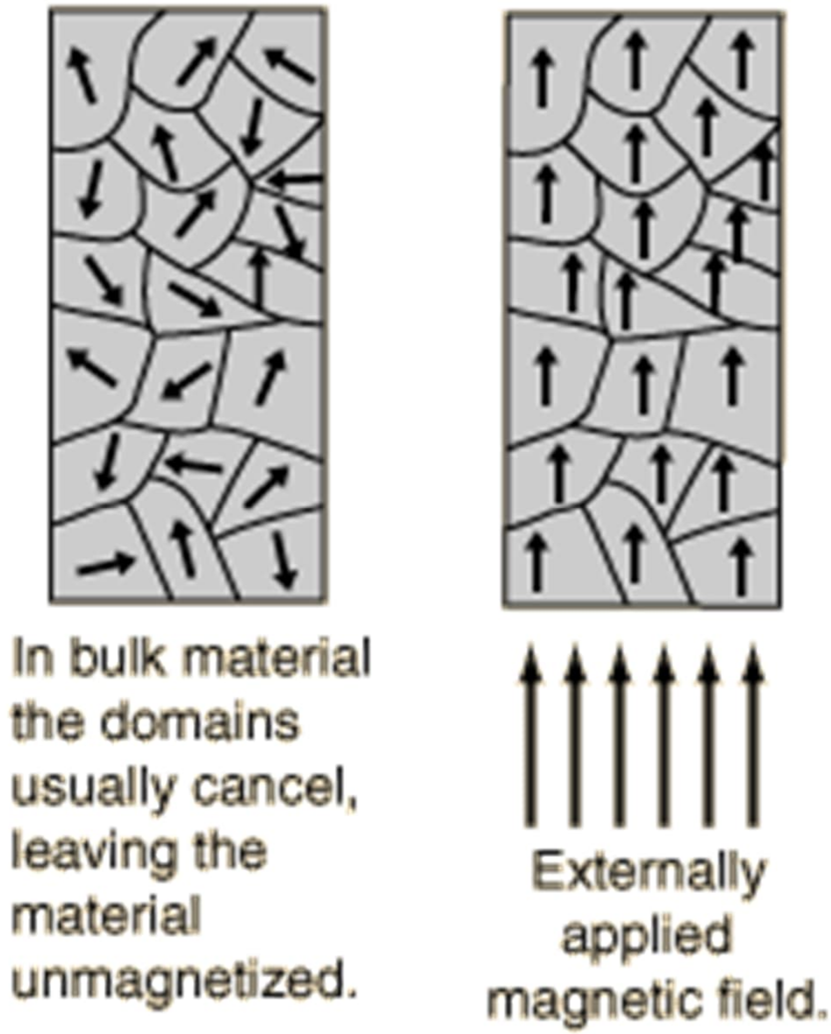
Spinel: $A^{II}B^{III}{}_2O_4$

Inverse spinel: $B^{III}(A^{II}B^{III})O_4$



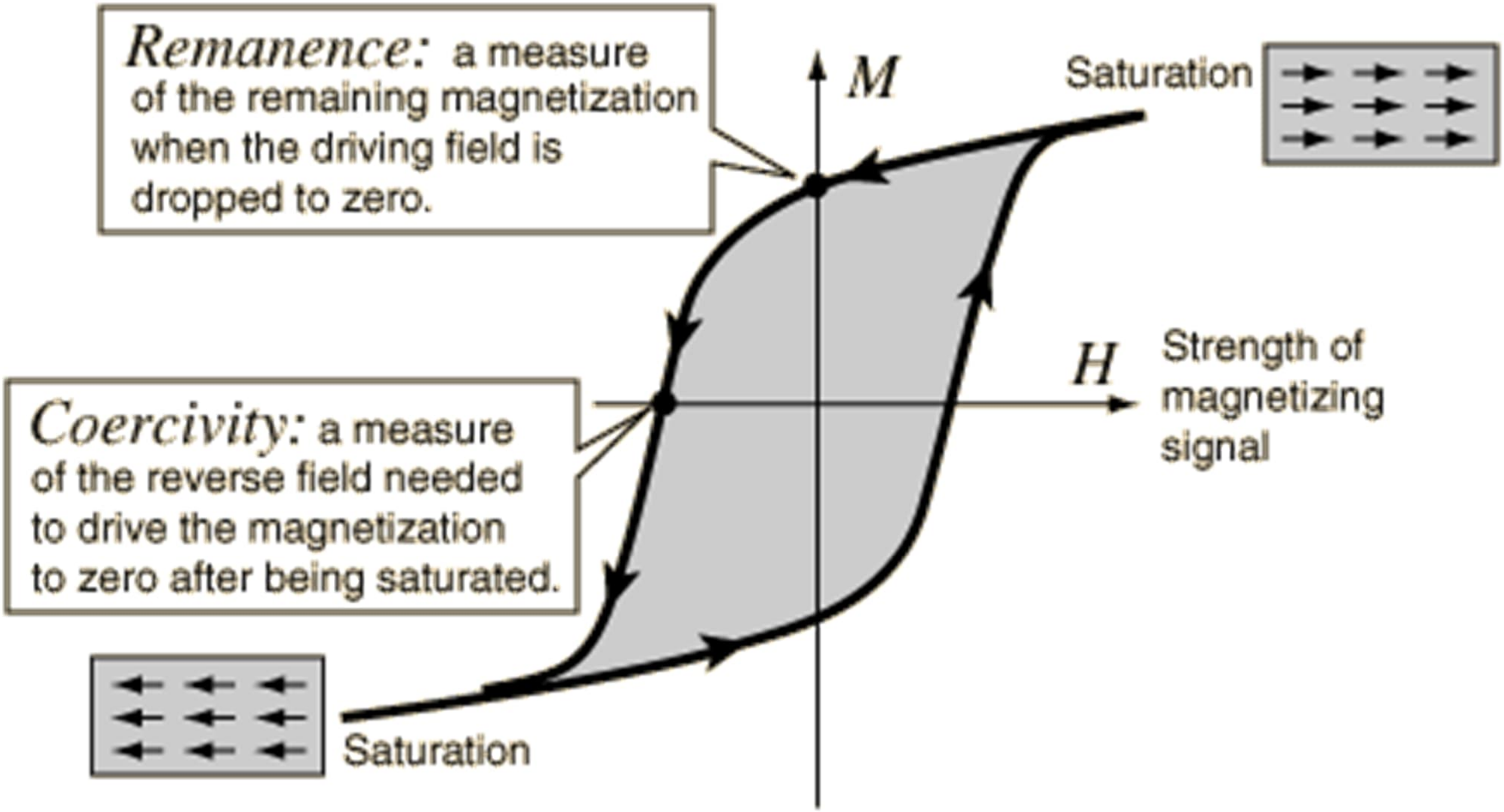


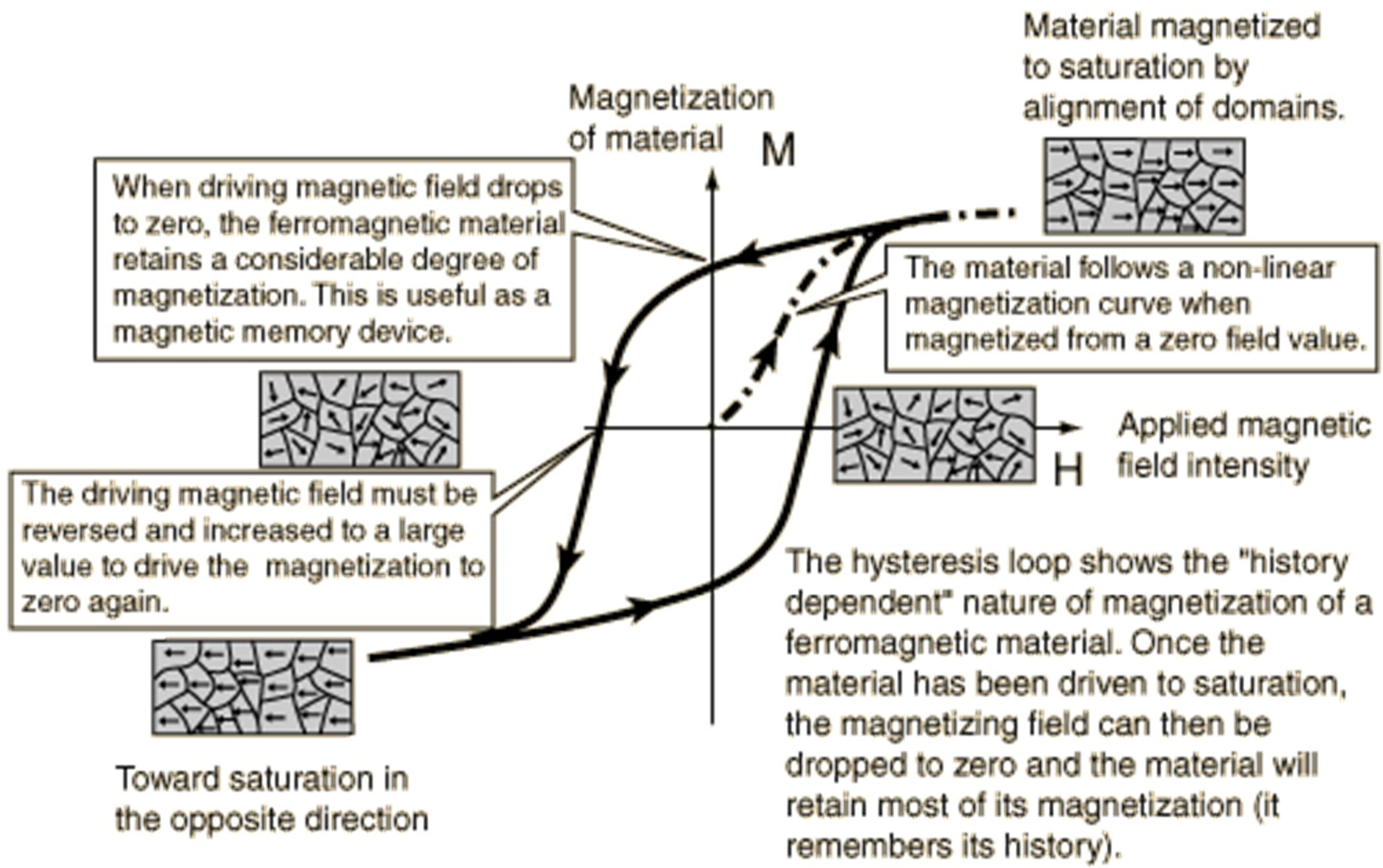
FERROMAGNETIC DOMAINS



Hystersis Loop of Ferromagnetic Materials

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

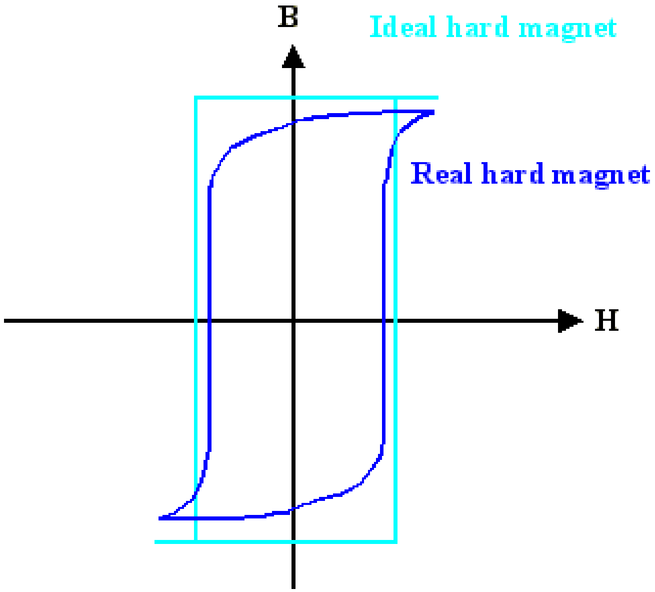


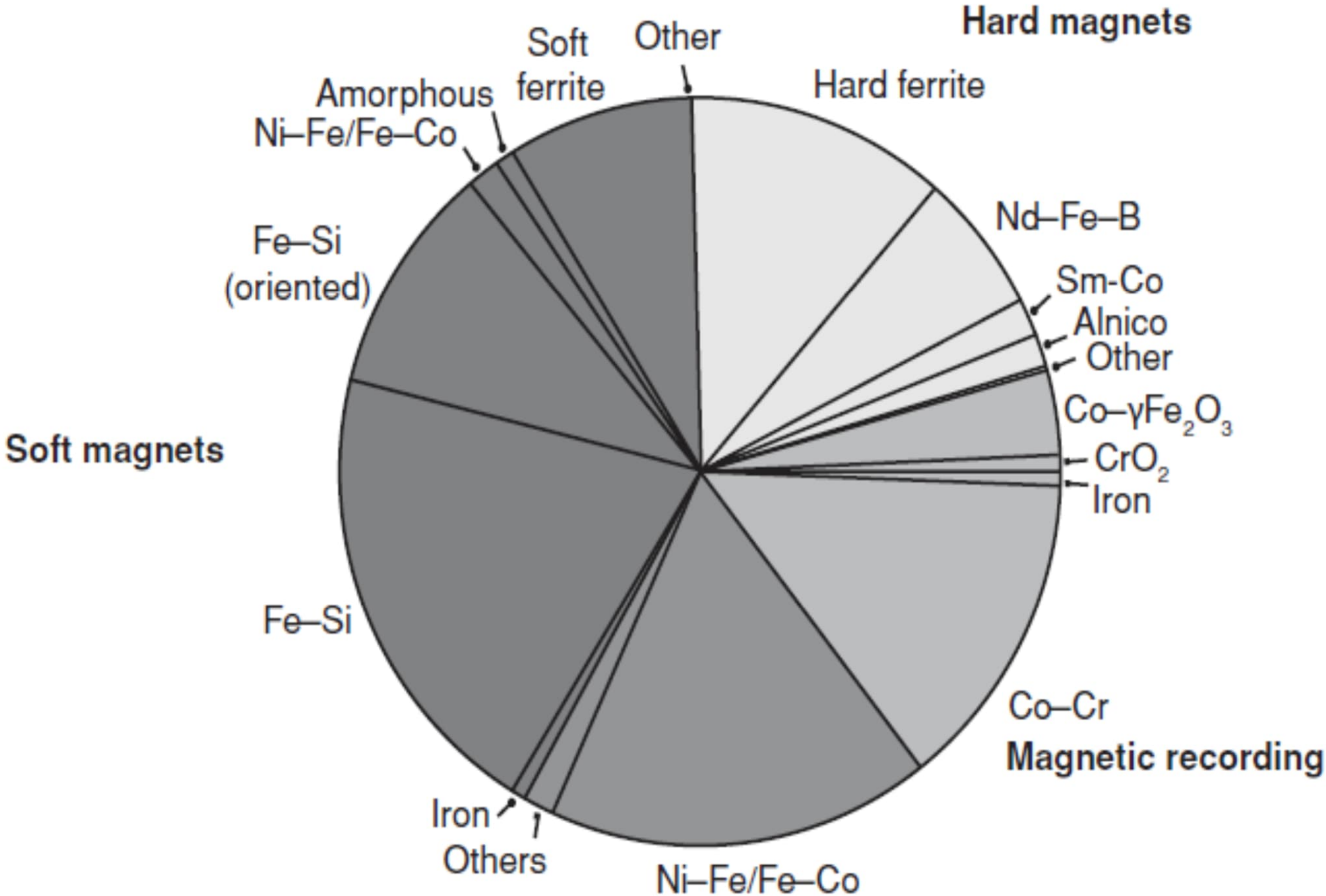

Material magnetized
to saturation by
alignment of domains.
Magnetization
of material
M
When driving magnetic field drops to zero, the ferromagnetic material retains a considerable degree of magnetization. This is useful as a magnetic memory device.
The material follows a non-linear magnetization curve when magnetized from a zero field value.
Applied magnetic
field intensity
H
The driving magnetic field must be reversed and increased to a large value to drive the magnetization to zero again.
The hysteresis loop shows the "history dependent" nature of magnetization of a ferromagnetic material. Once the material has been driven to saturation, the magnetizing field can then be dropped to zero and the material will retain most of its magnetization (it remembers its history).
Toward saturation in
the opposite direction

HARD MAGNETS

- Magnetically hard (true permanent magnets)
- Retain magnetic properties well when external field is removed/reversed
- Large coersivity
- Needed for many applications (soft magnets needed too for some applications)

Material	Coercivity [T]	Remanence [T]
$BaFe_{12}O_{19}$	0.36	0.36
Alnico IV	0.07	0.6
Alnico V	0.07	1.35
Alcomax I	0.05	1.2
MnBi	0.37	0.48
$Ce(CuCo)_5$	0.45	0.7
$SmCo_5$	1.0	0.83
Sm_2Co_{17}	0.6	1.15
$Nd_2Fe_{14}B$	1.2	1.2

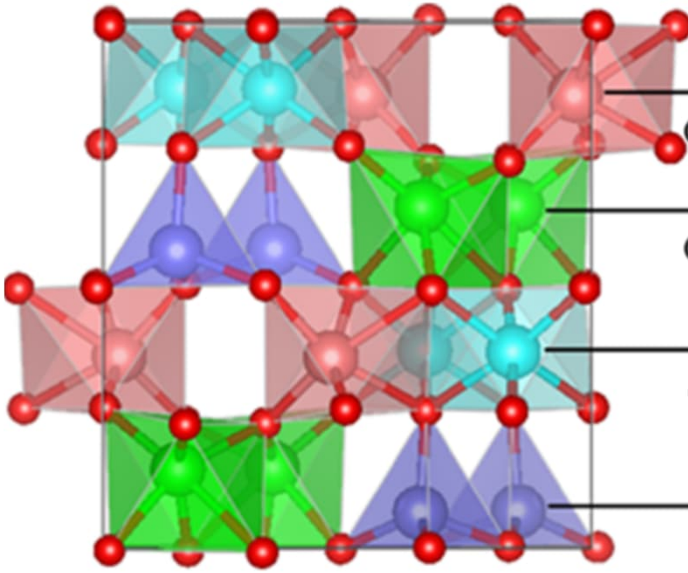




Hard magnets
Other
Soft
ferrite
Amorphous
Ni–Fe/Fe–Co
Hard ferrite
Nd–Fe–B
Sm-Co
Alnico
Other
Fe–Si
(oriented)
Co–γFe2O3
CrO2
Iron
Soft magnets
Fe–Si
Co–Cr
Magnetic recording
Iron
Others
Ni–Fe/Fe–Co

ε-Fe_2O_3

- Simple & critical-raw-material-free
- Rarest of the Fe_2O_3 polymorfs
- RT ferrimagnet ($T_C \approx 490$ K)
- Colossal coercivity
- Magnetoelectric
- BUT: Challenging synthesis



1934: First observed by Forestier and Guiot-Guillain

1963: Named by Schrader and Buttner

2004: Synthesis of pure ε-Fe_2O_3 with giant coercive field values (up to 2 T)
- J. Jin, S.I. Ohkoshi & K. Hashimoto, Adv. Mater. 16, 48 (2004)

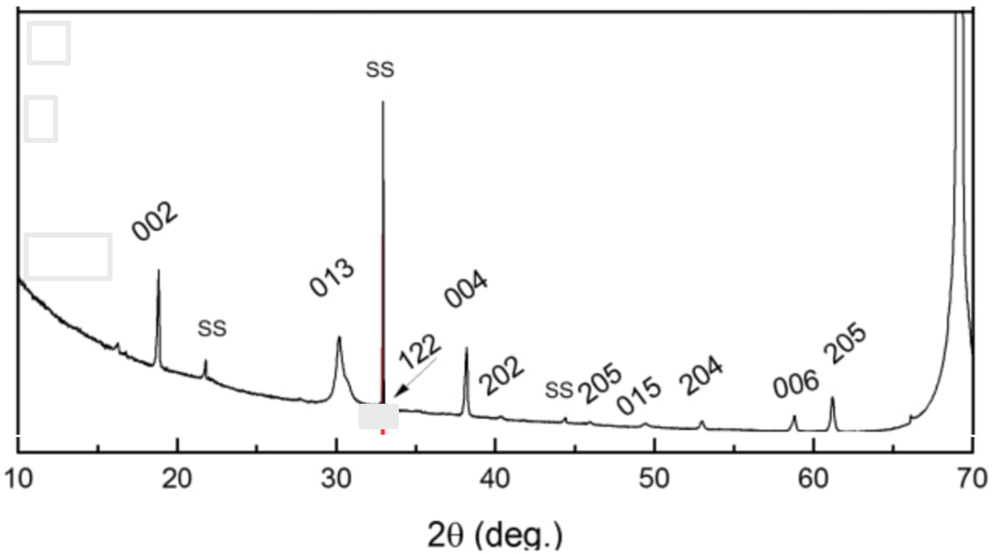
State-of-the-art: Synthesized in nano-scale/trace amounts only
- J. Tuček, R. Zbořil, A. Namai & S.I. Ohkoshi, Chem. Mater. 22, 6483 (2010)

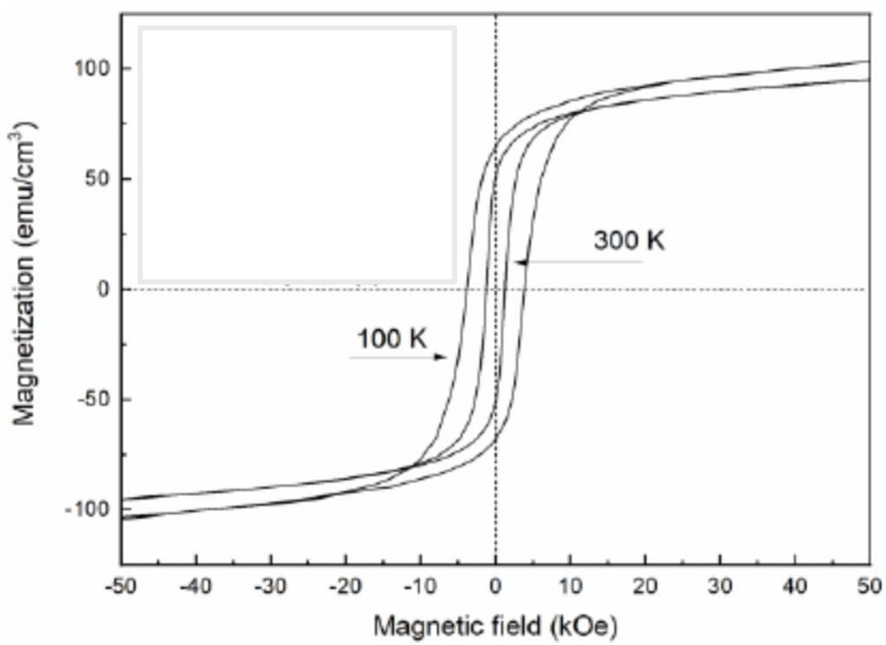
2017: ALD of ε-Fe_2O_3 thin films
- A. Tanskanen, O. Mustonen & M. Karppinen, APL Mater. 5, 056104 (2017)

Facile ALD process for stable ε-Fe_2O_3 thin films

- Just "most common" precursors: $FeCl_3$ & H_2O
- Deposition temperature: 280 ºC
- Substrate: silicon, flexible glass, Kapton, polyimide, etc.

ALD: large-area homogeneity & conformality over porous templates → "MASS production"

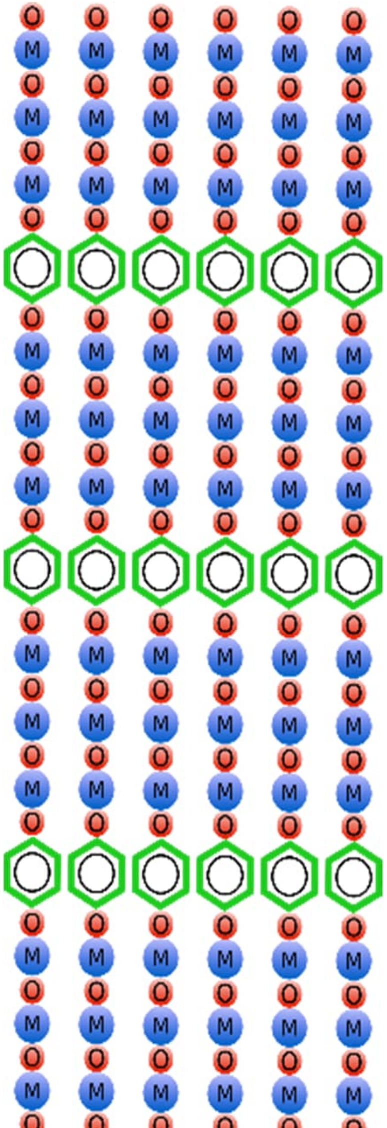




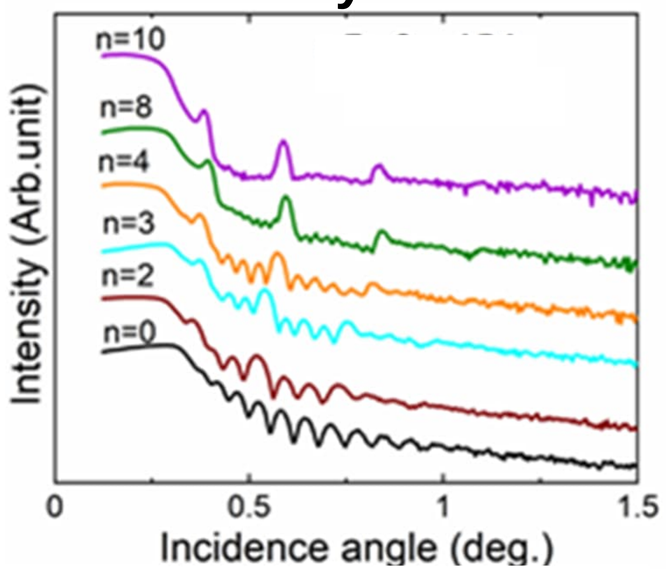
A. Tanskanen, O. Mustonen & M. Karppinen, Simple ALD process for ε-Fe_2O_3 thin films, *APL Materials* **5**, 056104 (2017).

ε-Fe_2O_3:Organic Superlattices (SL) by ALD/MLD

ORGANICS: terephthalic acid (TPA) or azobenzene (AZO)

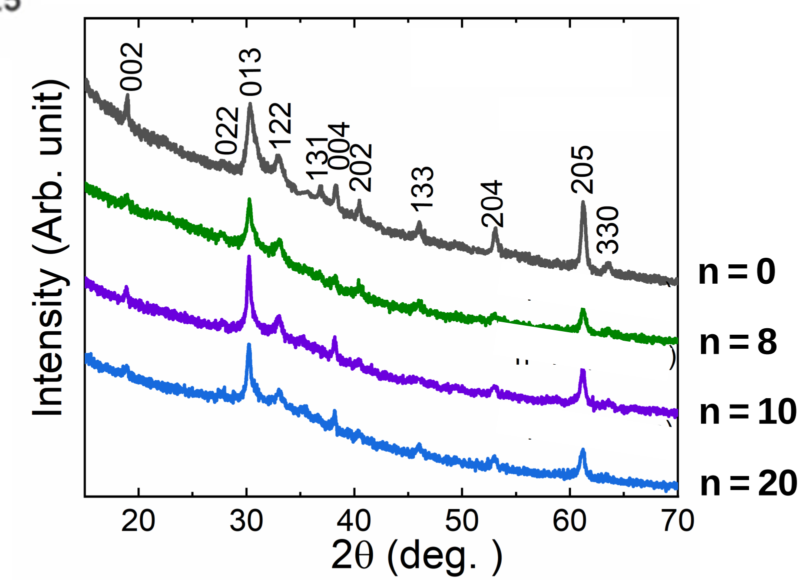


XRR: X-ray reflection

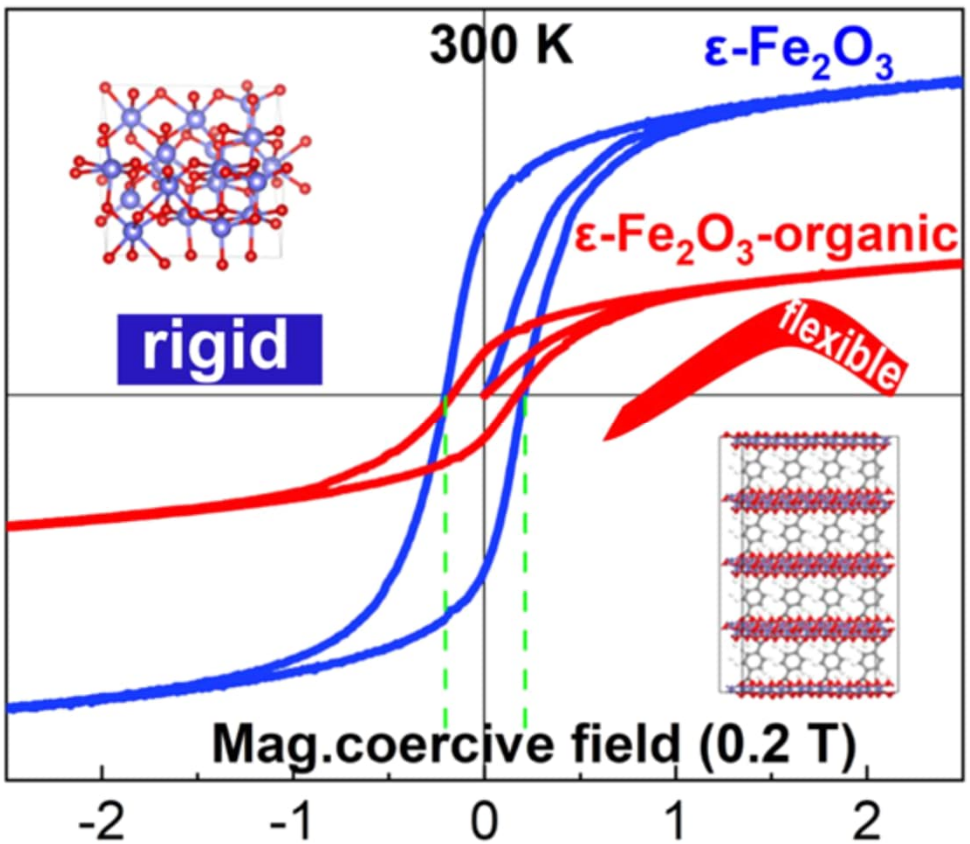


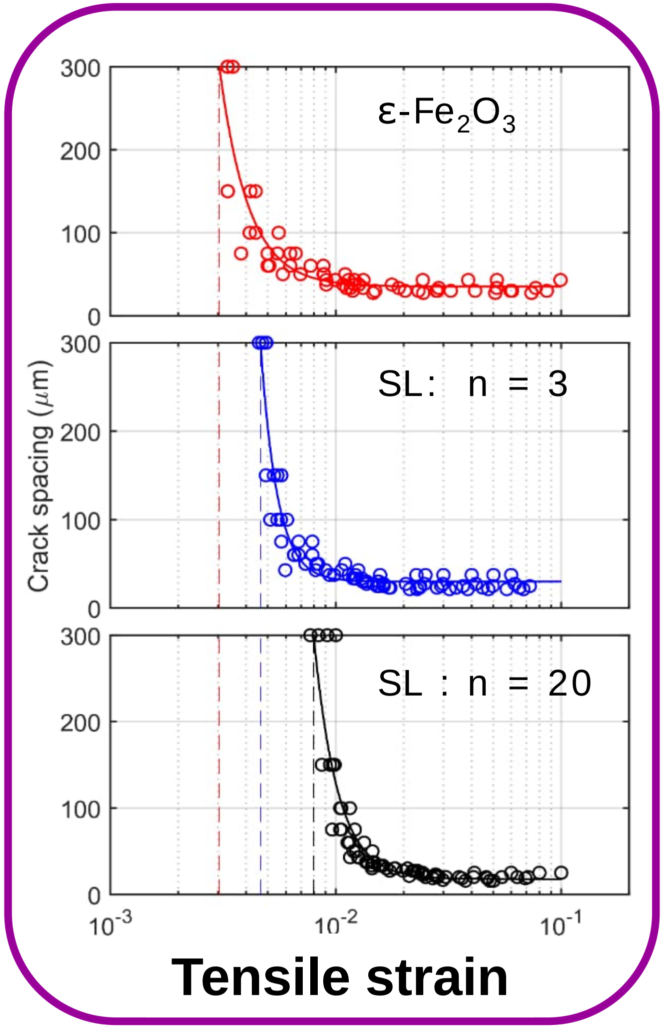
n: number of organic layers

GI-XRD



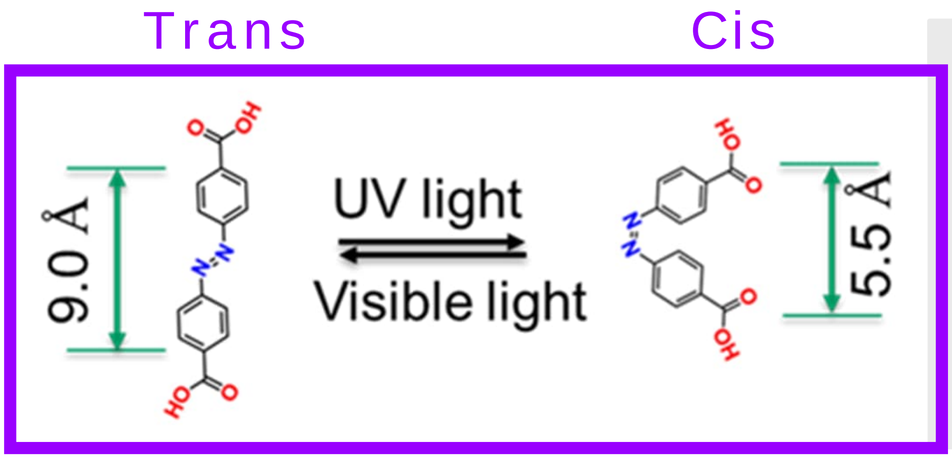
MECHANICALLY FLEXIBLE: ε-Fe_2O_3:TPA

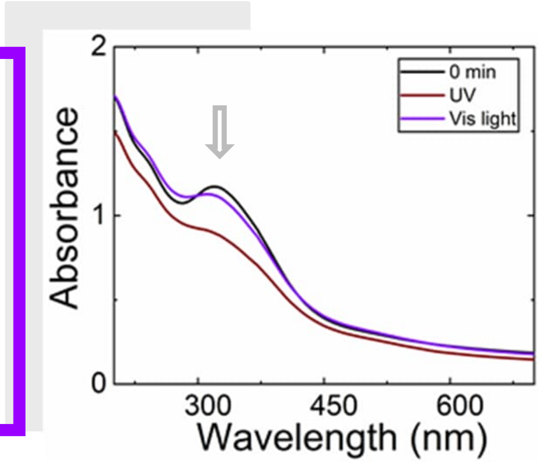




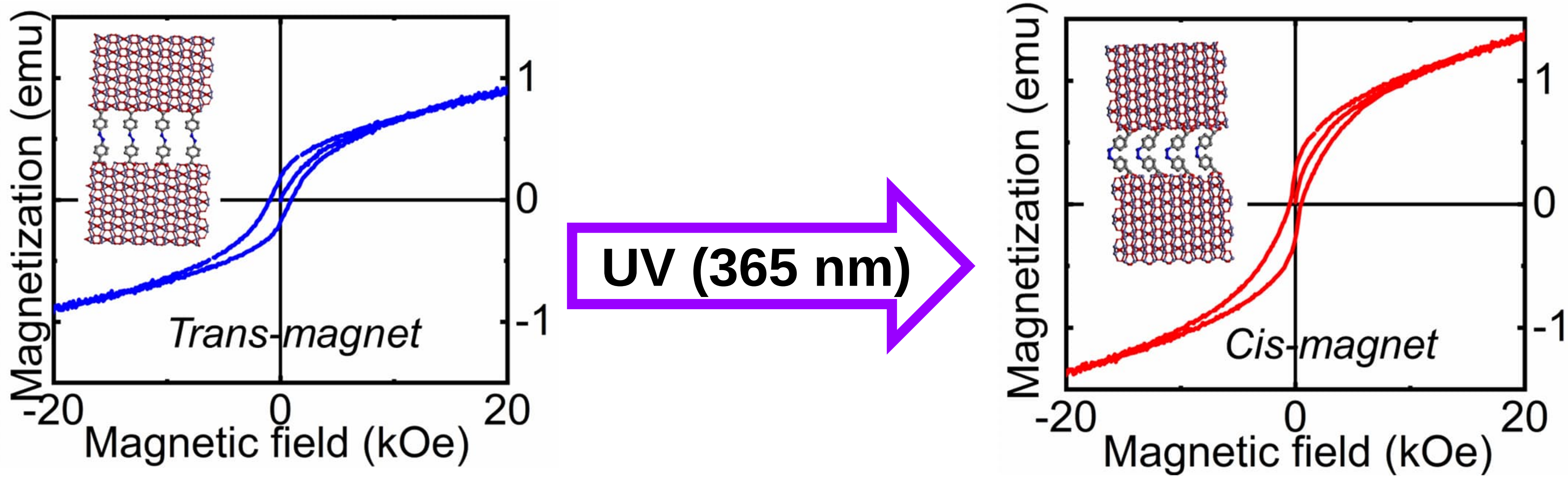
A. Philip, J.-P. Niemelä, G.C. Tewari, B. Putz, T.E.J. Edwards, M. Itoh, I. Utke & M. Karppinen, Flexible ε-Fe_2O_3-terephthalate thin-film magnets through ALD/MLD, *ACS Appl. Mater. Interfaces* 12, 21912 (2020).

PHOTOSWITCHABLE: ε-Fe_2O_3:AZO





UV absorption: trans-cis transition is reversible



- **Magnetization** **(remanent and saturation)** **increased** **(doubled)**
- **Coercivity decreased** **(into half)**

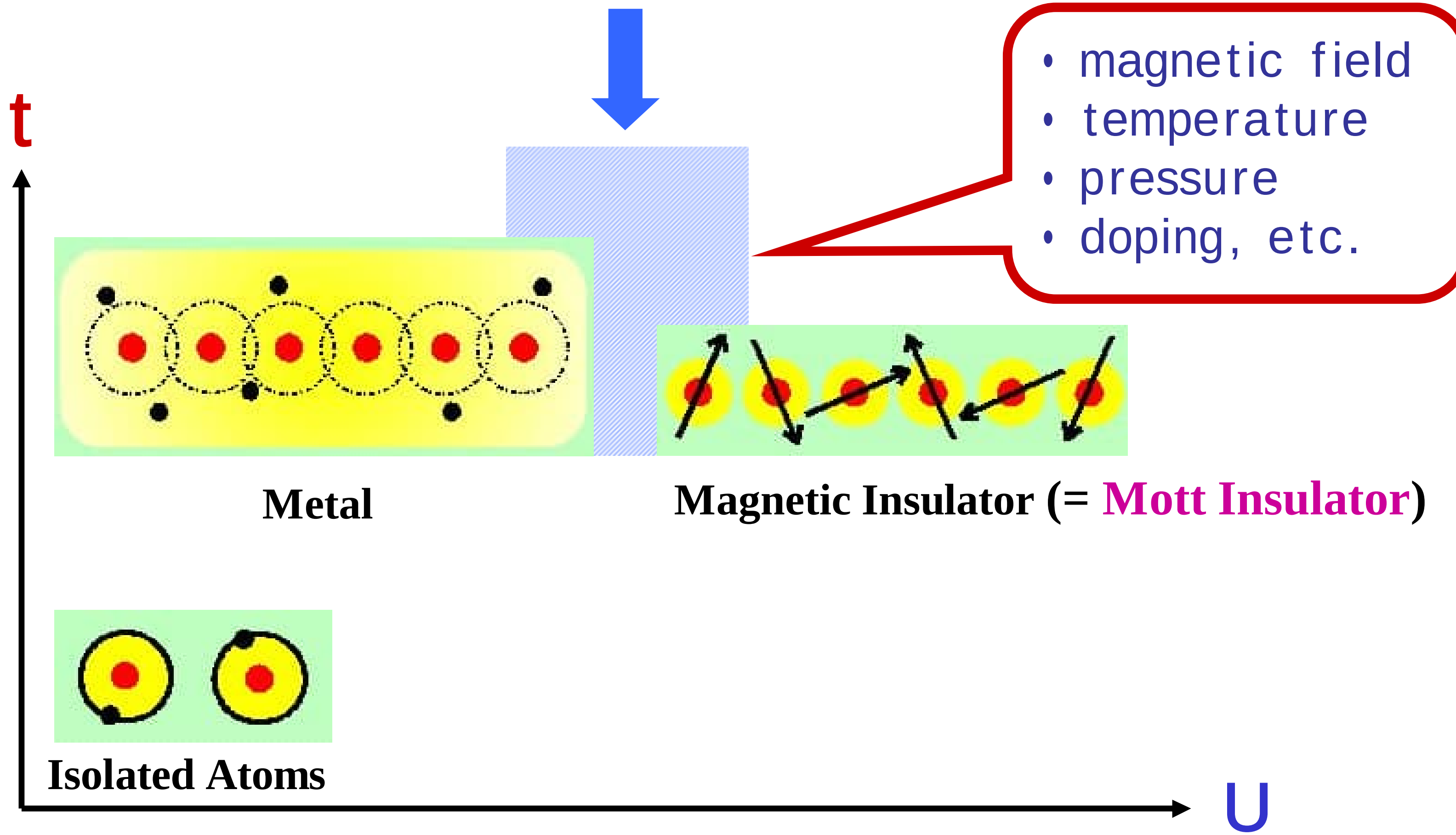
STRONGLY-CORRELATED-ELECTRON MATERIALS

- "Electron correlation" ≈ "Repulsion between (outer) electrons"
- Strongly-correlated-electron materials show unusual (but useful) electronic and magnetic properties
- Many transition metal oxides are strongly-correlated-electron materials: high-T_c superconductors, thermoelectrics, halfmetallic magnetoresistors, Mott insulators, heavy-fermion materials, *etc*.
- Strongly-correlated-electron materials typically have partially-filled *d* or *f* orbitals with narrow bands
- Once the electron correlations are strong, each single electron has a complex influence on its neighbours and ordinary electronic band structure calculation techniques do not work

Strongly-Correlated Finns

Strongly-Correlated-Electron Materials

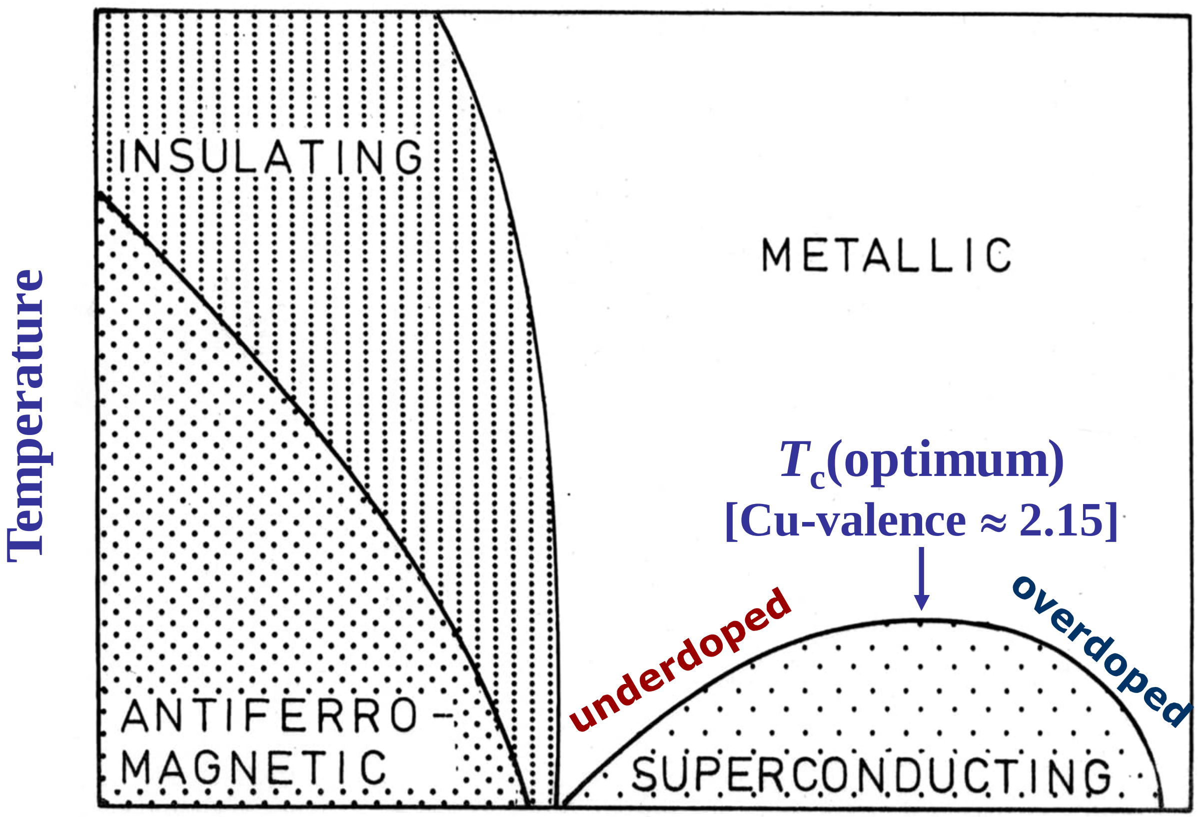
- **Band-picture does not work**
- NOVEL FUNCTIONS

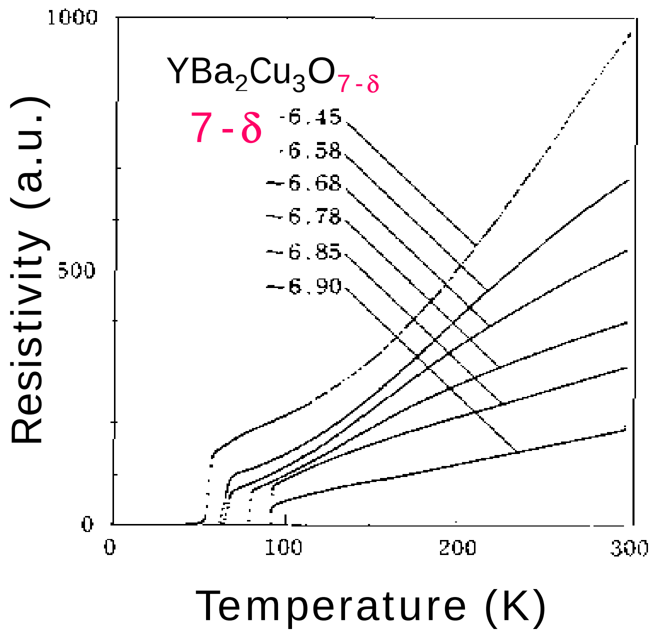


t : overlap of wave functions (= orbitals)

U : strength of electron repulsion (= correlation)

Phase Diagram of HTSC





CuO_2-plane hole concentration (valence of copper)

Chemistry