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 Complexes & MOFs
10.	Fri	08.10.	Cr, Mo, W & 2D materials
11.	Mon	11.10.	Mn, Fe, Co, Ni, Cu & Magnetism & Superconductivity
12.	Wed	13.10.	EXTRA
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

PRESENTATION TOPICS/SCHEDULE

Wed	06.10.	Nb:	Toivonen
Fri	08.10.	Mo:	Ahmed, Shamshad, Svinhufvud
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
		Te:	Huhtakangas, Wallin, Kaarne
Mon	18.10.	Eu:	Sonphasit, Tuisku
		Nd:	Jussila, Siuro, Perttu
		U:	Sinkkonen, Wennberg, Partanen

INSTRUCTIONS for SEMINAR PRESENTATIONS

- Presentation (~20 min) is given in a group of two or three persons
- It is evaluated in the scale: 15 ~ 25 points
- Presentation is given in English, and the slides are put up in MyCourses afterwards (by Maarit)
- Content of the presentation:

- ELEMENT: discovery, origin of name, abundancy, world production, special features if any, etc.

- CHEMISTRY: position in Periodic Table, electronic configuration, oxidation states, metal and ionic sizes, reactivity, etc.

- COMPOUNDS: examples of important compounds, their properties and applications, etc.

- SPECIFIC FUNCTIONALITIES/APPLICATIONS: Two or three examples of exciting topics/functionalities/applications related to the element or its compounds. If possible, please try to clarify/discuss why this chosen topic/functionality/application is specific to the element. For this, you will be given one or two scientific articles for a reference, and you should search from literature couple of more (recent) articles to be discussed in the presentation.

QUESTIONS: Lecture 8

- In octahedral crystal field, transition metal cations with the electron configurations of d^4, d^5, d^6 and d^7 have the choice of showing two different spin states, high-spin state or low-spin state. Give the electron configurations for which the same applies in tetrahedral crystal field.
- How many unpaired electrons the following ions have in high-spin state in (a) octahedral, and (b) tetrahedral crystal fields: Cr^{3+}, Mn^{2+}, Fe^{2+} and Co^{+2}?
- For which of the following ions (assume high-spin) would you expect to see (strong) Jahn-Teller distortion: Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}, Cu^{2+}. **Explain why!**

Crystal (or ligand) field SPLITTING of d (or f) ORBITAL energies

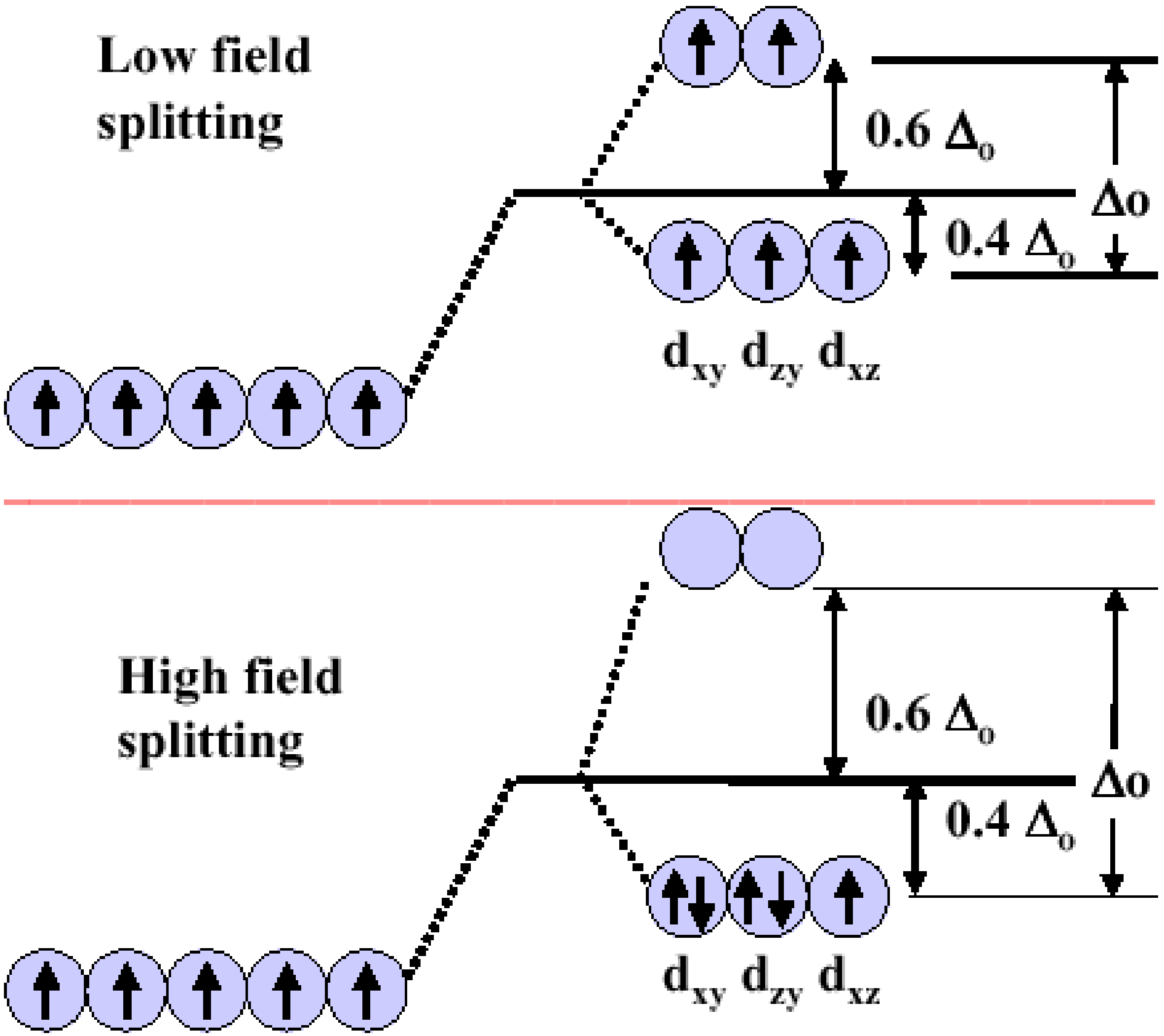
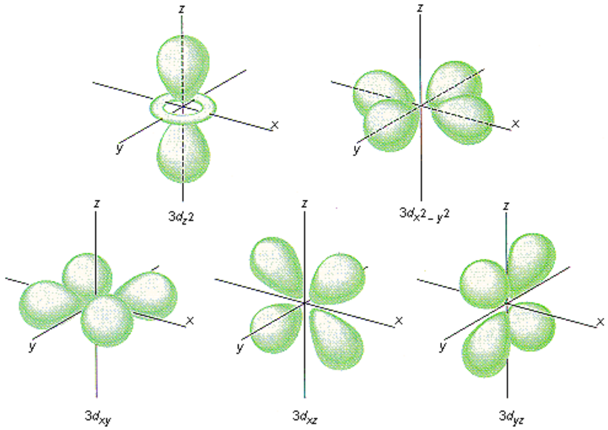


Figure 5. The two cases of crystal field splitting for the octahedral geometry.

d-orbital energies



In an isolated atom the different *d*-orbitals of the same shell all have the same energy (but different shapes & orientations)

COLOURS of d-BLOCK METAL IONS

- **partly filled *d*-orbitals**
- **electrons can transfer from one *d*-orbital to another**
- **energy needed for the transfer is small**
- **corresponds to visible light wavelengths**
- **ions absorb certain wavelengths within the visible light spectrum**
- **if ion absorbs certain colour (e.g. red) the transmitted or reflected light contains relatively more other colours (blue and green), and the ion looks coloured (bluish green)**
- **ions with empty or full orbitals (d^0 ja d^{10}) are colourless**
- **ions with half-filled orbitals (d^5) are colourless or faintly coloured**

CRYSTAL (or LIGAND) FIELD THEORY

- Electron configuration of n-period transition metal (T) : $ns^2 (n-1)d^x$
- For free T atom: all d-orbitals degenerated (= have the same energy)
- For T surrounded by neighbours (crystal, molecule or solution):

  ns^2 electrons and possibly also a portion of the d-electrons (y) participate in the formation of the chemical bond

  $\rightarrow \quad T^{(2+y)+} : d^{x-y}$
- Portion of d-electrons (x-y) remain non-bonded
- These remaining d-electrons are the source of exciting properties

WHEN the T atom is BONDED:

- Each T atom (cation) likes simultaneously to:

  (1) get the nearest-neighbour anions (e.g. O^{2-}) as close as possible (such that the bond can form)

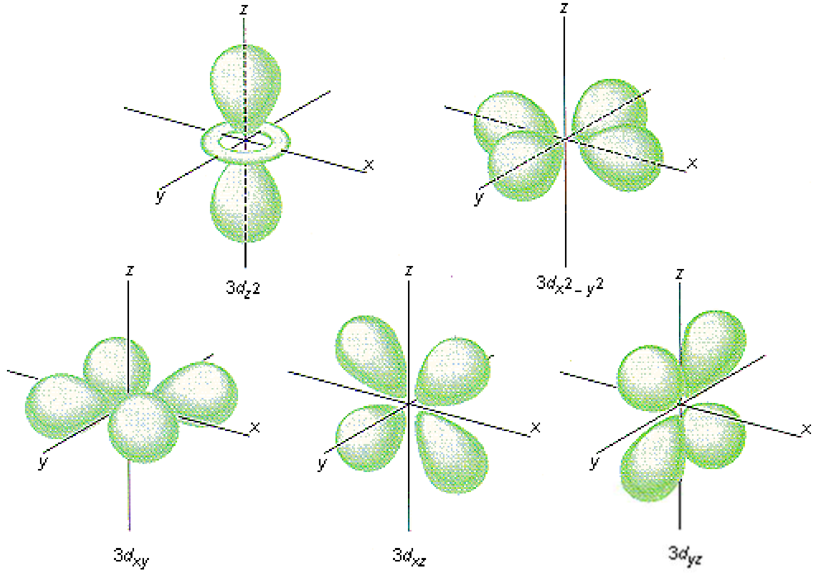
  (2) keep the non-bonded d-electrons as far as possible from the nearest-neighbour anions (to minimize electron-anion repulsion)

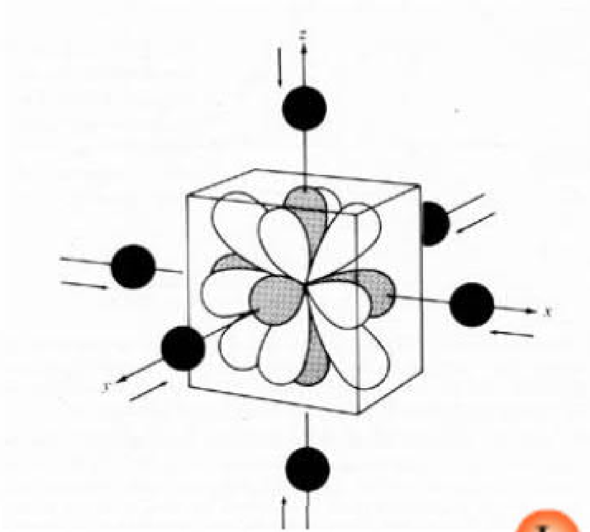
  → this repulsion determines the orientation of the d-orbitals related to the nearest-neighbour anions

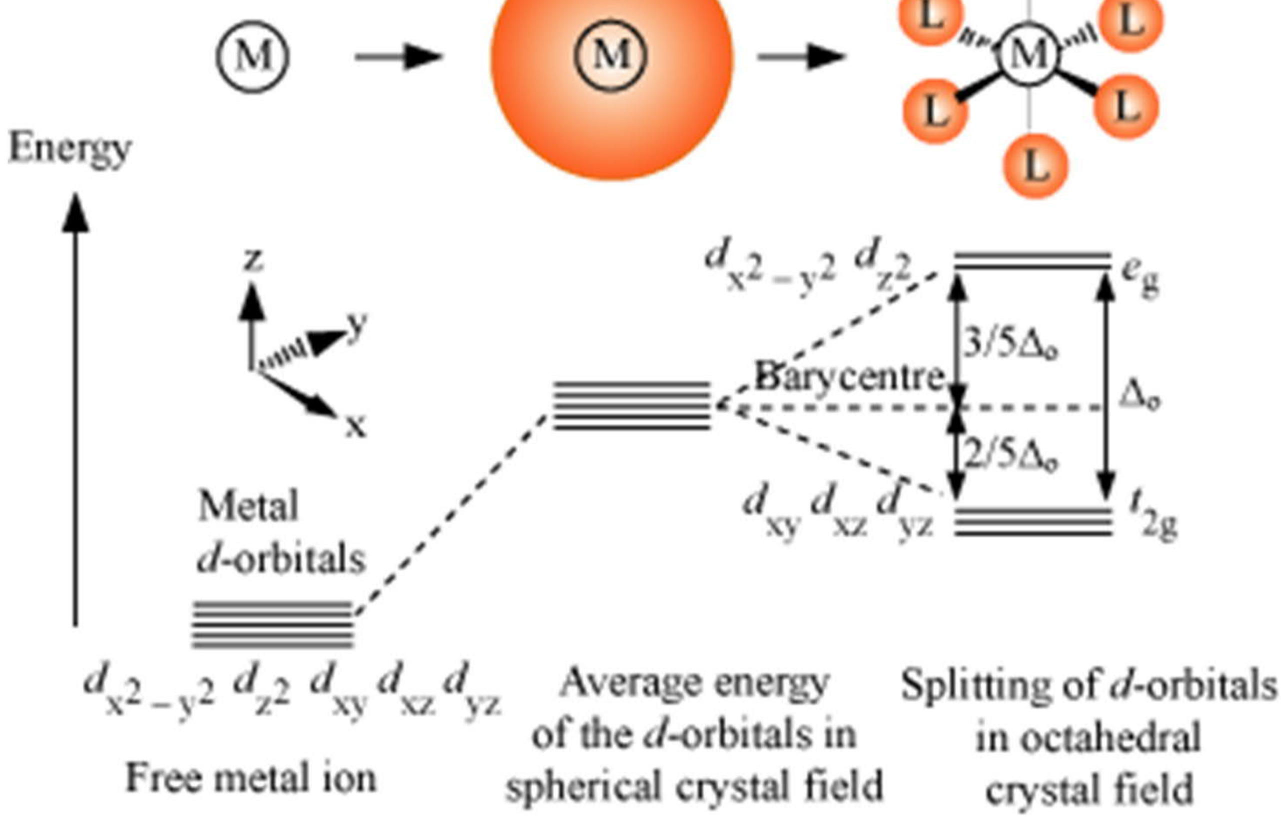
- All the five d-orbitals feel the repulsion → energy increased in comparison to the energy level in free T atom

- d-orbitals that are closest to the nearest-neighbour anions feel the strongest repulsion and are with the highest energy, while those that are farther are with the lower energy

- d-orbitals have different shapes and spatial orientations
  → energies of the orbitals split (Δ) when the T cation is surrounded by anions (i.e. degeneration of the d orbitals disappears)


z
x
y
$3d_{z^2}$
$3d_{x^2-y^2}$
$3d_{xy}$
$3d_{xz}$
$3d_{yz}$

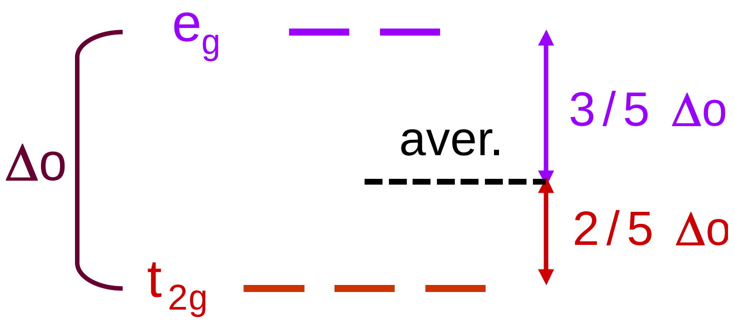

z
x

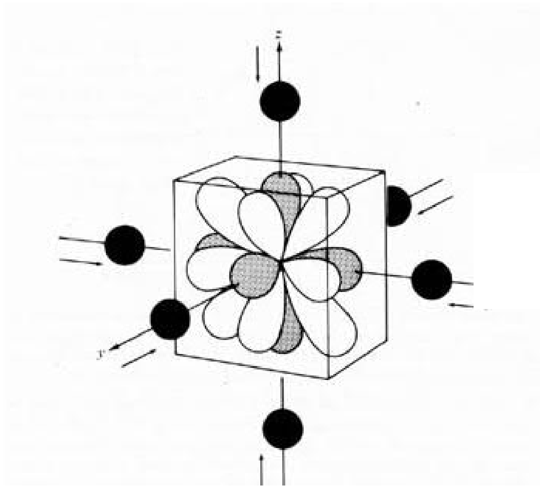

M
L
Energy
z
y
x
Metal d-orbitals
$d_{x^2-y^2}$ d_{z^2} d_{xy} d_{xz} d_{yz}
Free metal ion
Average energy of the d-orbitals in spherical crystal field
$d_{x^2-y^2}$ d_{z^2}
e_g
$3/5\Delta_o$
Barycentre
Δ_o
$2/5\Delta_o$
d_{xy} d_{xz} d_{yz}
t_{2g}
Splitting of d-orbitals in octahedral crystal field

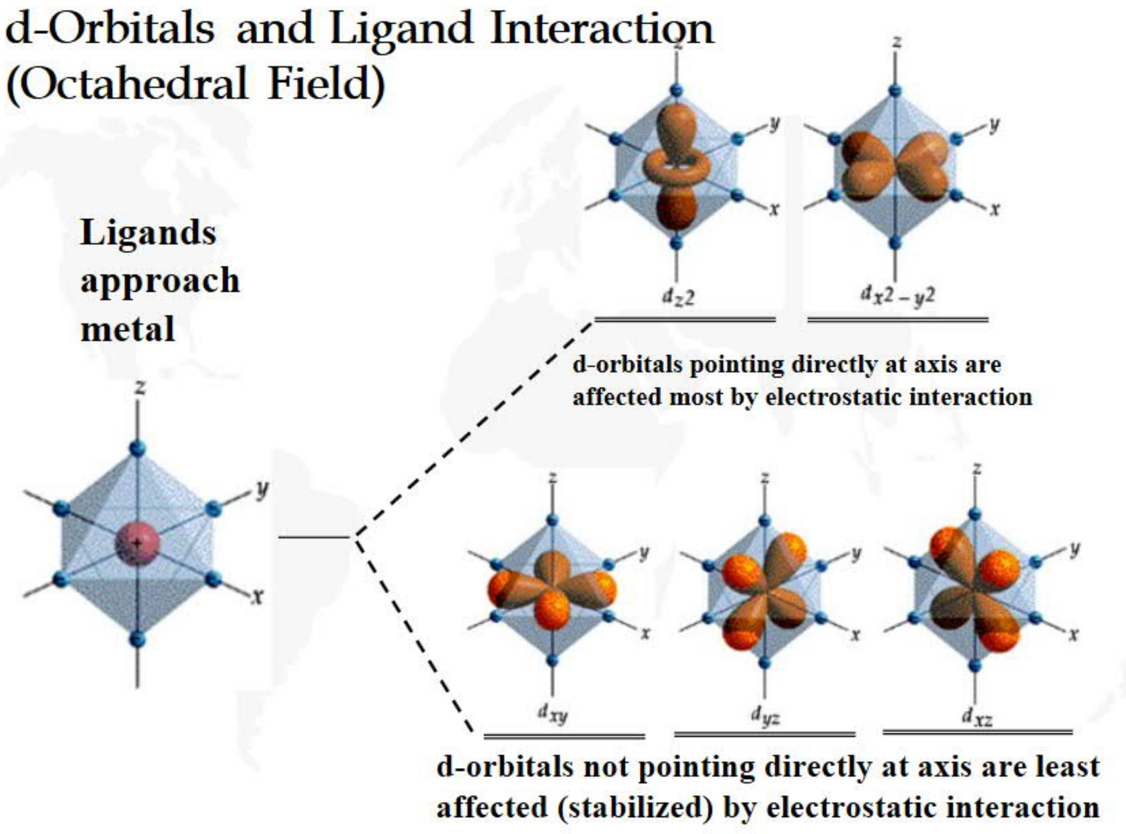
Octahedral crystal / ligand field

- three d orbitals (d_{xy}, d_{yz} ja d_{zx}) orient towards the empty spaces between the anions → **lower energy (2/5 Δ_o) t_{2g} orbitals**

- two d-orbitals (d_{z2} ja d_{x2-y2}) orient towards the anions → **higher energy (3/5 Δ_o) e_g orbitals**





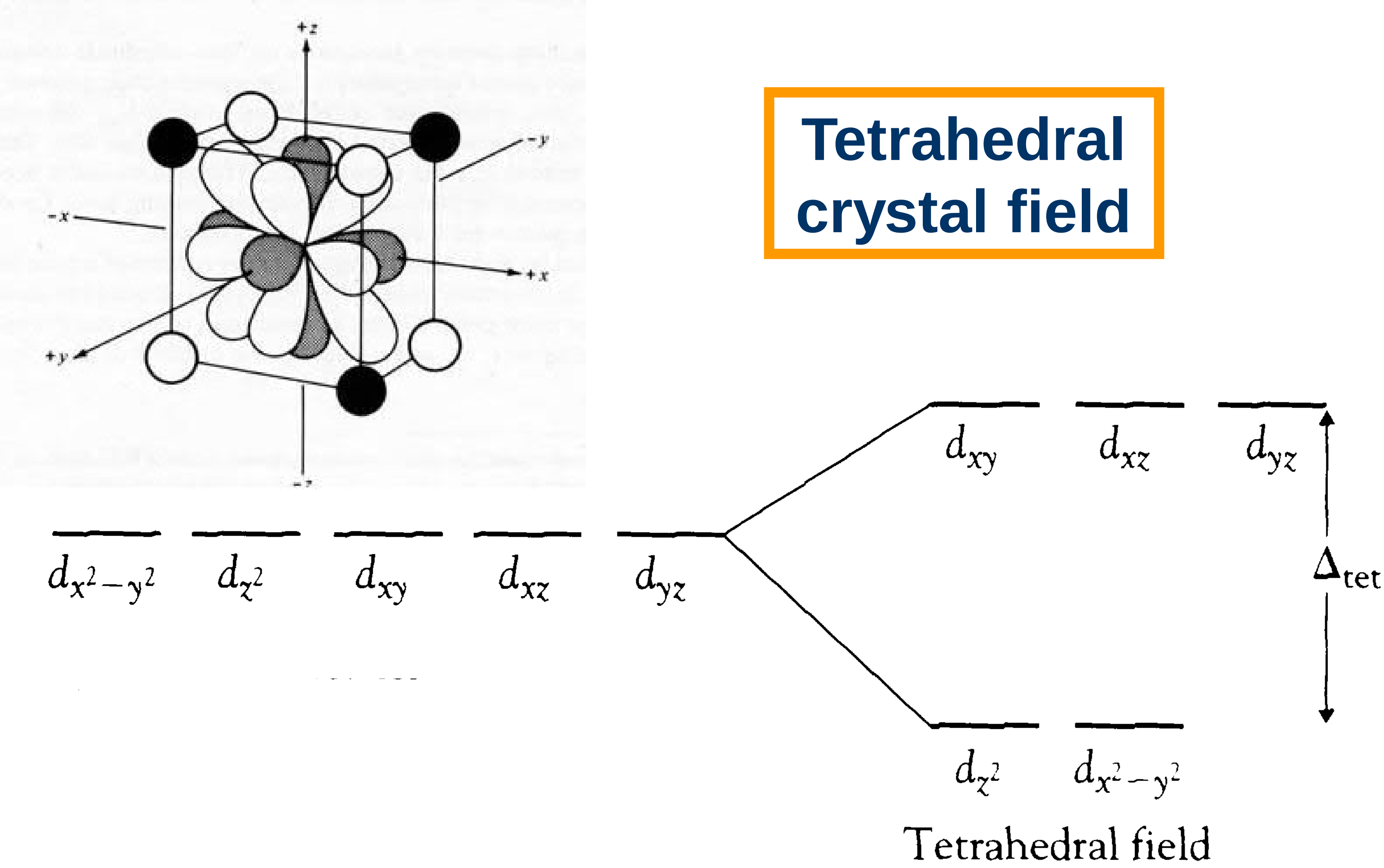

d-Orbitals and Ligand Interaction (Octahedral Field)

Ligands approach metal

d-orbitals pointing directly at axis are affected most by electrostatic interaction

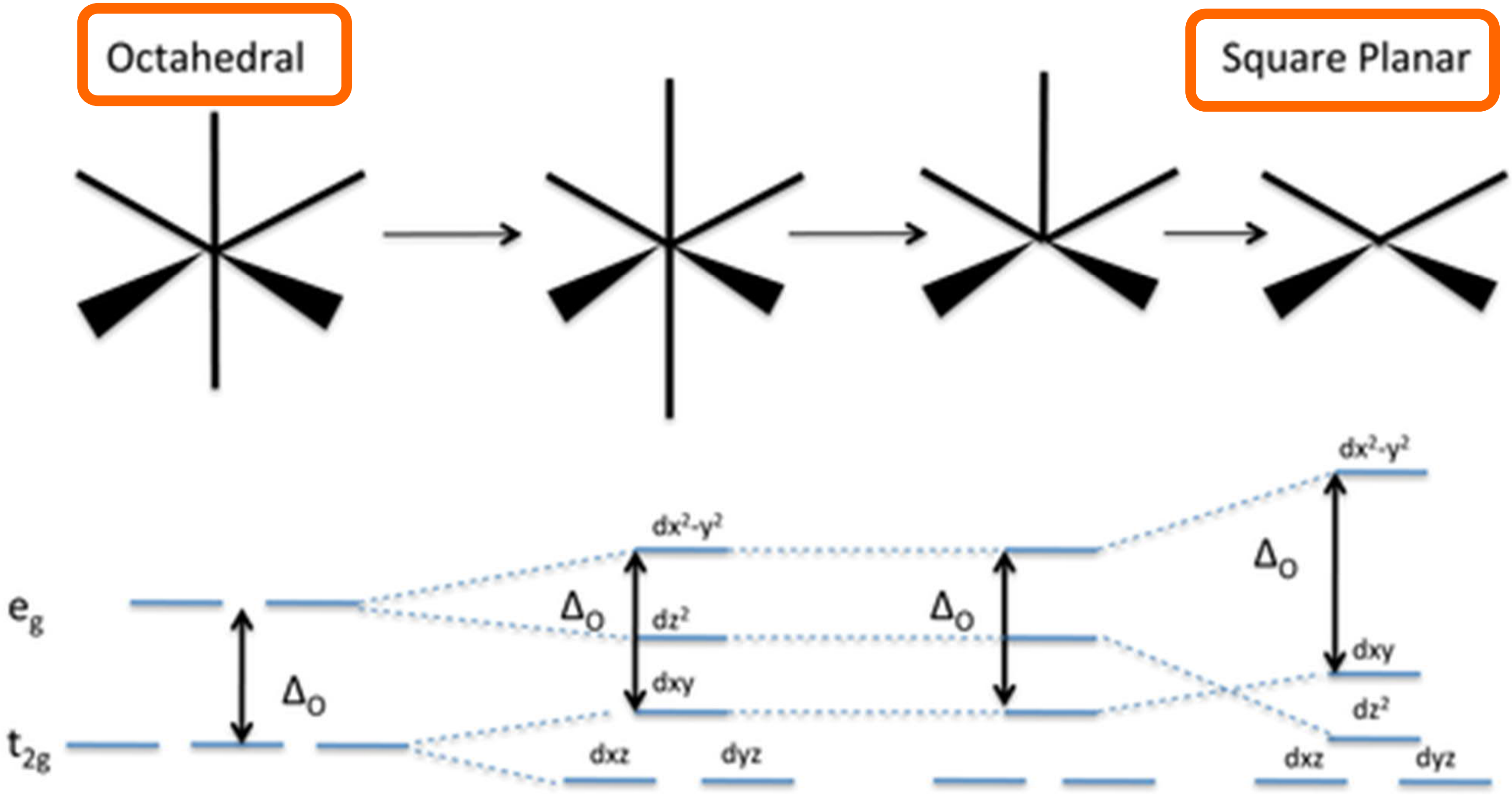
d-orbitals not pointing directly at axis are least affected (stabilized) by electrostatic interaction

Tetrahedral crystal field



Tetrahedral field

- **4 anions/ligands around transition metal T cation**
- **compared to octahedral case, splitting is less: typically $\Delta_{tet} = 4/9\ \Delta_{oct}$ for the same metal/anion pair**



elongation of octahedron

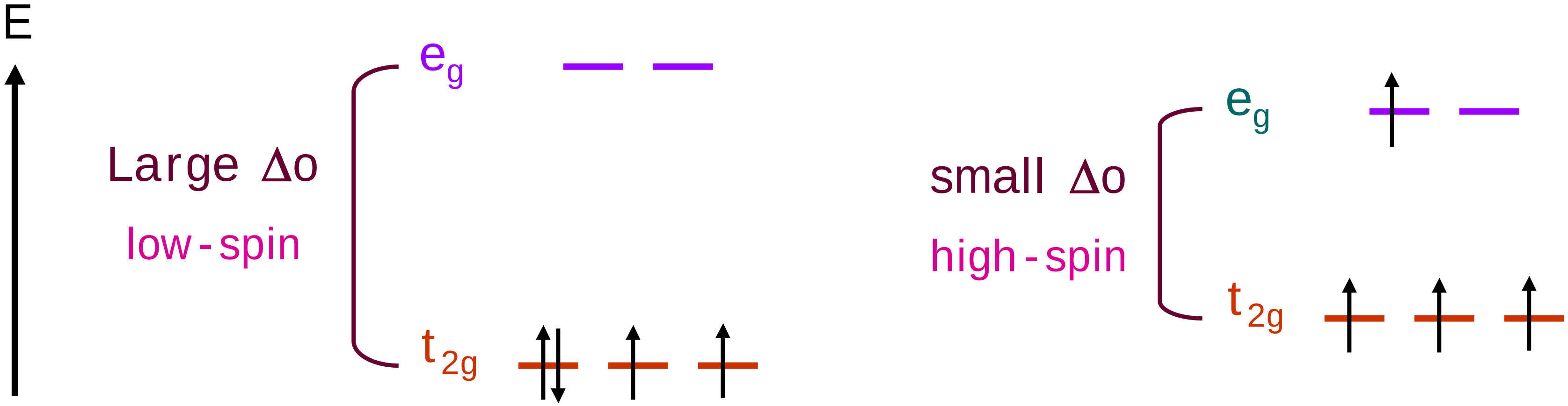
How the d electrons occupy the splitted orbitals?

Two contadictory goals:

(1) Minimum energy → low spin (if large Δ)

(2) Hund's rule (avoid electron pairs) → high spin (if small Δ)

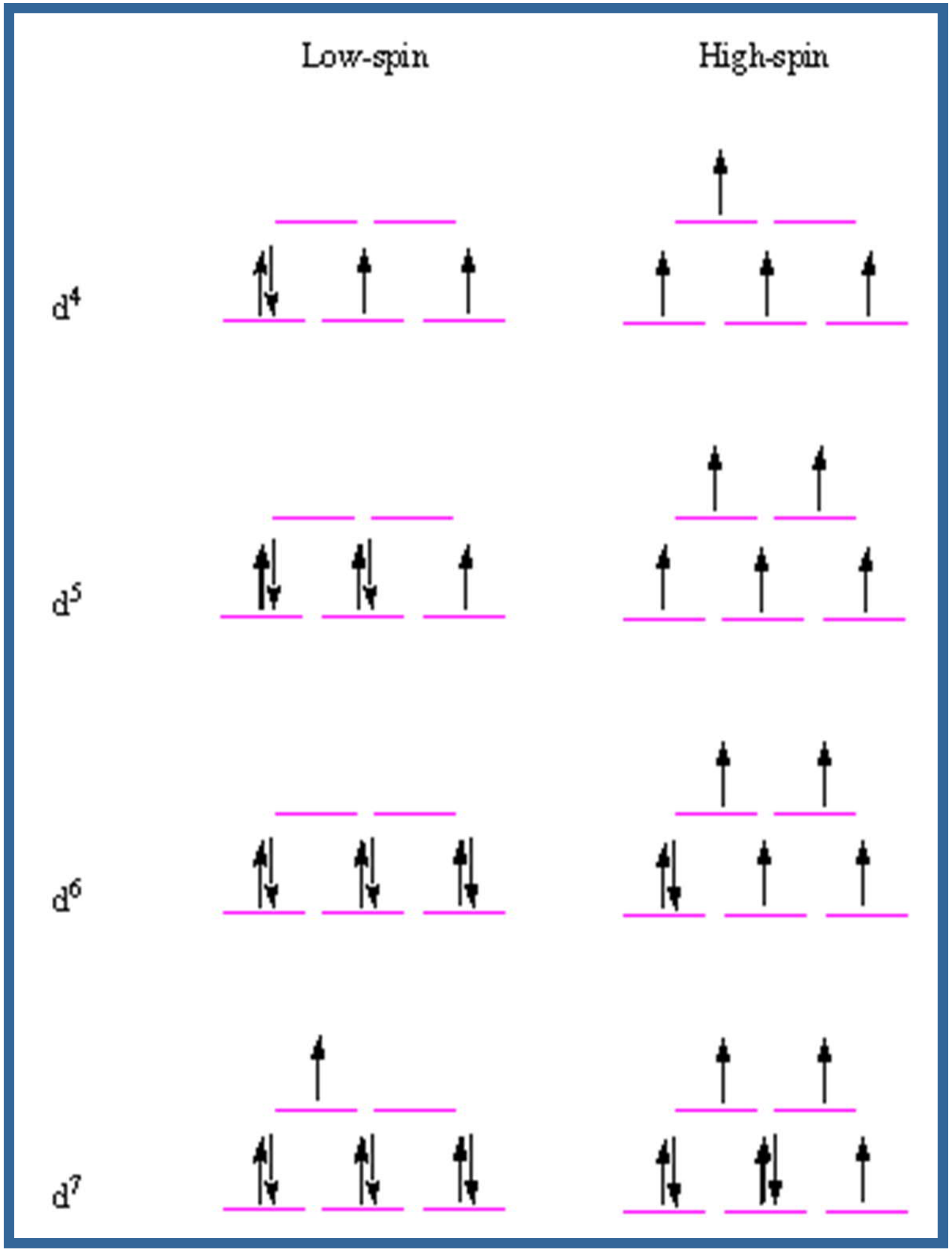
As $\Delta_{tet} = 4/9\ \Delta_{oct}$, tetrahedral case almost always high-spin



Let's consider

the OCTAHEDRAL case

(in your lecture exercise
you will consider
the tetrahedral case)



SPECTROCHEMICAL SERIES

- **Empirically found order for ligands/anions**
- **Ligands in the order of the magnitude of splitting Δ they produce**
- **Below is just part of the series**

$CO > CN^{-} > NO^{2-} >> O^{2-} >> H_2O > OH^{-} > F^{-} > N^{3-} > NO^{3-} > Cl^{-} > SCN^{-} > S^{2-} > Br^{-} > I^{-}$

π acceptors ↔ π donors

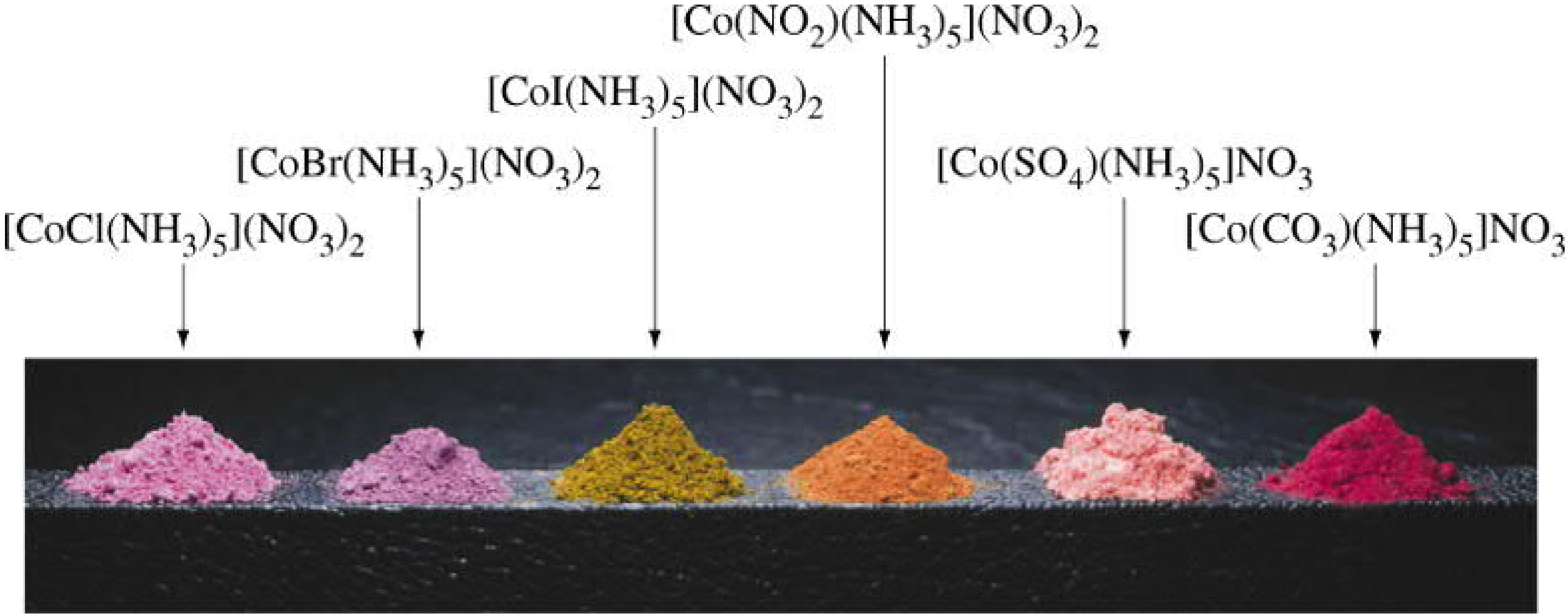
EXAMPLE: **For O^{2-} : Δ is still relatively small**

→ high-spin configurations common in oxide materials

EXAMPLE: **Fe^{2+}: d^6**

- $[Fe(H_2O)_6]^{2+}$: high-spin → paramagnetic

- $[Fe(CN)_6]^{4-}$: low-spin → diamagnetic


$[CoCl(NH_3)_5](NO_3)_2$
$[CoBr(NH_3)_5](NO_3)_2$
$[CoI(NH_3)_5](NO_3)_2$
$[Co(NO_2)(NH_3)_5](NO_3)_2$
$[Co(SO_4)(NH_3)_5]NO_3$
$[Co(CO_3)(NH_3)_5]NO_3$

Magnitude of the splitting energy depends also on:

(1) Transition metal T itself

- 50% larger for 4d metals than for 3d metals
- 25% larger for 5d metals than for 4d metals

  → 4d and 5d metals almost always: low-spin

(2) Oxidation state of T

- With increasing oxidation state of T

  → anions become closer

  → larger repulsion between d electrons and anions

  → larger Δ

- 3d metals: when $T^{2+} \rightarrow T^{3+}$, Δ is doubled

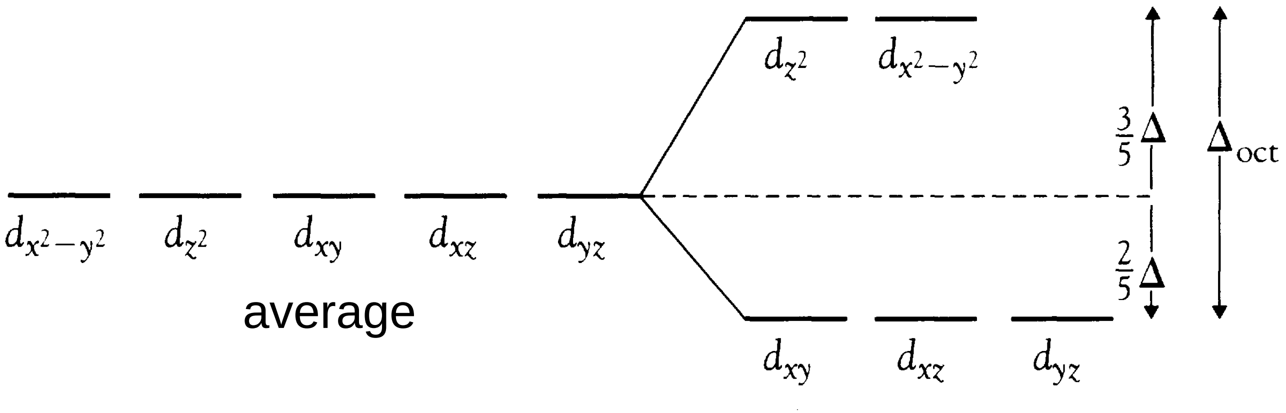
(3) Number of anions/ligands

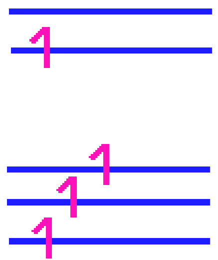
- The more ligands the larger Δ : $\Delta_{tet} \approx 4/9 \times \Delta_{oct}$

Crystal Field Stabilization Energy (CFSE)

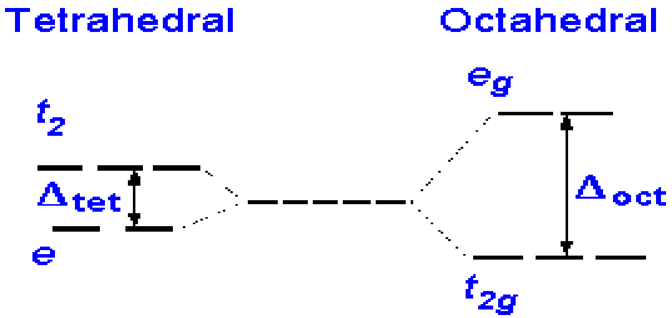
For example: octahedral crystal field

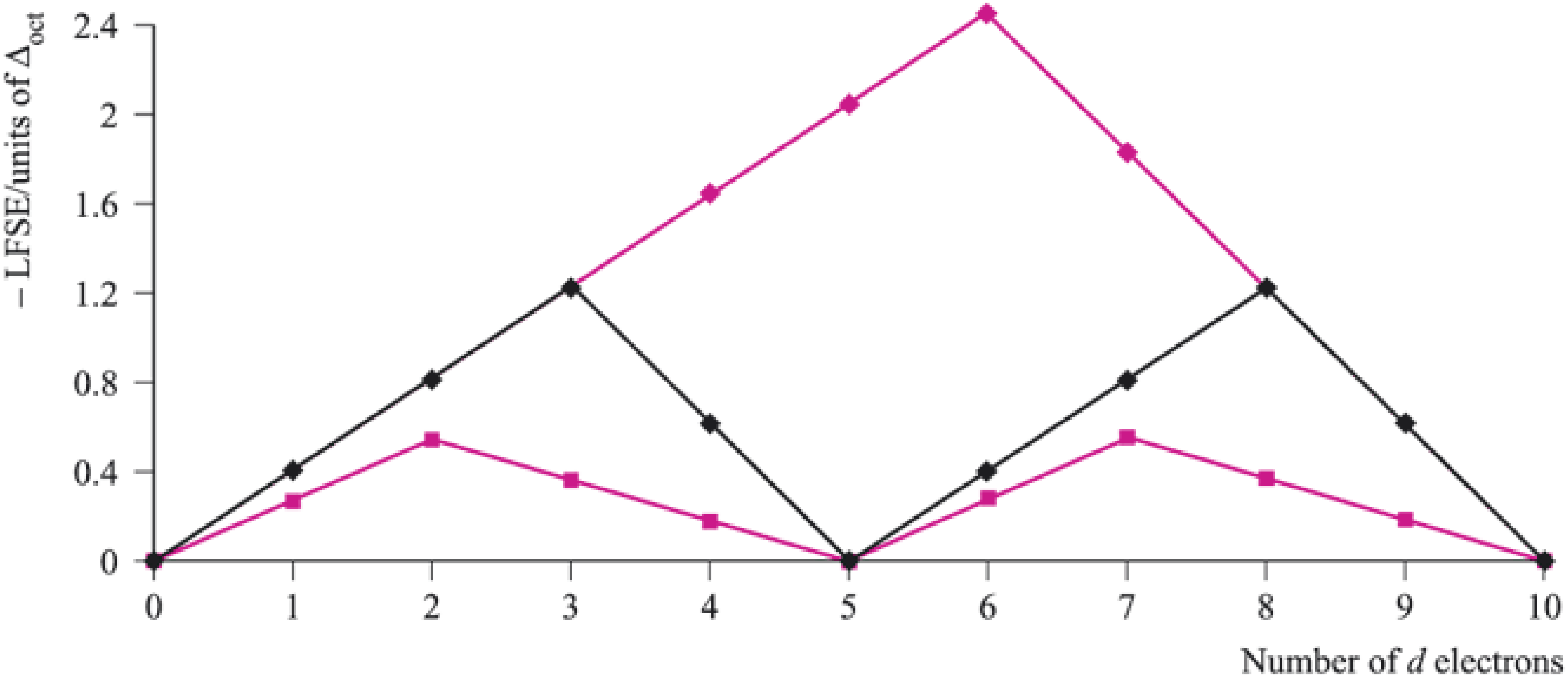
- **each t_{2g} electron stabilizes (relatively) the compound**
- **each e_g electron destabilizes (relatively) the compound**





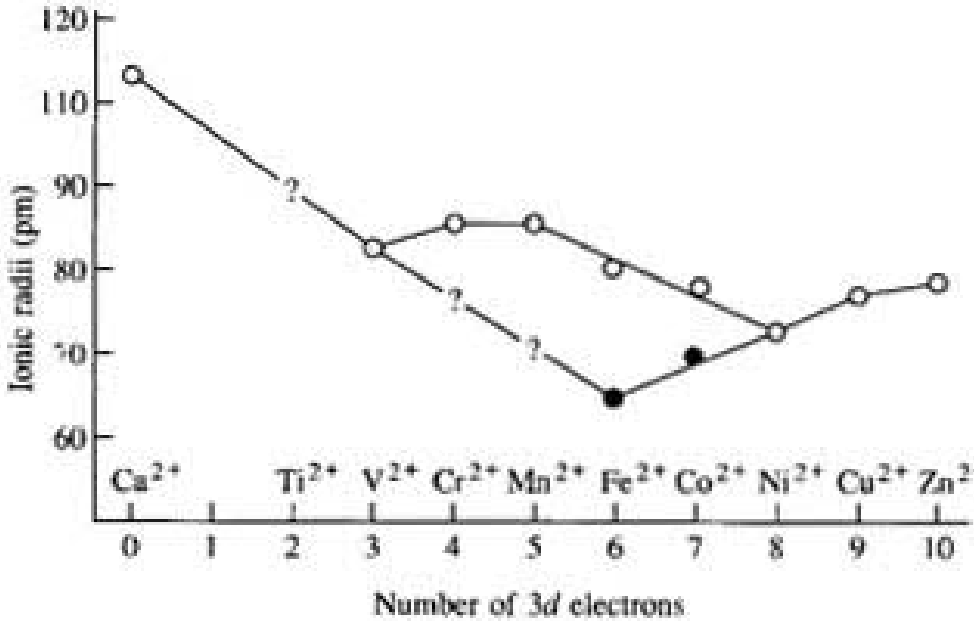
$$\mathrm{CFSE} = [3 \times (-2/5) + 1 \times (3/5)]\Delta o = -3/5\ \Delta o$$


Tetrahedral
Octahedral
e_g
t_2
Δ_{tet}
e
Δ_{oct}
t_{2g}

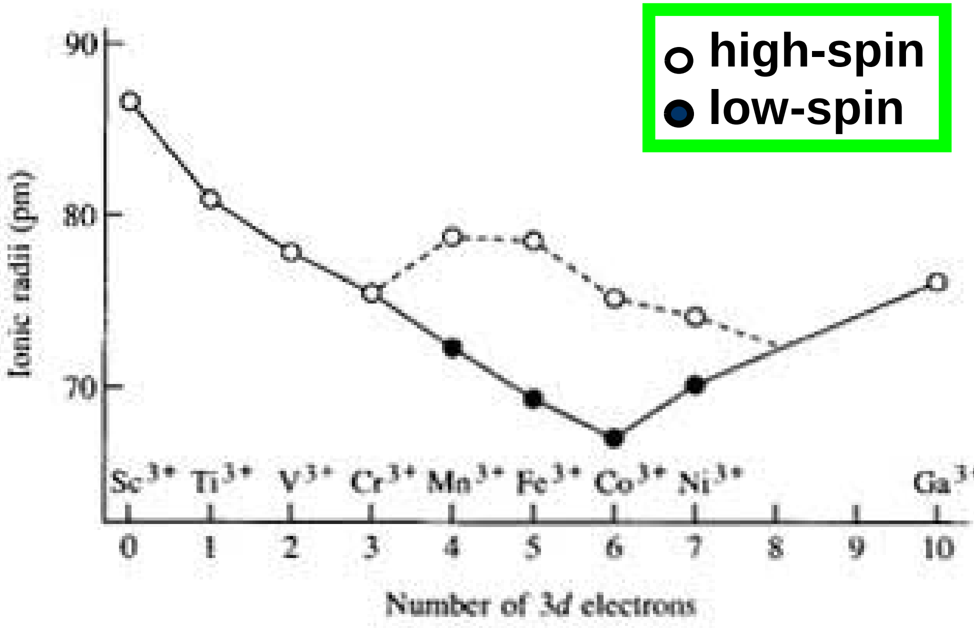

− LFSE/units of Δ_{oct}
2.4
2
1.6
1.2
0.8
0.4
0
0
1
2
3
4
5
6
7
8
9
10
Number of *d* electrons

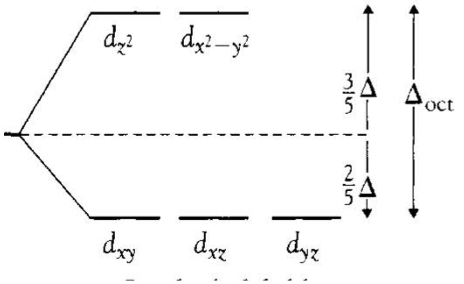
How CFSE is seen in ionic radius

- **FOR EXAMPLE: 3d metals in octahedral coordination**
- **At a fixed oxidation state, ionic radius decreases from left to right**
- **HOWEVER: each electron in e_g orbital increases the ionic radii**
- **Ionic radius depends on spin state !**

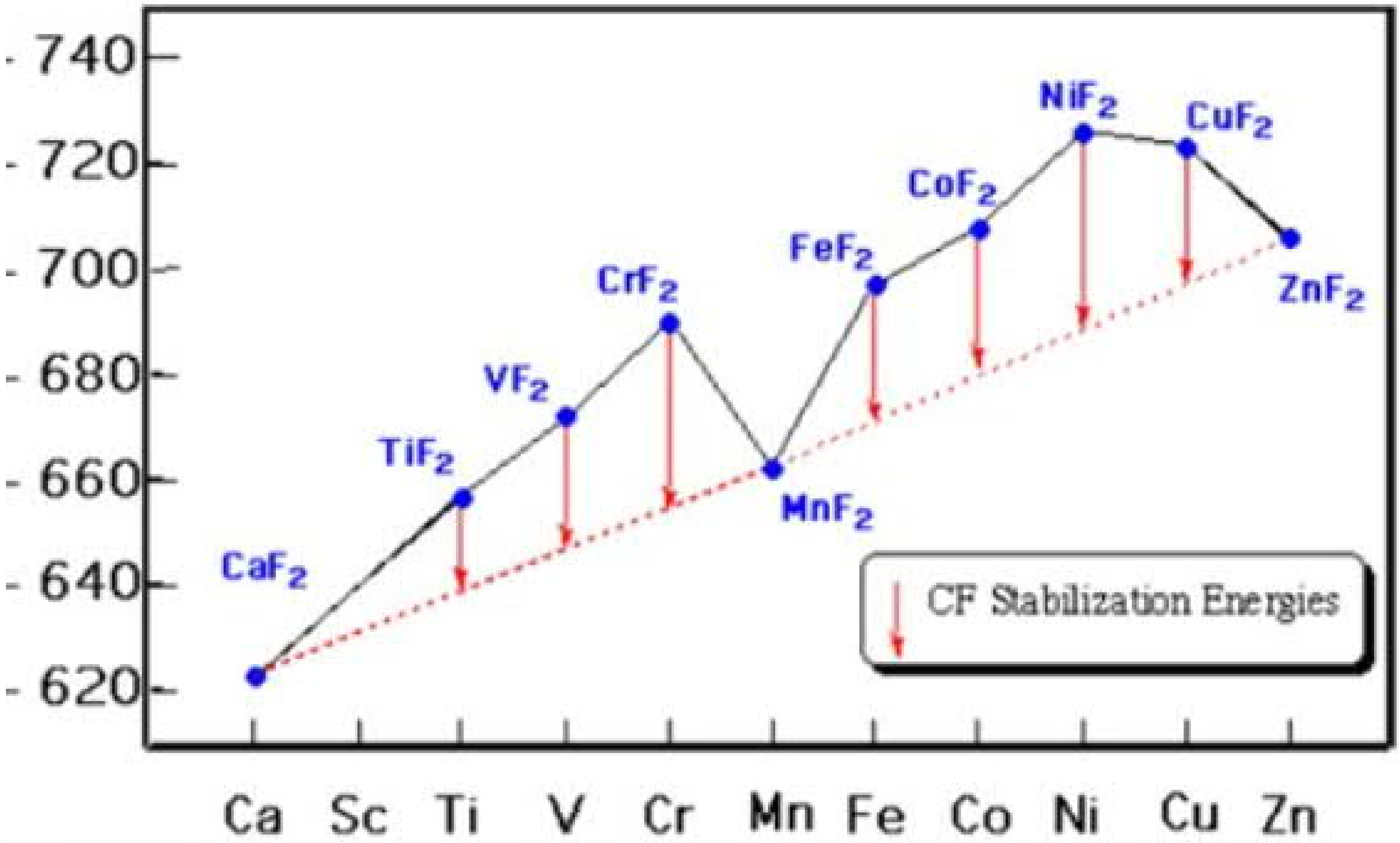


○ **high-spin**
● **low-spin**





Lattice Energy of Transition Metal Fluorides [kcal / mol]

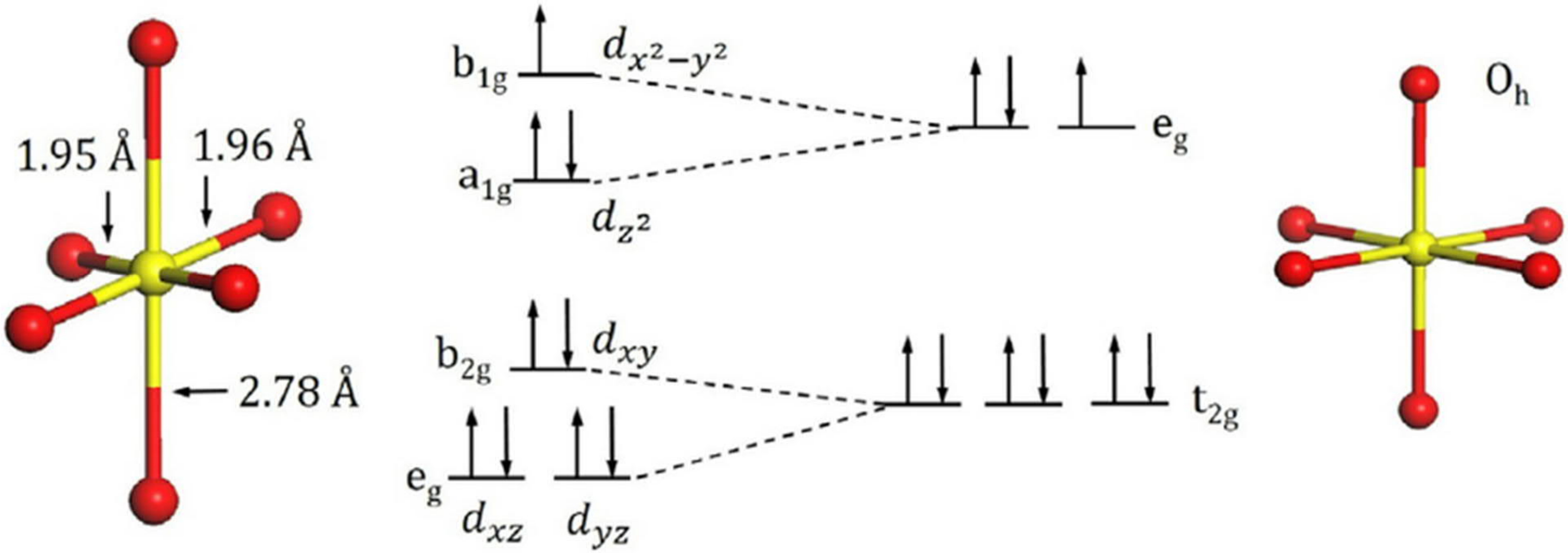


C.S.G. Phillips, R. J. P Williams, Inorganic Chemistry, Volume 1, p. 179.

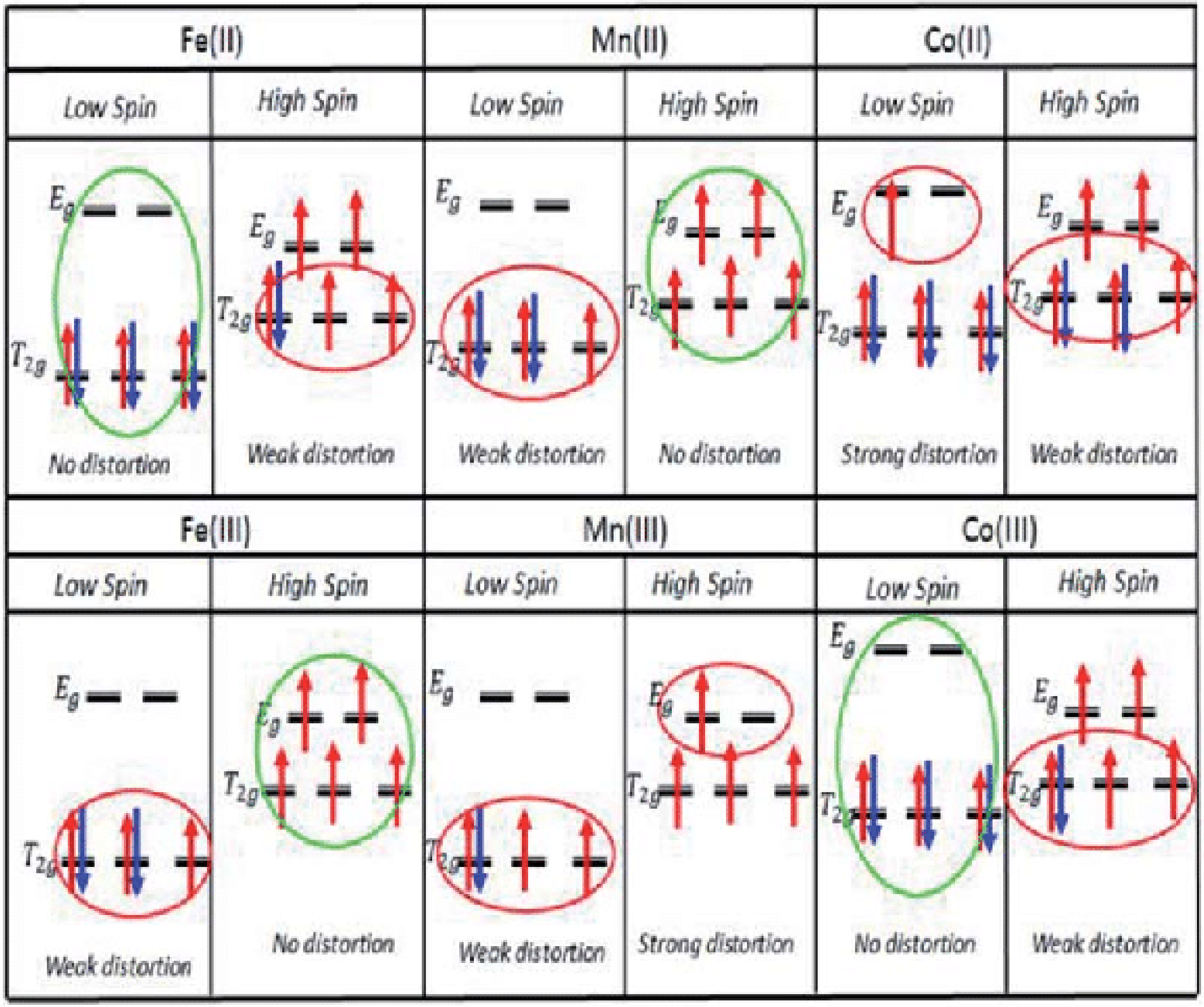
Jahn–Teller Effect (or Distortion)

- 1937: Hermann Arthur Jahn & Edward Teller
- Important in explaining: spectroscopy, stereochemistry, crystal chemistry, solid-state physics and materials science
- All is explained by the repulsions between ligands/anions and electrons at outer-most orbitals
- Crystal field effect: ligands raise the (closer) orbital energy
- Jahn-Teller effect: electrons at the higher-energy orbital push the ligand/anion farther
- JT effect is most visible in octahedral environment when there is different electron occupancies at the two e_g orbitals (as the ligands/anions come closest to these orbitals)
  → **Distortion** (typically elongation) of the octahedron

Distorted **Regular**



We come back to this when we discuss high-temperature superconducting copper oxides later in this course


Fe(II)
Mn(II)
Co(II)
Low Spin
High Spin
Low Spin
High Spin
Low Spin
High Spin
E_g
T_{2g}
No distortion
Weak distortion
Weak distortion
No distortion
Strong distortion
Weak distortion
Fe(III)
Mn(III)
Co(III)
Low Spin
High Spin
Low Spin
High Spin
Low Spin
High Spin
Weak distortion
No distortion
Weak distortion
Strong distortion
No distortion
Weak distortion