Transition Elements

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Definition

- What is transition metal ?

  One of which forms one or more stable ions which have incompletely filled *d* orbitals.

$_{30}Zn$?

Definition

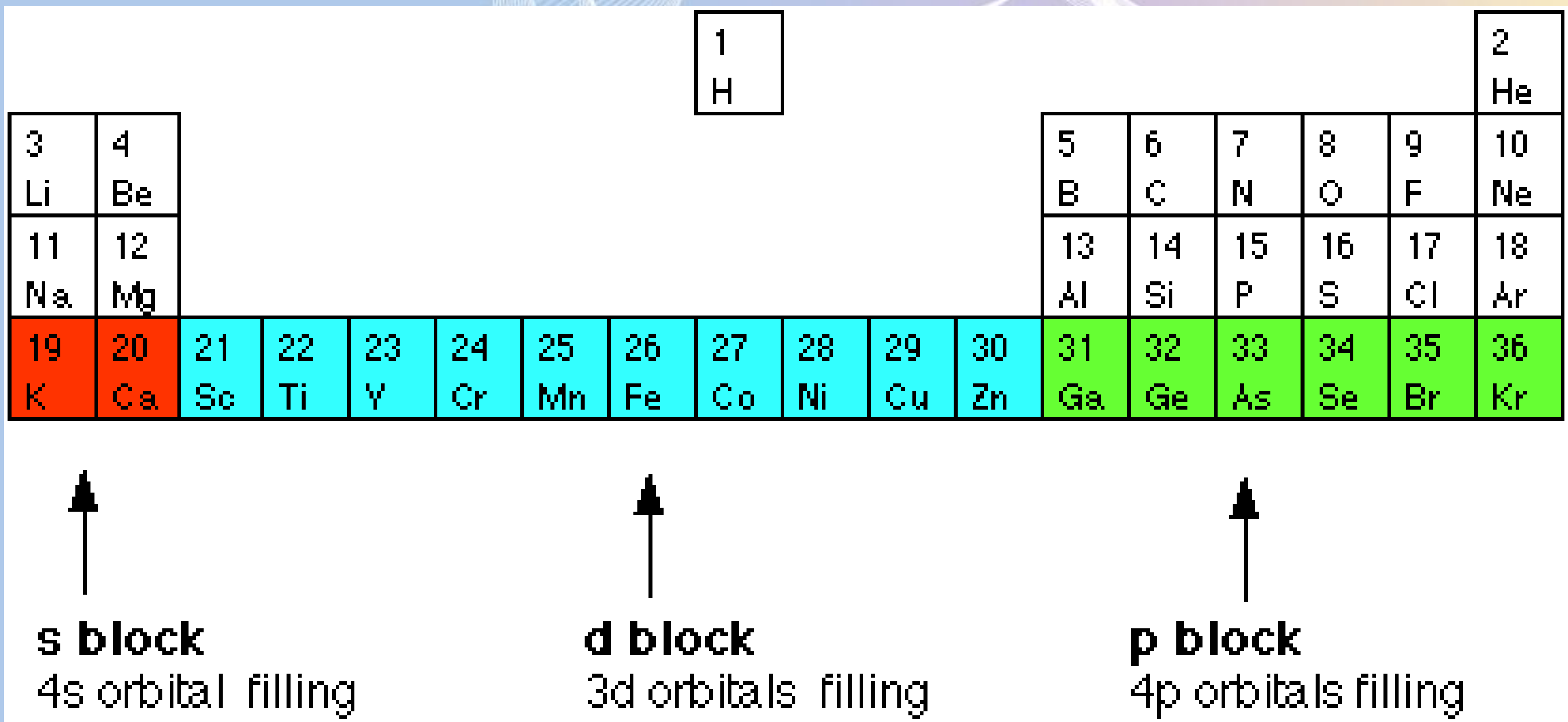
- Zink is not transition elements
  - Zn → has fully filled *d* orbital

Electronic configuration

- charge (atomic number) >>, stability of (n-1)d >> ns
- ionization energy of (n-1)d >> ns
- filled orbital energy of (n-1) d << ns
- electronic configuration writing
  - (n-1)d ns not ns (n-1)d

Electronic configuration

Electronic structures of the d block elements



Electronic configuration

- $_{21}Sc$: [18Ar] $3d^{1}4s^{2}$
- $_{22}Ti$: [18Ar] $3d^{2}4s^{2}$
- $_{23}V$: [18Ar] $3d^{3}4s^{2}$
- $_{24}Cr$: [18Ar] $3d^{5}4s^{1}$
- $_{25}Mn$: [18Ar] $3d^{5}4s^{2}$

$_{26}Fe$: [18Ar] $3d^{6}4s^{2}$

$_{27}Co$: [18Ar] $3d^{7}4s^{2}$

$_{28}Ni$: [18Ar] $3d^{8}4s^{2}$

$_{29}Cu$: [18Ar] $3d^{10}4s^{1}$

$_{30}Zn$: [18Ar] $3d^{10}4s^{2}$

Several energy terms to think about

- The amount of energy needed to ionize the metal

- The amount of energy released when the compound formed (as lattice enthalpy in solids, or the hydration enthalpies of the ions in solution)

Several energy terms to think about

- Charged the ion >>, electrons to be removed >> ionization energy >>

- Charged the ion >>, energy to be released (as lattice enthalpy or the hydration enthalpy of the metal ion) >>

Several energy terms to think about

- The more energy released, the more stable the compound

Oxidation state

- ${}_{21}Sc$: +1, +2, +3 → +3 is most stable oxidation state

- ${}_{22}Ti$: +1, +2, +3,+4 → +4 is the most stable oxidation state

Oxidation state

- Iron
  - Iron has two common oxidation states (+2 and +3), for example, Fe^{2+} or $[Fe(H_2O)_6]^{2+}$ and Fe^{3+}or $[Fe(H_2O)_6]^{3+}$
  - It also has a less common +6 oxidation state in the ferrate(VI) ion, FeO_4^{2-}.

Oxidation state

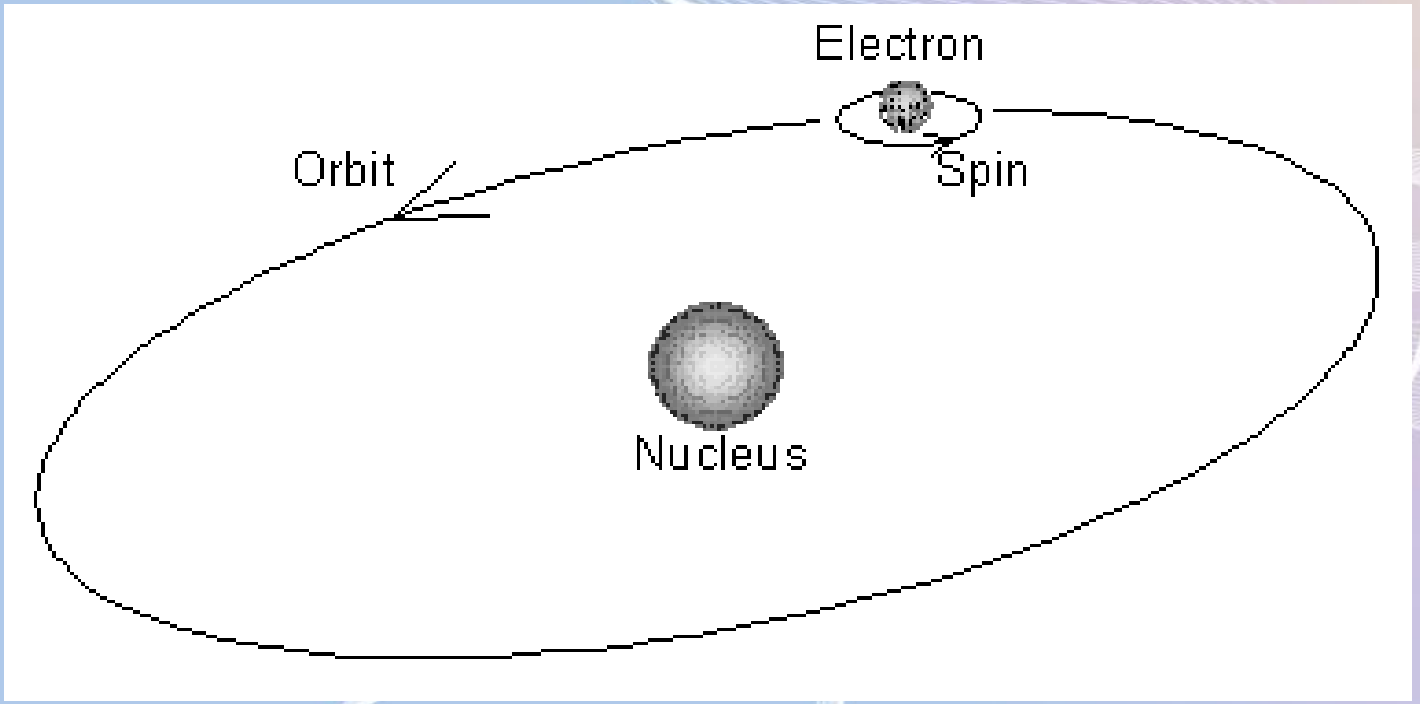
- Manganese

Manganese has a very wide range of oxidation states in its compounds. For example:

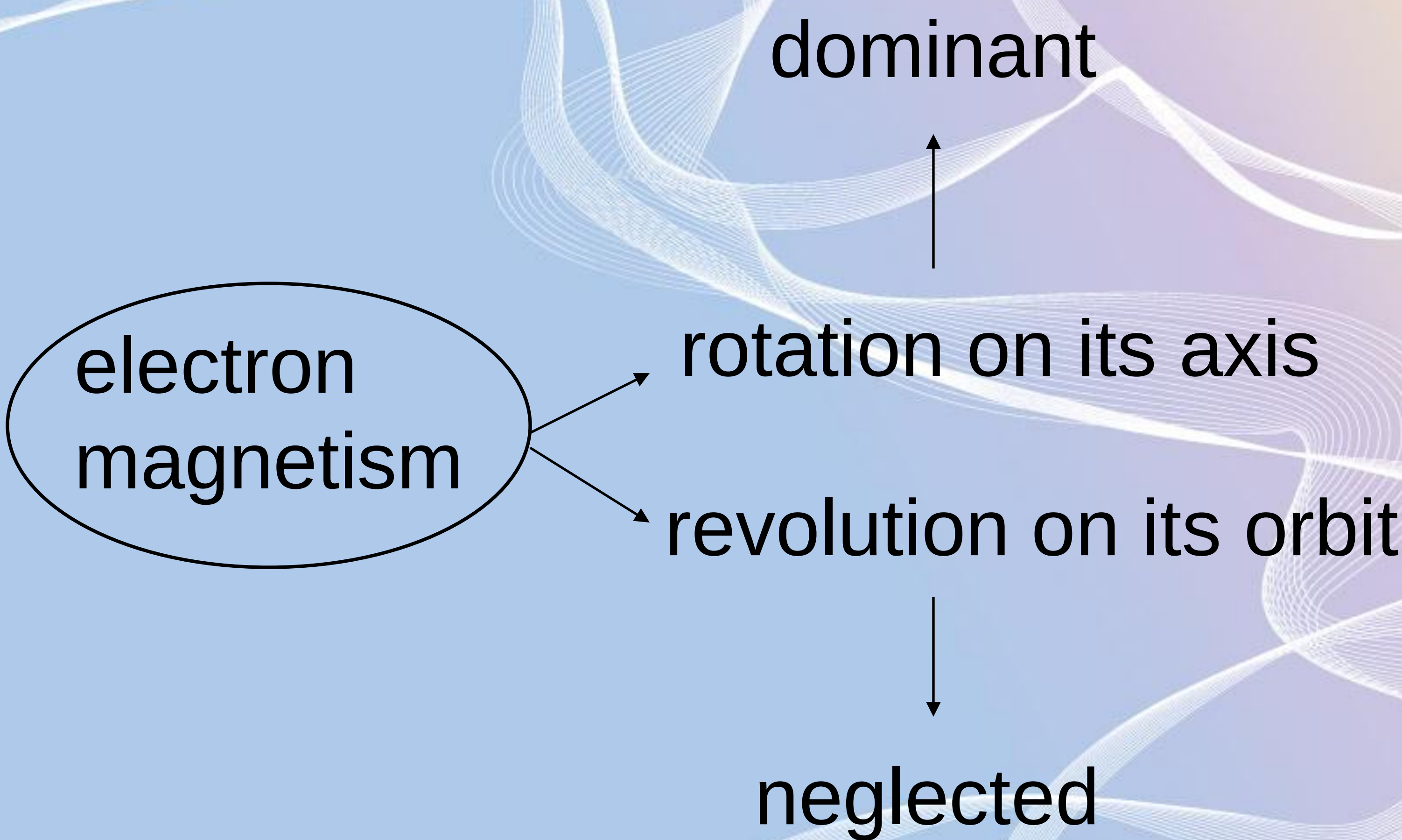
+2 (Mn^{2+}),
+3 (Mn_2O_3),
+4 (MnO_2),
+6 (MnO_4^{2-}),
+7 (MnO_4^-)

The origin of magnetism

- Electron (as particle → mass) → spinning on its axis → magnetism→ magnet elemental



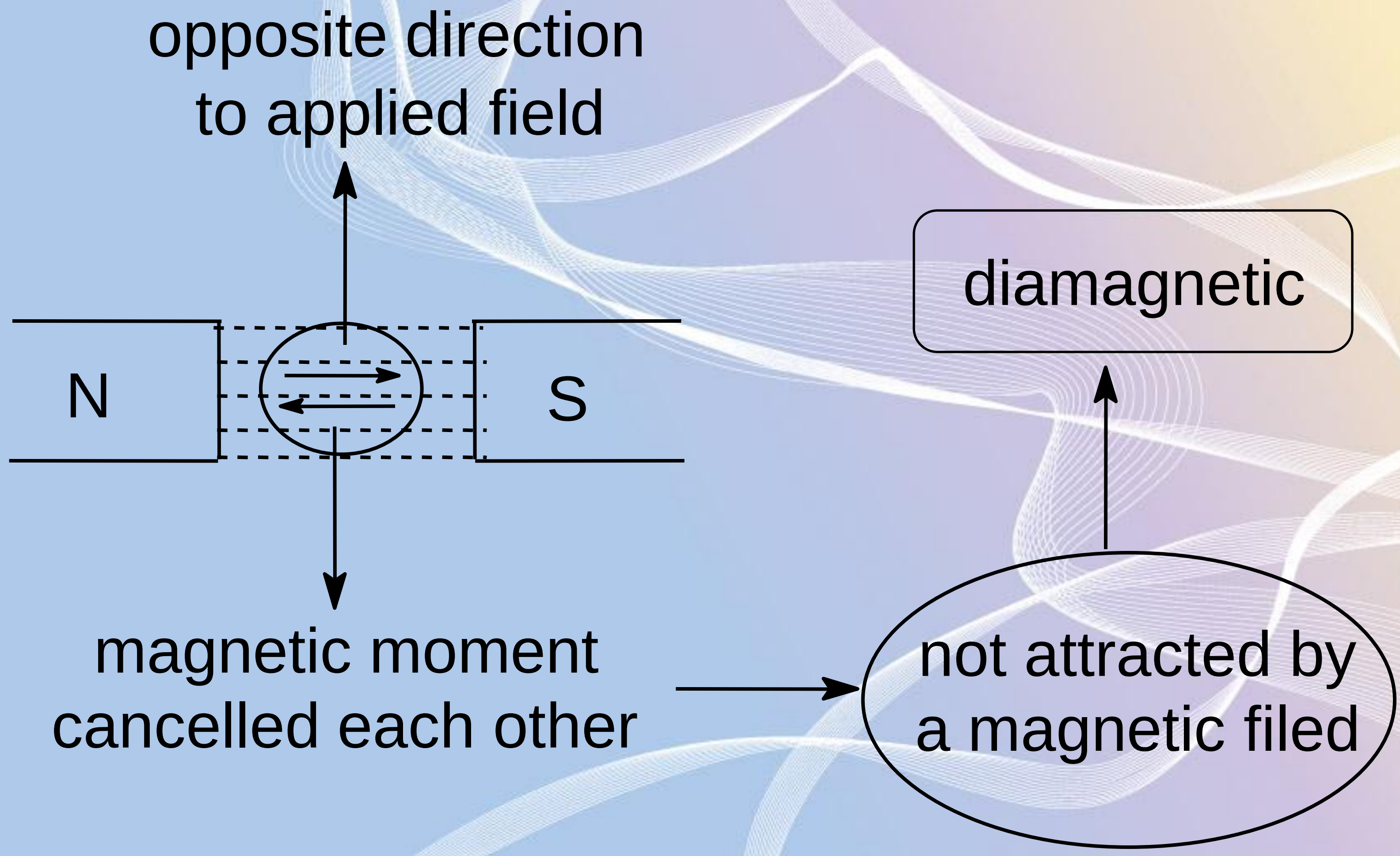
The origin of magnetism



Diamagnetic

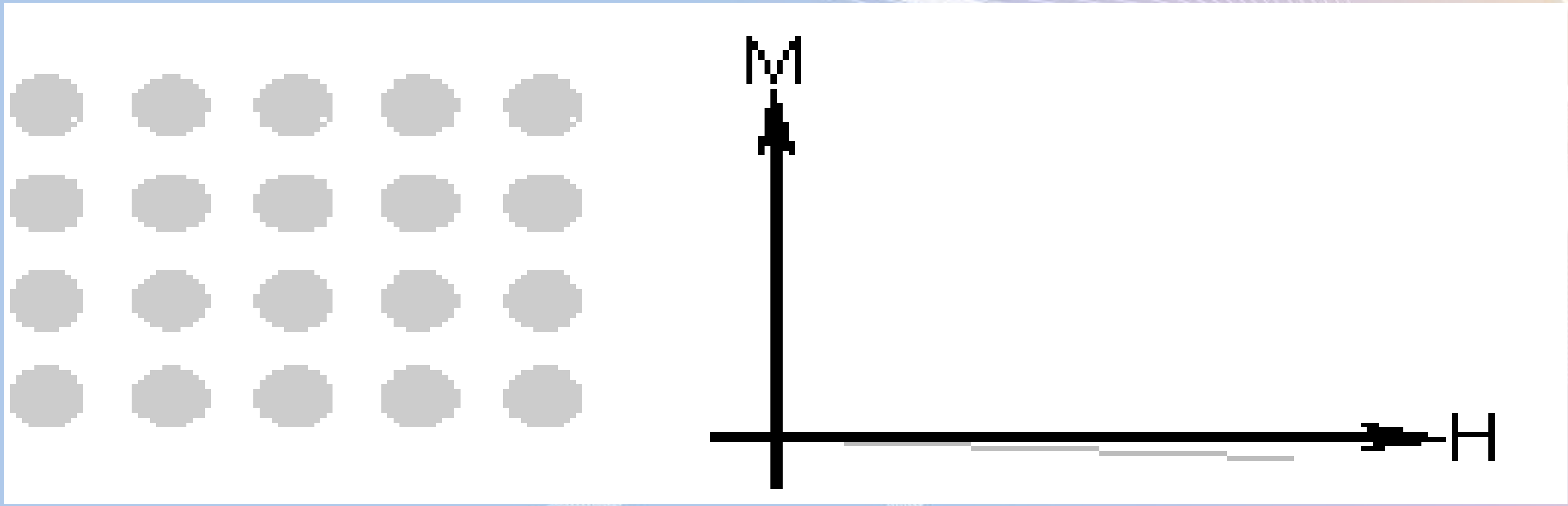
- All materials have a diamagnetic effect → masked by larger "para or ferro""-magnetic term
- All electron are paired
- Atoms have no net magnetic moment (no applied field)
- The spinning electrons produce a magnetization (M) in the opposite direction to that of the applied field (applied field)

Diamagnetic



Diamagnetic

- Magnetic moment alignment
  - Has no magnetic moment



Paramagnetic

- Permanent magnetism from the spinning of unpaired electron

Paramagnetism ≈ unpaired electron

Paramagnetic

paramagnetism → electronic configuration of central atom / cation

paramagnetism → influenced by ligand

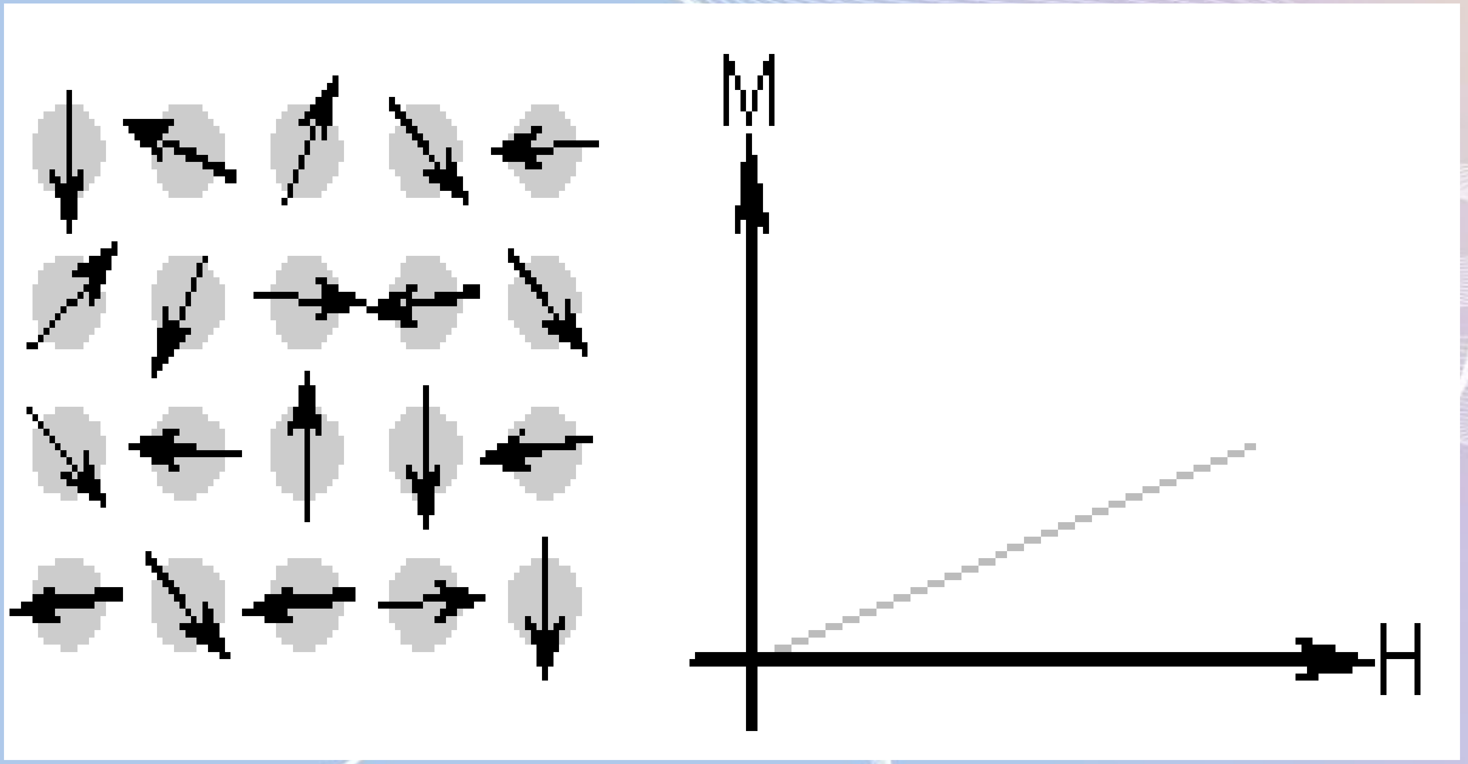
Paramagnetic

The strength of ligands

$I^- < Br^- < Cl^- < OH^- < H_2O$
$< NCS^- < NH_3 < en < CO < CN^-$

Paramagnetic

- Magnetic moment alignment
  - Randomly magnetic moment alignment



Paramagnetic vs. Diamagnetic

What is the magnetism of each compound below?

?

$[NiCl_4]^{2-}$

$[Ni(CN)_4]^{2-}$

Paramagnetic vs. Diamagnetic

- $[NiCl_4]^{2-}$:
  - paramagnetic
  - sp^3
  - tetrahedral
- $[Ni(CN)_4]^{2-}$
  - diamagnetic
  - dsp^2
  - square planar

Ferromagnetic (super magnet)

– Atoms are arranged in a lattice and the atomic magnetic moments can interact to align parallel to each other.

– Only Fe, Co and Ni are ferromagnetic at and above room temperature.

Ferromagnetic (super magnet)

- As ferromagnetic materials are heated or vibrated
  - alignment of the atomic magnetic moments decreases
  - saturation magnetization also decreases
  - paramagnetic

Ferromagnetic (super magnet)

– Curie temperature, TC
  - transition temperature of ferro → para

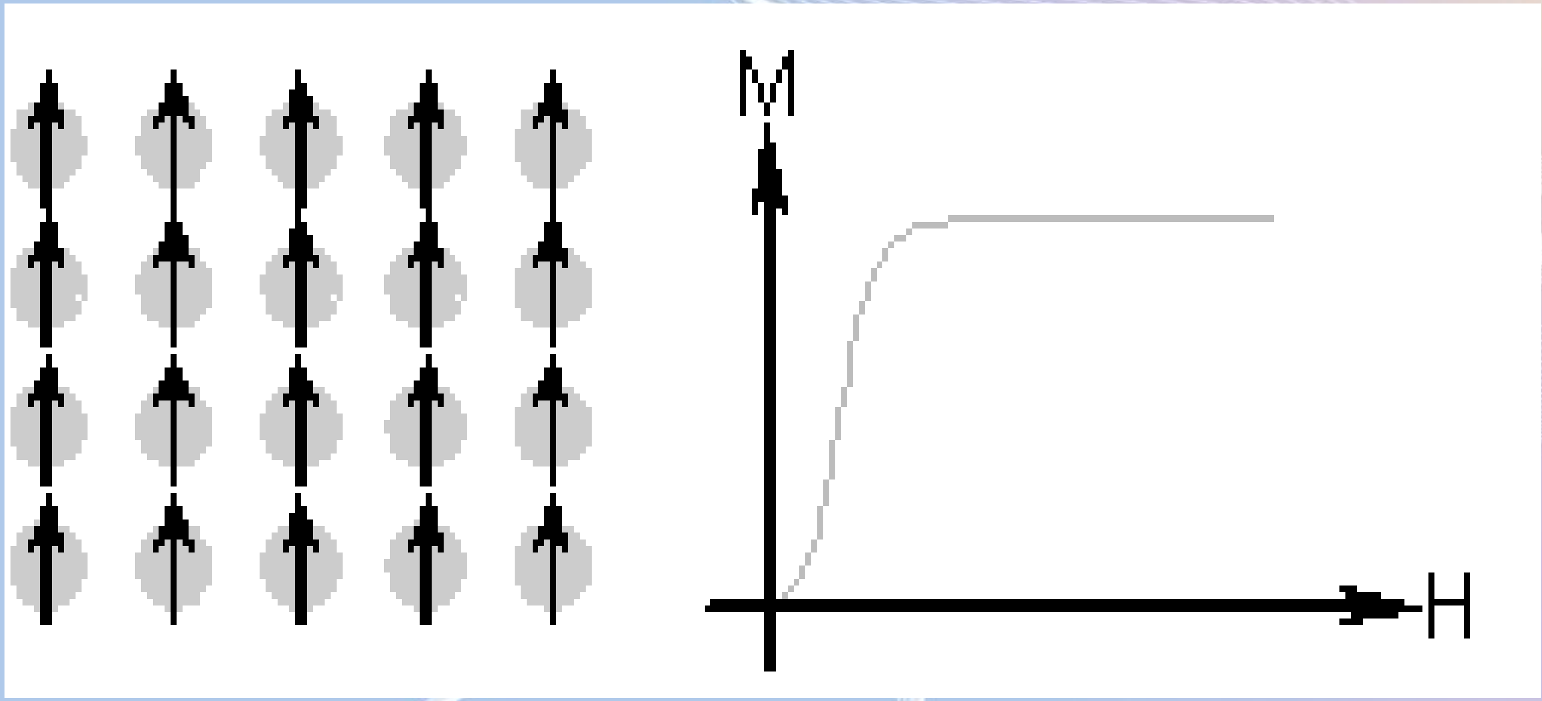
    Fe : 770°C

    Co :1131°C

    Ni : 358°C

Ferromagnetic (super magnet)

- Magnetic moment alignment
  - Parallel magnetic moment alignment



Ferrimagnetic

- Only observed in compounds, which have more complex crystal structures than pure elements.
- Parallel alignment of atoms in some of the crystal sites and anti-parallel alignment of others.
- Ferrimagnetic materials usually have lower saturation magnetizations than ferromagnetic materials

Ferrimagnetic

Barium ferrite ($BaO.6Fe_2O_3$)

- The unit cell contains 64 ions
  - barium and oxygen ions have no magnetic moment
  - 16 Fe^{3+} ions have moments aligned parallel

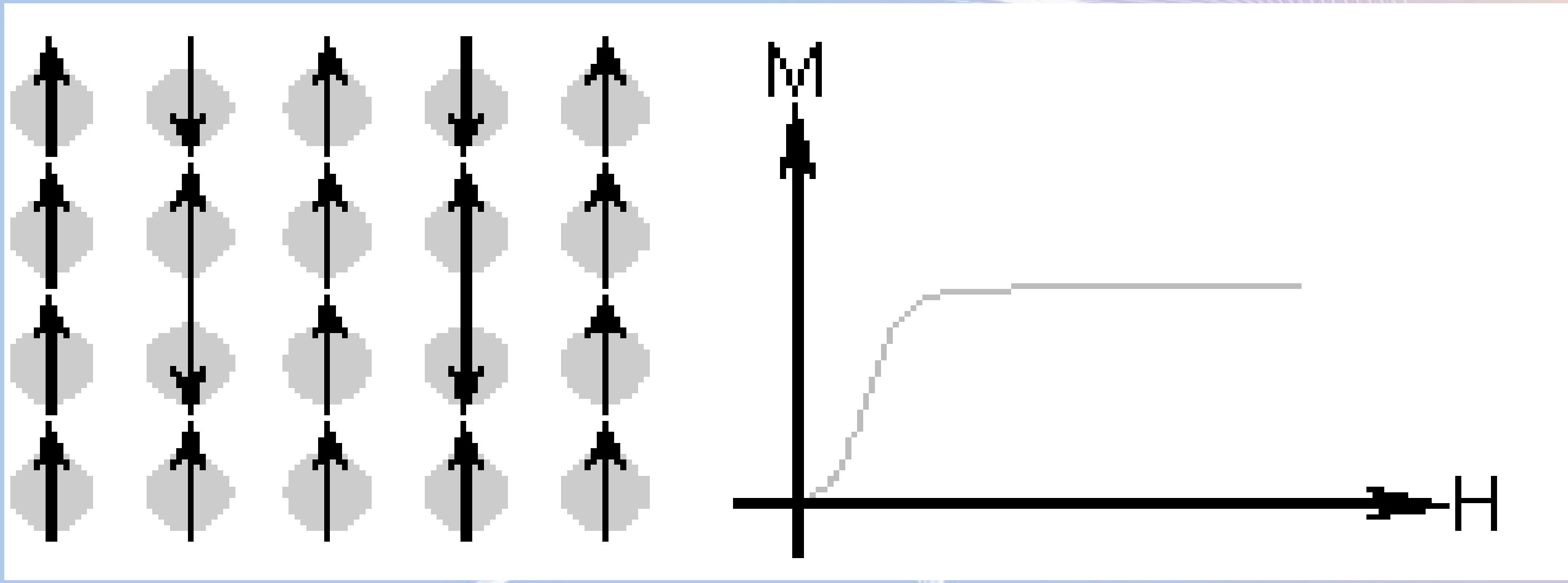
Ferrimagnetic

Barium ferrite ($BaO.6Fe_2O_3$)

- 8 Fe^{3+} aligned anti-parallel giving a net magnetization parallel to the applied field,
- only ⅛ of the ions contribute to the magnetization of the material.

Ferrimagnetic

- Magnetic moment alignment
  - Parallel magnetic moment in one site and anti-parallel in the other site



Antiferromagnetic

- Very similar to ferromagnetic materials
- The exchange interaction between neighboring atoms are anti-parallel alignment

Antiferromagnetic

- The magnetic field cancelled out
- Appears to behave in the same way as a paramagnetic material

Antiferromagnetic

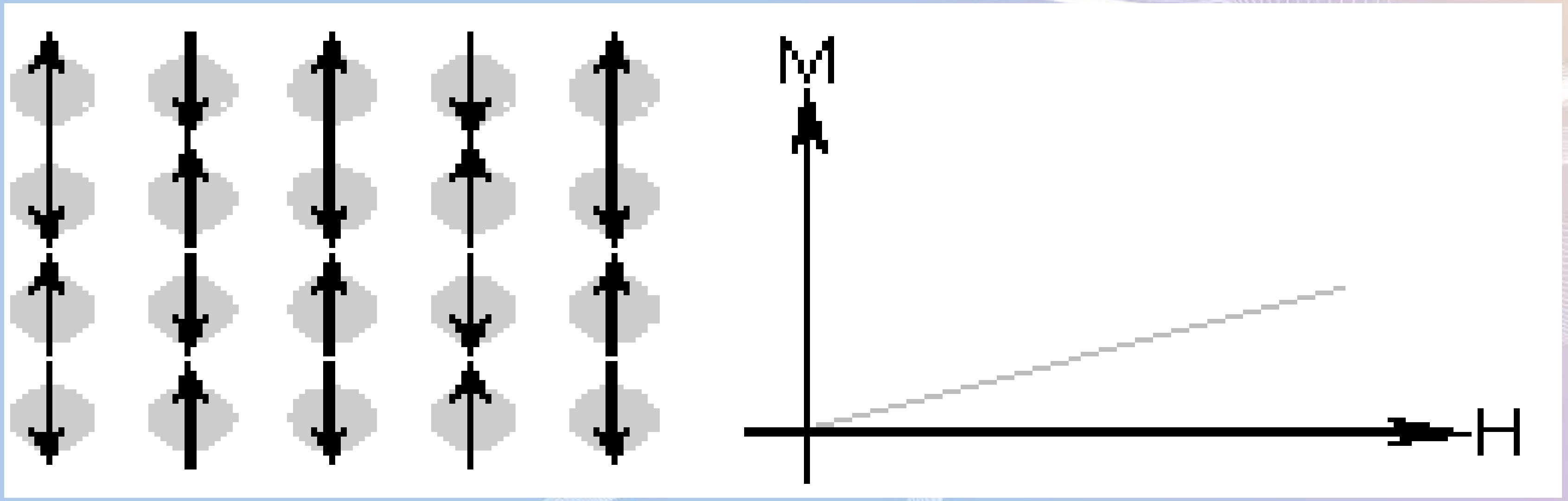
- Only chromium is antiferromagnetic at room temperature

- Néel temperature, TN.
  - transition temperature of antiferro → para

Cr: 37ºC

Antiferromagnetic

- Magnetic moment alignment
  - Anti-parallel magnetic moment with neighboring atoms



Summary of different types of magnetic behavior

Type of Magne-tism	Susceptibility, Example	Atomic Behaviour
Dia-magne-tism	Small & negative Au (-2.74×10^{-6})	Atoms have no magnetic moment

Summary of different types of magnetic behavior

Type of Magne-tism	Susceptibility, Example	Atomic Behaviour
Para-magne-tism	Small & positive Cu (0.77×10^{-6}) β-Sn (0.19×10^{-6}) Pt (21.04×10^{-6}) Mn (66.10×10^{-6})	Atoms have randomly oriented magnetic moments

Summary of different types of magnetic behavior

Type of Magne-tism	Susceptibility, Example	Atomic Behaviour
Ferro-magne-tism	Large & positive function of applied magnetic moments field, microstructure dependent Fe (~100,000)	Atoms have parallel aligned

Summary of different types of magnetic behavior

Type of Magne-tism	Susceptibility, Example	Atomic Behaviour
Antiferro-magne-tism	Small & positive Cr ($3.6x10^{-6}$)	Atoms have anti-parallel aligned

Summary of different types of magnetic behavior

Type of Magne-tism	Susceptibility, Example	Atomic Behaviour
Ferri-magne-tism	Large & positive function of applied magnetic moments field, microstructure dependent Ba ferrite (~3)	Atoms have mixed parallel and anti-parallel aligned magnetic moments

Problem:

- Cr, Mo and W locate in the same group (group 6 or group VIB)
- Radius of:
  - $_{24}Cr$ = 128 pm
  - $_{42}Mo$ = 139 pm
  - $_{74}W$ = 139 pm
- Explain the radius phenomena of this group.