LECTURE SCHEDULE

	Date	Topic
1.	Wed 28.10.	Course Introduction & Short Review of the Elements
2.	Fri 30.10.	Periodic Properties & Periodic Table & Main Group Elements (starts)
3.	Fri 06.11.	Short Survey of the Chemistry of Main Group Elements (continues)
4.	Wed 11.11.	Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)
5.	Fri 13.11.	Redox Chemistry
6.	Mon 16.11.	Transition Metals: General Aspects & Crystal Field Theory
7.	Wed 18.11.	Zn + Ti, Zr, Hf & Atomic Layer Deposition (ALD)
8.	Fri 20.11.	V, Nb, Ta & Metal Complexes and MOFs
9.	Mon 23.11.	Cr, Mo, W & 2D materials
10	Wed 25.11.	Mn, Fe, Co, Ni, Cu & Magnetism and Superconductivity
11.	Fri 27.11.	Resources of Elements & Rare/Critical Elements & Element Substitutions
12.	Mon 30.11.	Lanthanoids + Actinoids & Pigments & Luminescence & Upconversion
13.	Wed 02.12.	Inorganic Materials Chemistry Research

EXAM: Thu Dec 10, 9:00-12:00 Ke1

QUESTIONS: Lecture 6

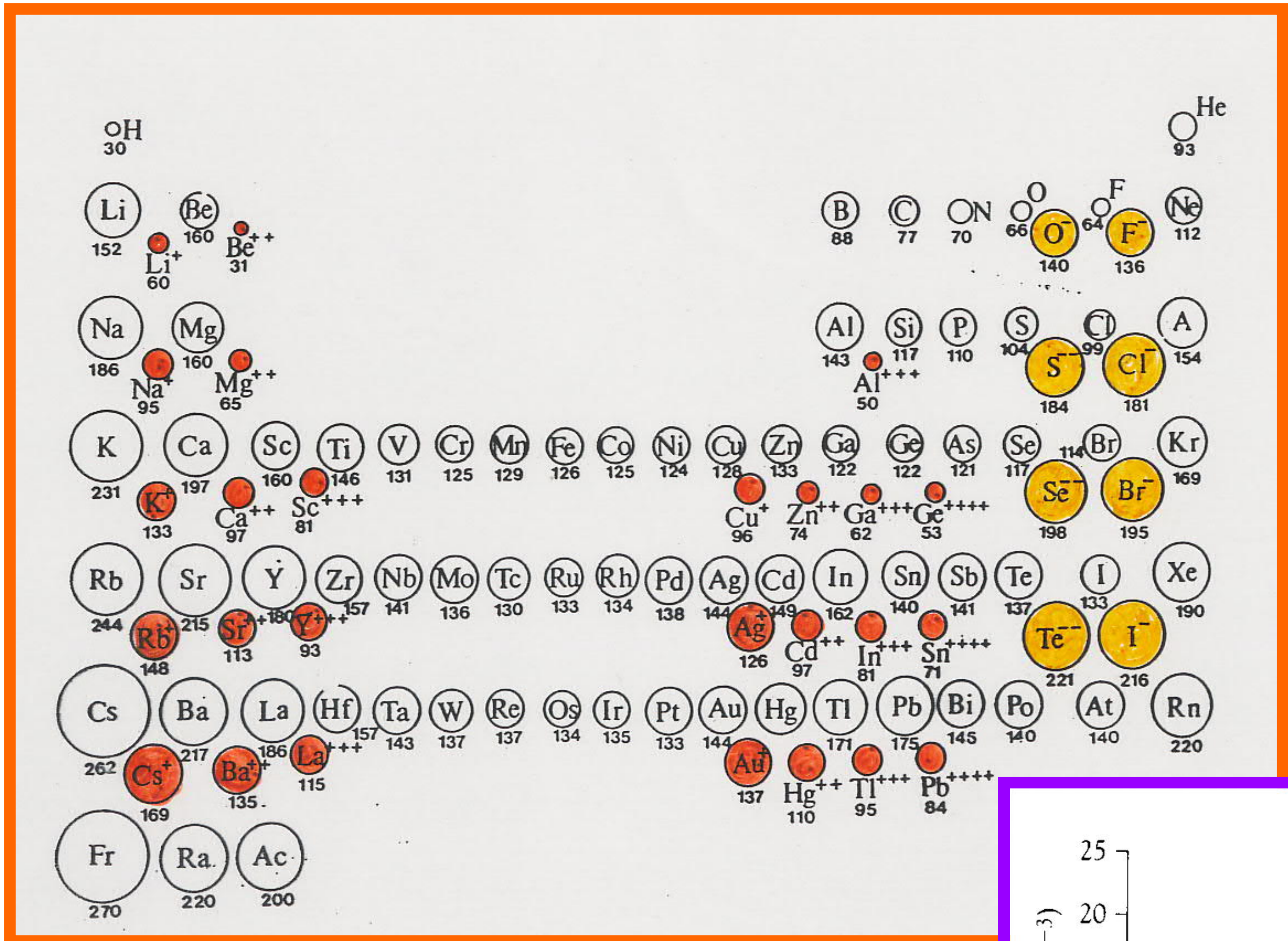
- **In octahedral crystal field, transition metal cations with the electron configurations of d^4, d^5, d^6 and d^7 have the possibility for two spin states. Give the electron configurations for which the same applies in tetrahedral crystal field.**

- **How many unpaired electrons the following ions have (assume high spin) in (a) octahedral, and (b) tetrahedral crystal fields: Cr^{3+}, Mn^{2+}, Fe^{2+} and Co^{+2}?**

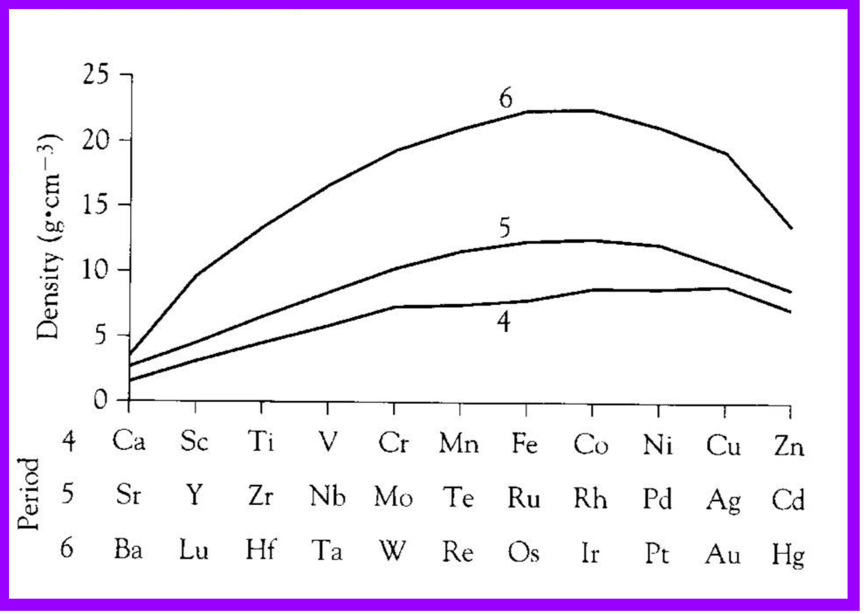
- **Which of the following ions is/are (a) colourless, (b) lightly coloured, (c) strongly coloured: Fe^{3+}, Co^{2+}, Cu^{+}?**

GENERAL FEATURES (d block transition metals)

- All are metals
- Multiple oxidation states → richness of chemistry
- Reactivity varies
- More electronegative than alkali and alkaline earth metals
- Both ionic and covalent compounds
- General rule: at lower oxidation states more ionic bond nature
- General rule: positive metal ions at low oxidation state, oxoanions at high oxidation states (e.g. Mn^{2+} and MnO_4^-)
- Coordination complexes



Atomic/ionic radius



Density

Ionic radii for 3d cations (CN = 6) in Å:

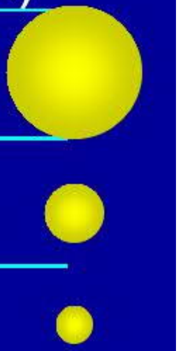
- with increasing oxidation state ionic radius decreases

Ox. state	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+II	0.86	0.79	0.80	0.83	0.78	0.75	0.69	0.73	0.74
+III	0.67	0.64	0.62	0.65	0.65	0.61	0.60	0.54	-
+IV	0.61	0.58	0.55	0.53	0.59	0.53	0.48	-	-

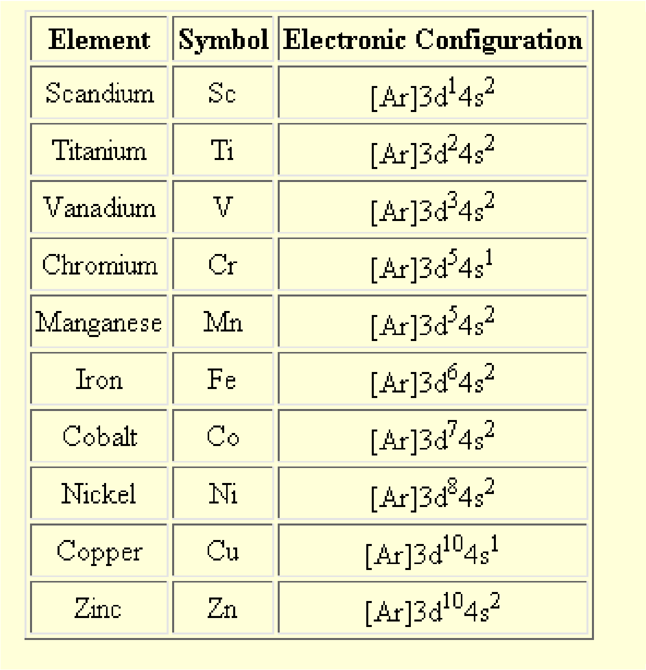
Rank the hydride ion, helium atom and lithium ion in terms of size

Explain the relative sizes.

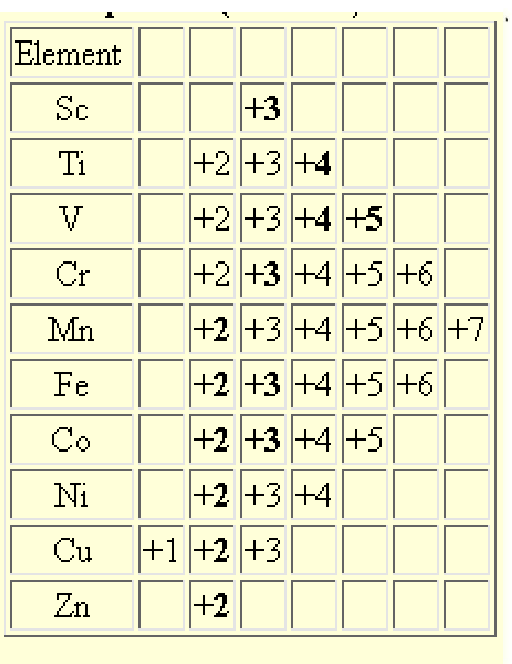
	Nuclear charge	Number of electrons	Ionic radii (Å)
H^-	1	2	2.08
He	2	2	0.93
Li^+	3	2	0.60



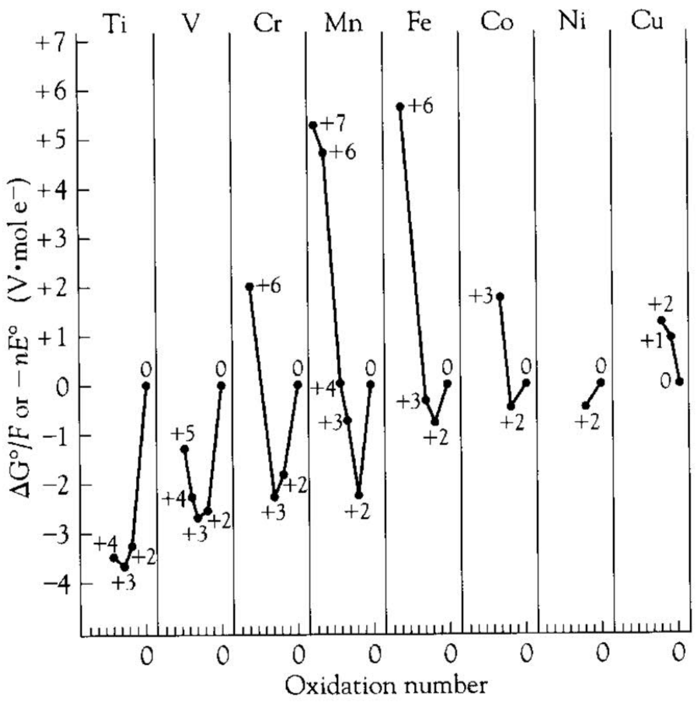
FROST DIAGRAMS



Element	Symbol	Electronic Configuration
Scandium	Sc	$[Ar]3d^14s^2$
Titanium	Ti	$[Ar]3d^24s^2$
Vanadium	V	$[Ar]3d^34s^2$
Chromium	Cr	$[Ar]3d^54s^1$
Manganese	Mn	$[Ar]3d^54s^2$
Iron	Fe	$[Ar]3d^64s^2$
Cobalt	Co	$[Ar]3d^74s^2$
Nickel	Ni	$[Ar]3d^84s^2$
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**					



OXIDATION STATES

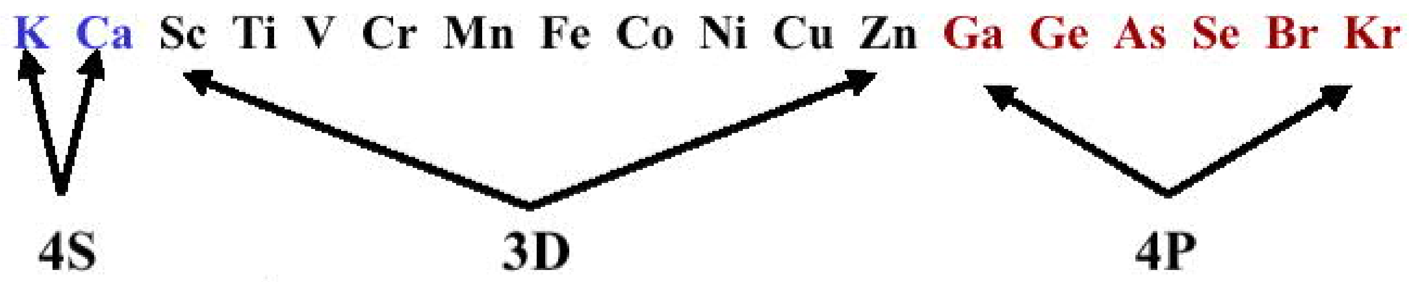


Figure 1. The 4th row of the periodic table. The transition metals are the elements that range from Sc (Scandium) to Zn (Zinc).

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	(Zn)
+VIII										
+VII					●					
+VI				●	o	o				
+V			●		●					
+IV		●	o		o			o		
+III	●	●	●	●	o	●	●			
+II		o	o	o	●	●	●	●	●	●
+I									●	

	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	(Cd)
+VIII						o				
+VII					●					
+VI				●	o	o				
+V			●	o						
+IV		●	o	o	o	●	o	o		
+III	●	o	o	o	o	o	●		o	
+II			o	o		o	o	●		●
+I						o	o		●	

	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	(Hg)
+VIII						●				
+VII					●					
+VI				●	o	●				
+V			●	o	o					
+IV		●	o	o	o	o	●	●		
+III	●		o	o	o		●		●	
+II			o	o				●		●
+I									o	●

$ns^2(n-1)d^x$

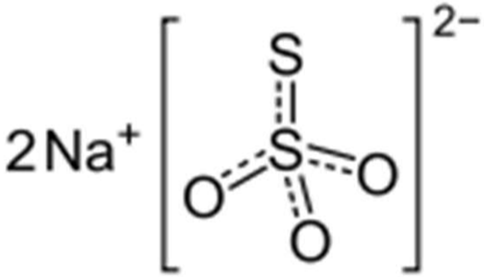
● : most stable

o : possible

MELTING POINTS (ºC)

Ti	1668	Zr	1852	Hf	2220
V	1890	Nb	1470	Ta	3000
Cr	1860	Mo	2620	W	3410
Mn	1245	Tc	2140	Re	3180
Fe	1535	Ru	2282	Os	3045
Co	1492	Rh	1960	Ir	2443
Ni	1452	Pd	1552	Pt	1769
Cu	1083	Ag	961	Au	1063

- compare to Zn 420, Cd 321, Hg -38
- compare to alkali metals 179→29, alkaline earth metals 1080 → 725
- many valence electrons
  → many electrons per atom in the metal bond
  → good electrical conductors
  → strong bonds
  → high melting points
  → hard



CLASSIFICATION OF MIXED-VALENCE COMPOUNDS

M.B. Robin & P. Day, Adv. Inorg. Chem. Radiochem. 10, 247 (1967).

Class-I

- e.g. $Na_2S_2O_3$ (S^{-II} & S^{VI})
- clearly different environments for the two different atoms
- large energy required for electron transfer between these atoms → no interaction → no special properties

Class-II

- e.g. Ag_2O_2 (Ag^{I} & Ag^{III})
- different but sufficiently similar environments → only a small energy required for electron transfer between the different atoms → semiconducting

Class-III

- e.g. Ag_2F ($Ag^{0.5}$) & $YBa_2Cu_3O_7$ ($Cu^{2.3}$)
- all mixed-valence atoms have identical environments → electrons delocalized → metallic conductivity

VALENCE SEPARATION (Verwey-type)

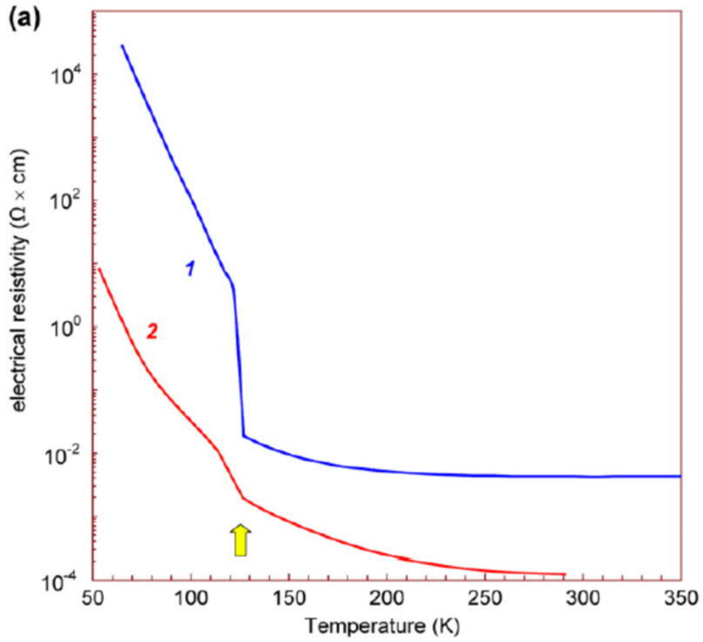
$$2\,M^{m+0.5} \rightarrow M^{m} + M^{m+1}$$

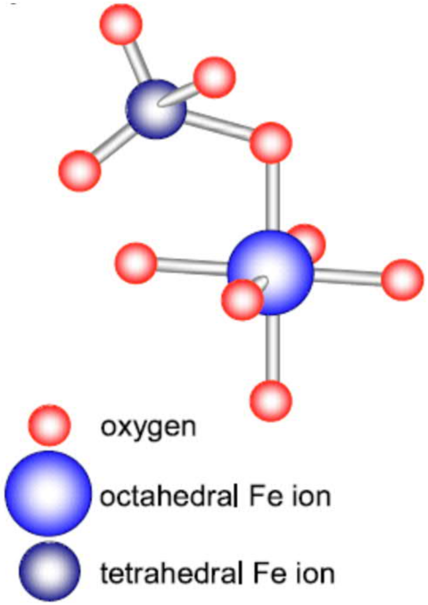
(mixed valence state) → (valence-separated state)

Example: Magnetite Fe_3O_4

- Inverse spinel structure: $Fe^{III}_{tet}[Fe^{2.5}]_{oct}O_4$
- Verwey transition (around 125 K): $2\,Fe^{2.5} \rightarrow Fe^{II} + Fe^{III}$

1 single crystal
2 thin film





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

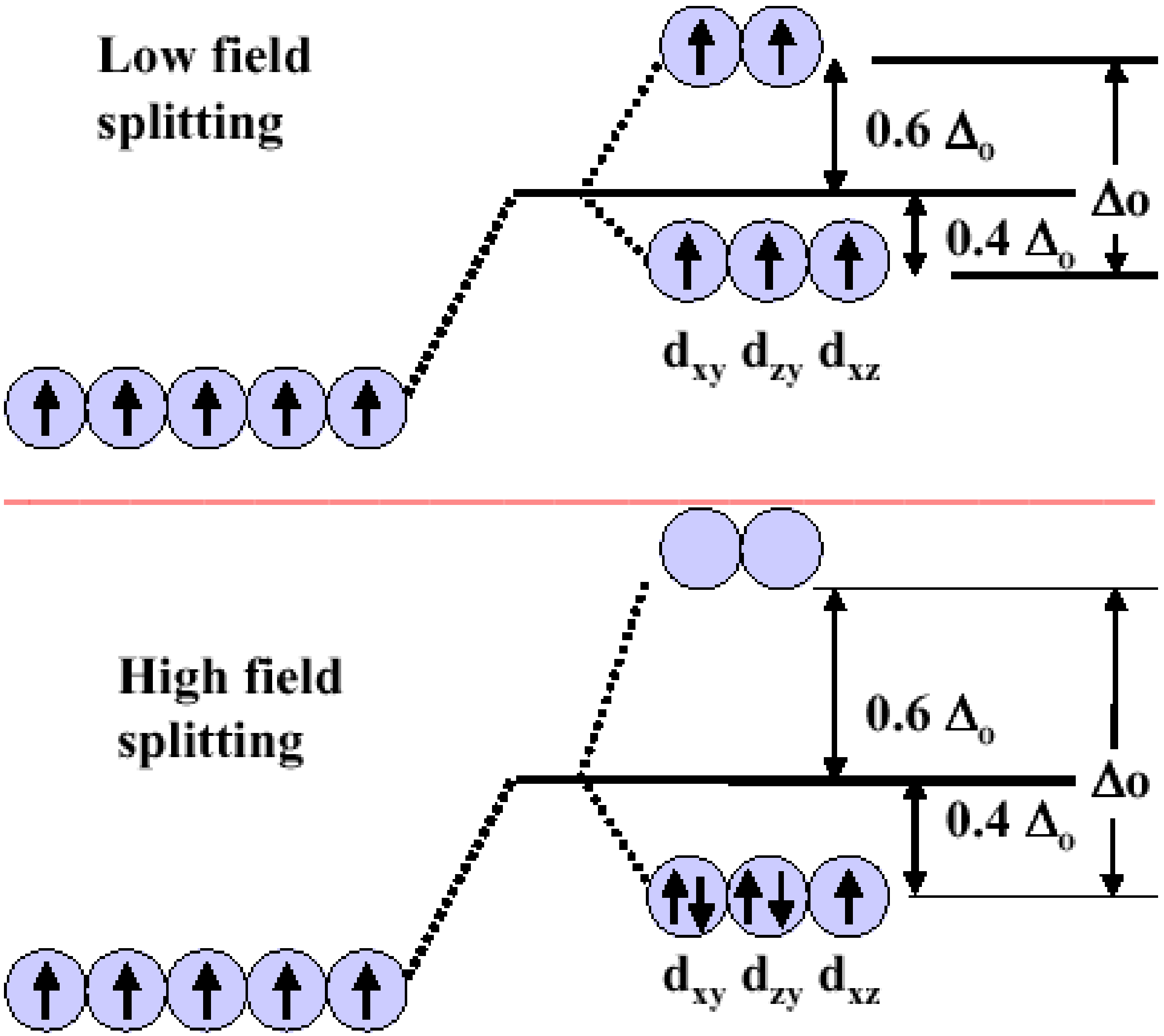
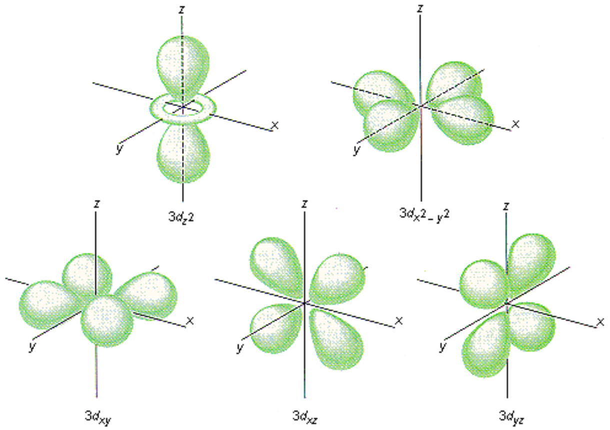


Figure 5. The two cases of crystal field splitting for the octahedral geometry.

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

- **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**

$[Fe(H_2O)_6]^{3+}$ $[Ni(H_2O)_6]^{2+}$ $[Zn(H_2O)_6]^{2+}$

$[Co(H_2O)_6]^{2+}$ $[Cu(H_2O)_6]^{2+}$

CRYSTAL / LIGAND FIELD THEORY

- **Electron configuration of transition metal (T) : $ns^2 (n-1)d^x$**
- **Free T atom:**

  - all the five d-orbitals are degenerated (= have the same energy)

- **T atom surrounded by neighbours (crystal, molecule or solution):**

  - outer s electrons and possibly also part of the d-electrons (y) participate in the formation of the chemical bond

  → $T^{(2+y)+}$: d^{x-y}

- **Part of d-electrons (x-y) remain non-bonded**

  (exciting properties of transition metals originate from these electrons)

WHEN the T atom is BONDED:

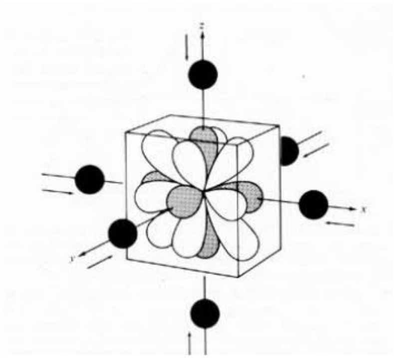
- **Each T atom (cation) likes to:**

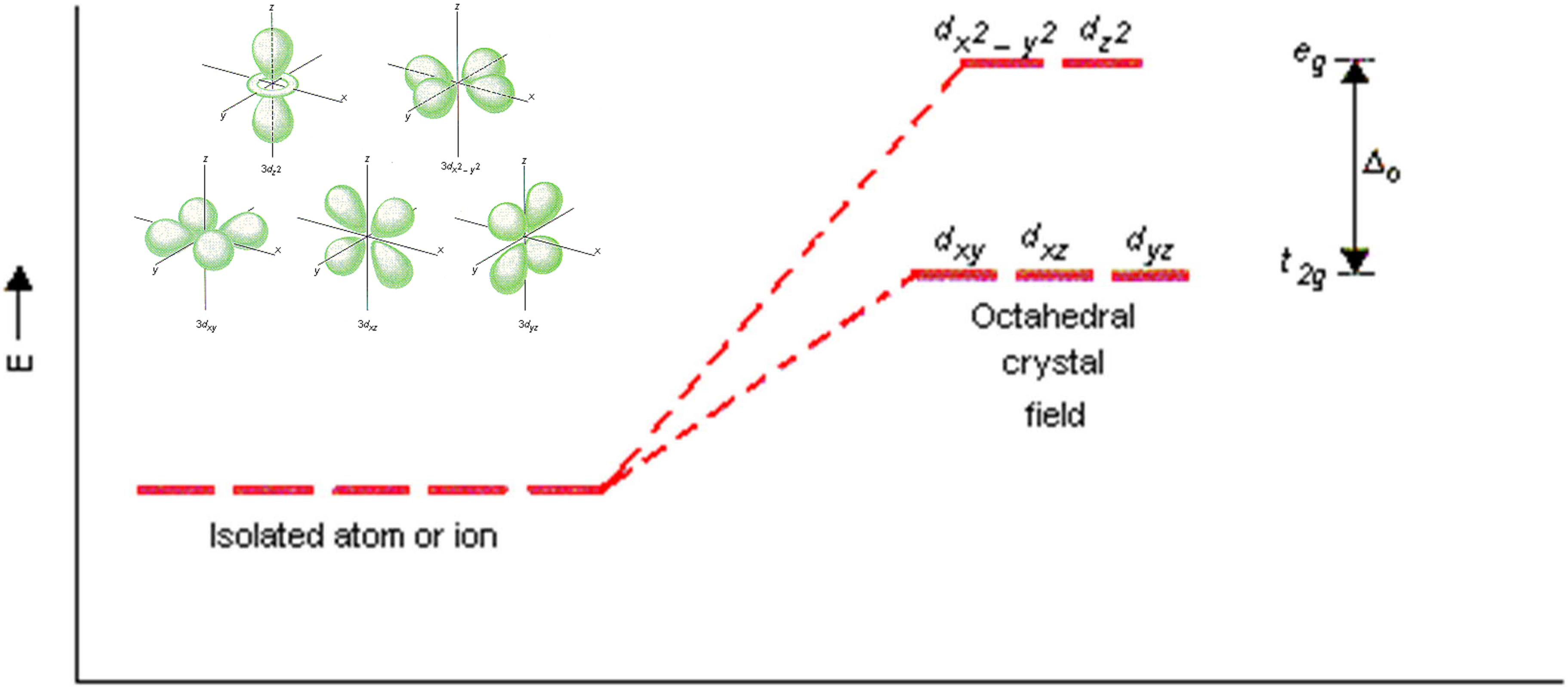
  (1) get the nearest-neighbour anions (e.g. O^{2-}) as close as possible **(such that the bond can form)**

  (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

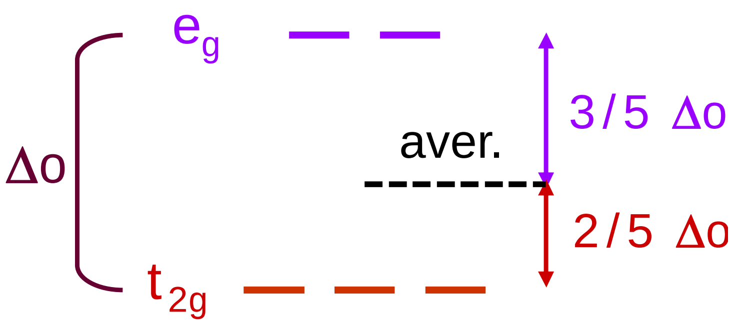
- **All the five d-orbitals feel the repulsion; in other words, their energy is increased in comparison to the case in free T atom**
- **d-orbitals that are closest to the nearest-neighbour anions feel the strongest repulsion and are with the highest energy, while those that are farther are with the 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)**

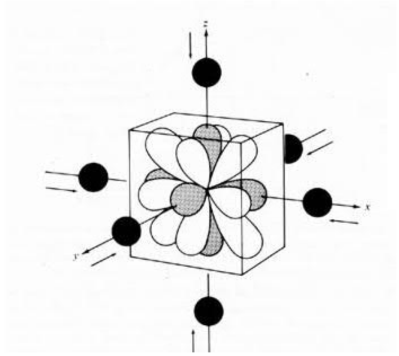

z
x
y

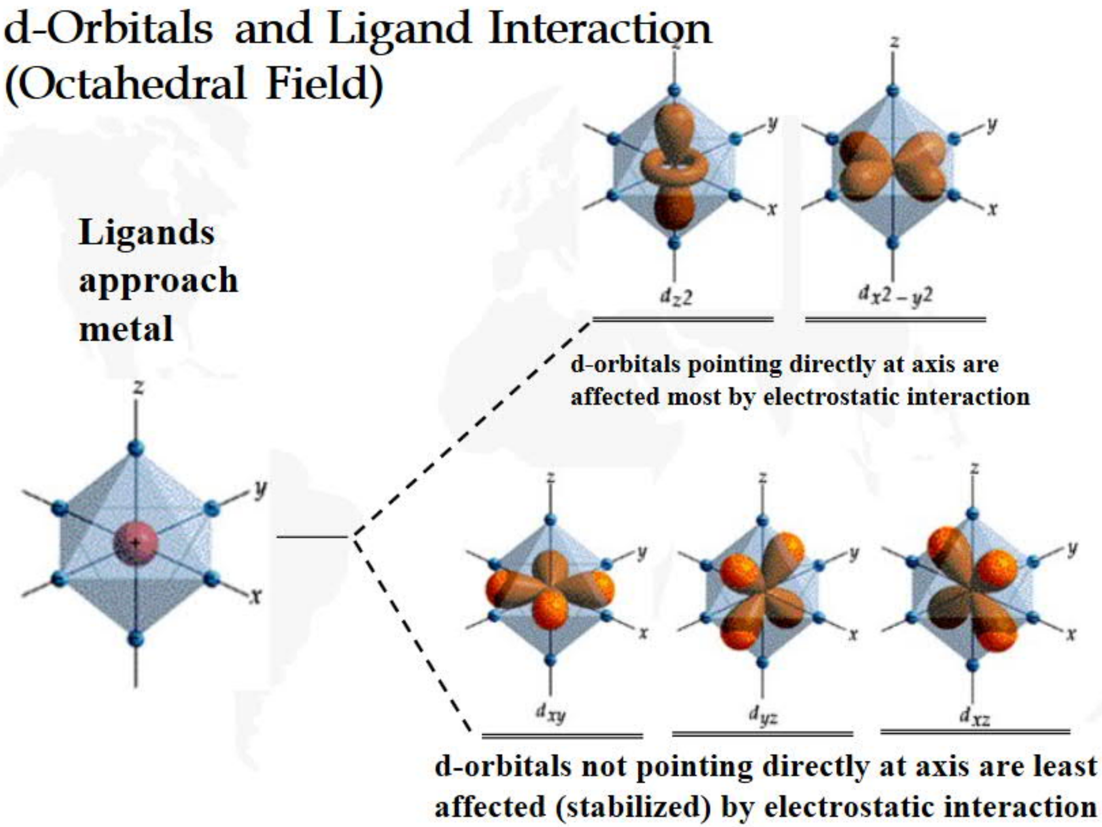

E
z
x
y
$3d_{z^2}$
$3d_{x^2-y^2}$
$3d_{xy}$
$3d_{xz}$
$3d_{yz}$
Isolated atom or ion
$d_{x^2-y^2}$
d_{z^2}
d_{xy}
d_{xz}
d_{yz}
Octahedral crystal field
e_g
Δ_o
t_{2g}

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 $d_{x2\text{-}y2}$) orient towards the anions → higher energy (3/5 Δ_o) e_g orbitals



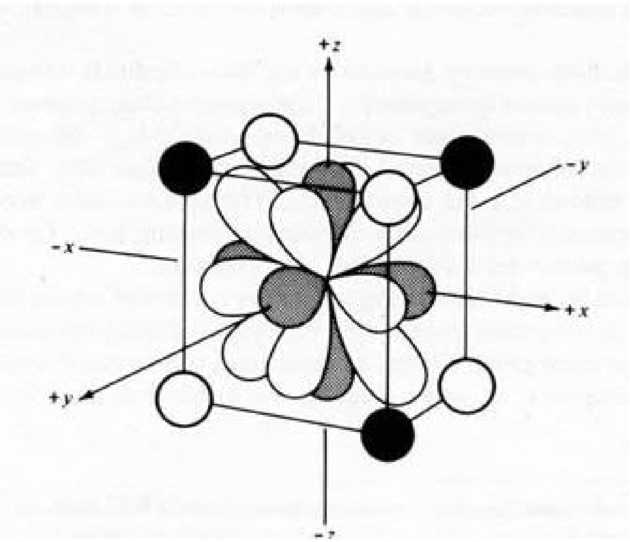



d-Orbitals and Ligand Interaction (Octahedral Field)

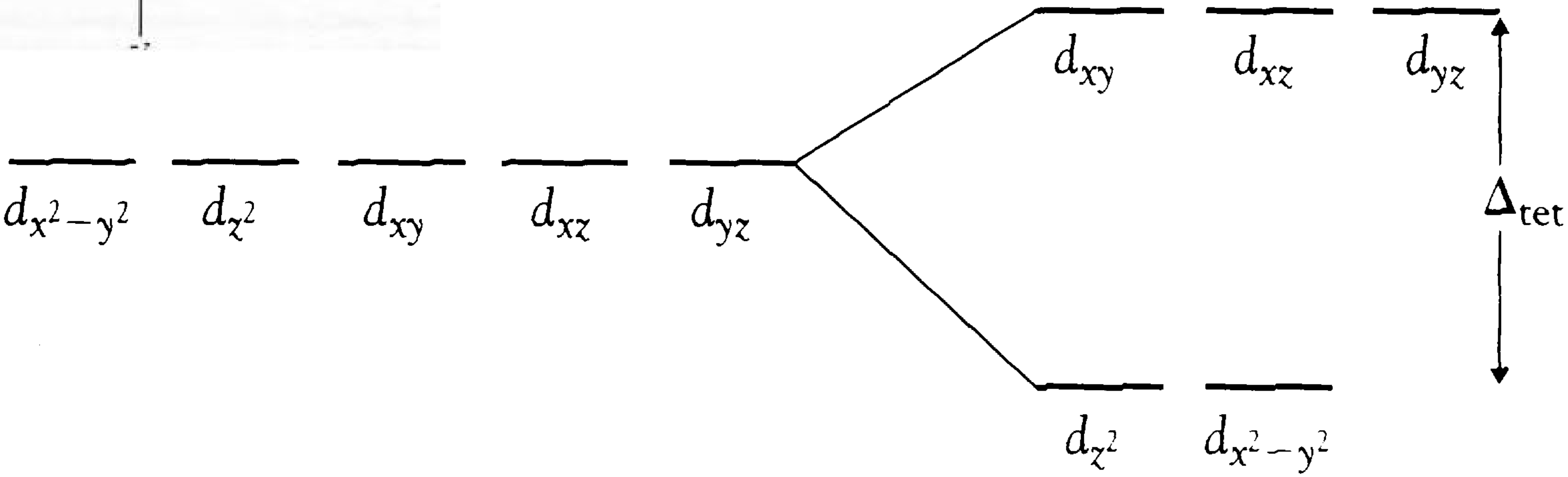
Ligands approach metal

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

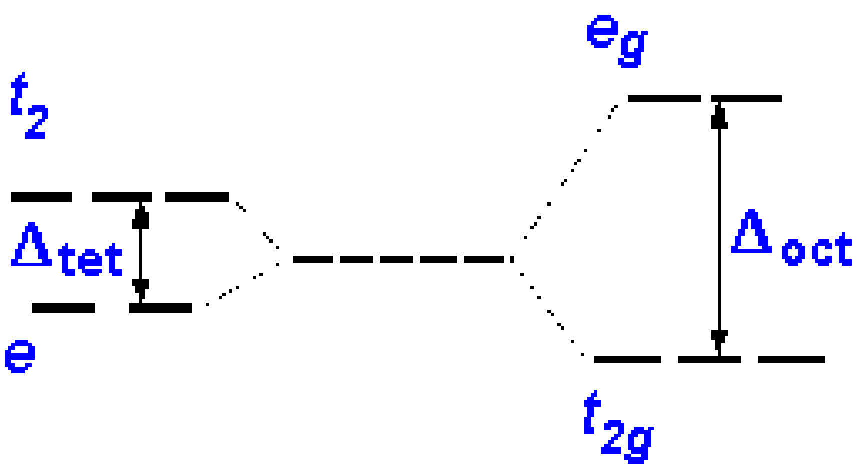


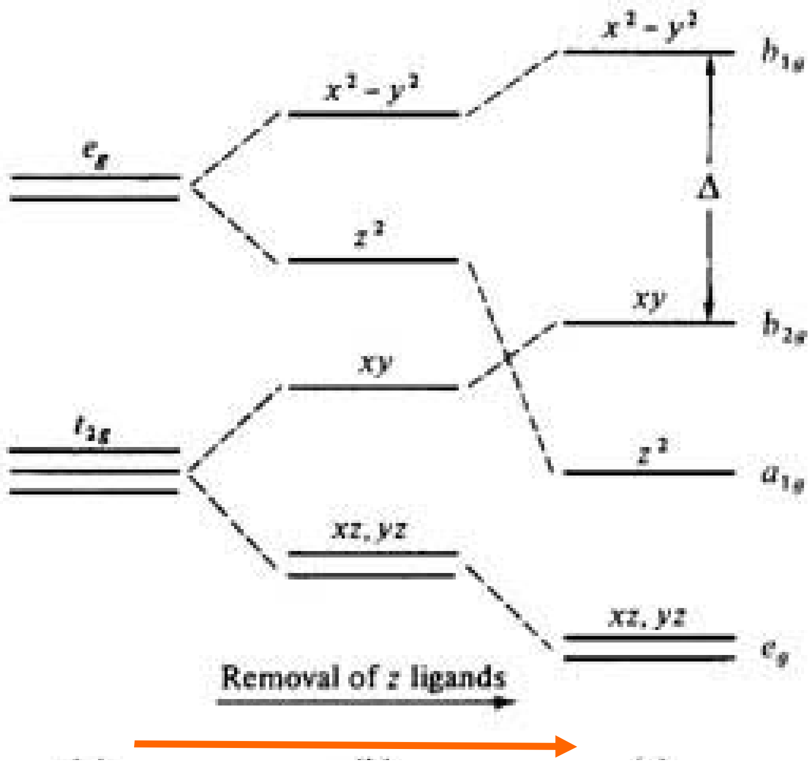
Tetrahedral field

- **4 anions/ligands around transition metal T cation**
- **$\Delta_{tet} = 4/9\ \Delta_{oct}$ for the same metal/anion pair→ usually high spin**

Square-planar

Tetrahedral **Octahedral**





elongation of octahedron

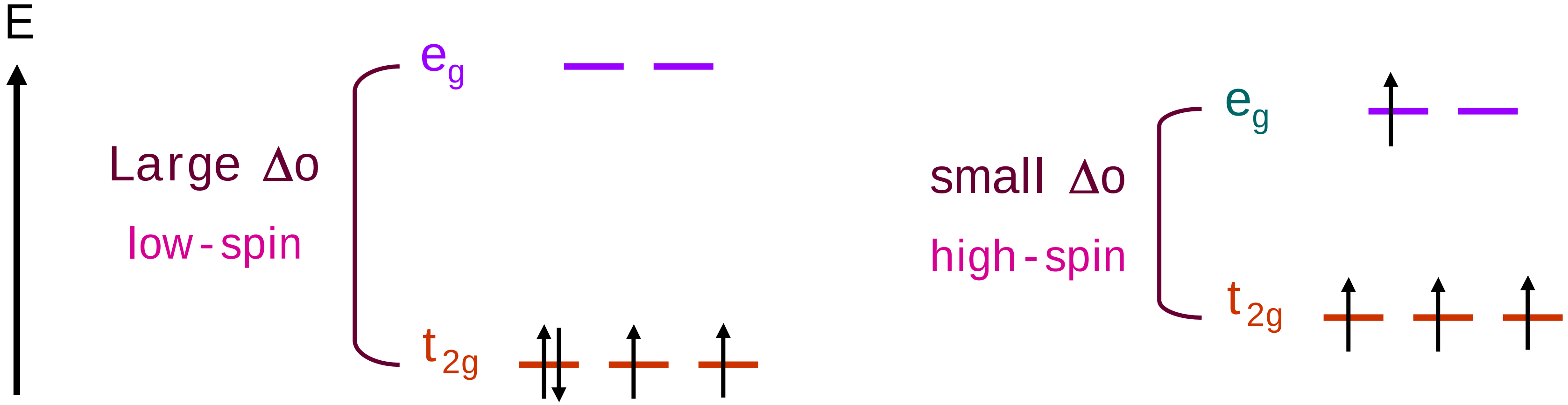
How the d electrons occupy the splitted orbitals?

Two contadictory goals:

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

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

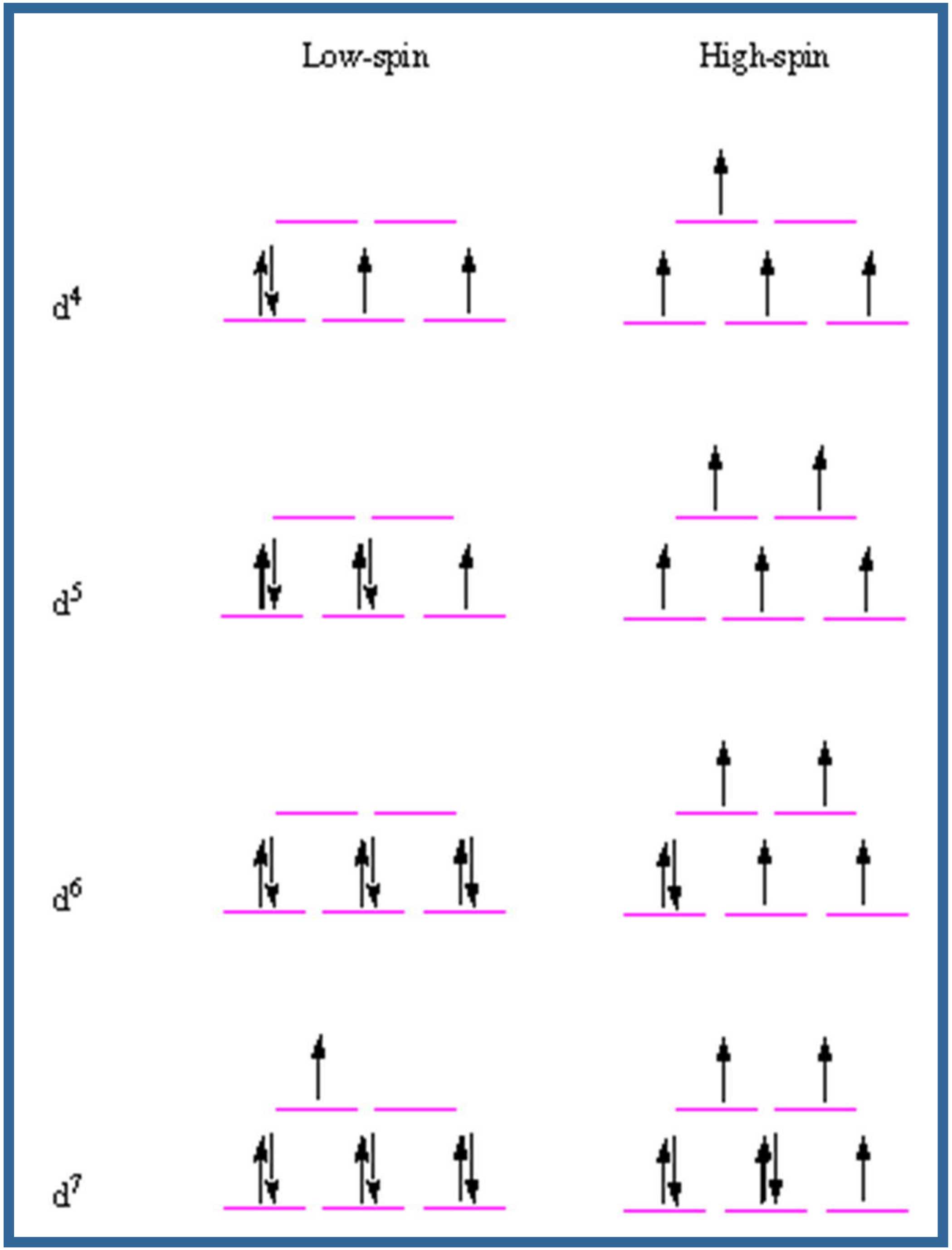
As $\Delta_{tet} = 4/9\ \Delta_{oct}$, tetrahedral case almost always high-spin



Let’s consider

the OCTAHEDRAL case

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



SPECTROCHEMICAL SERIES

- **Empirically derived order for ligands/anions**
- **Ligands ordered by the size of the splitting Δ they produce**

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

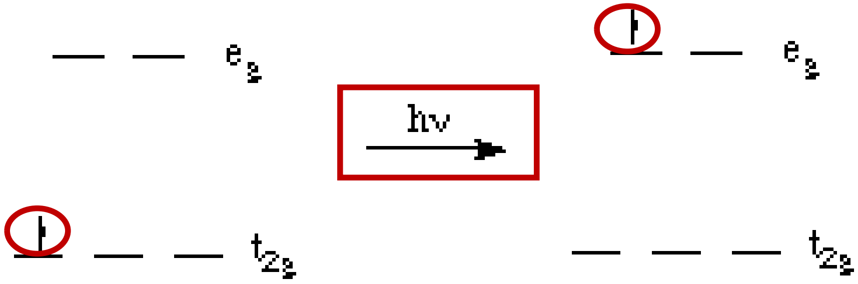
π acceptors ⟷ π donors

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

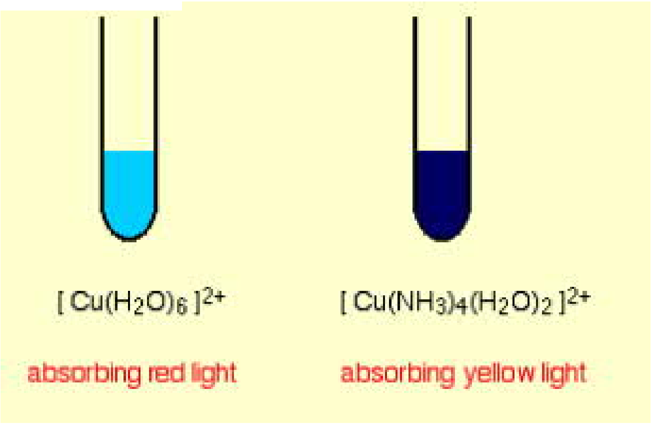
→ high-spin configurations common in oxide materials

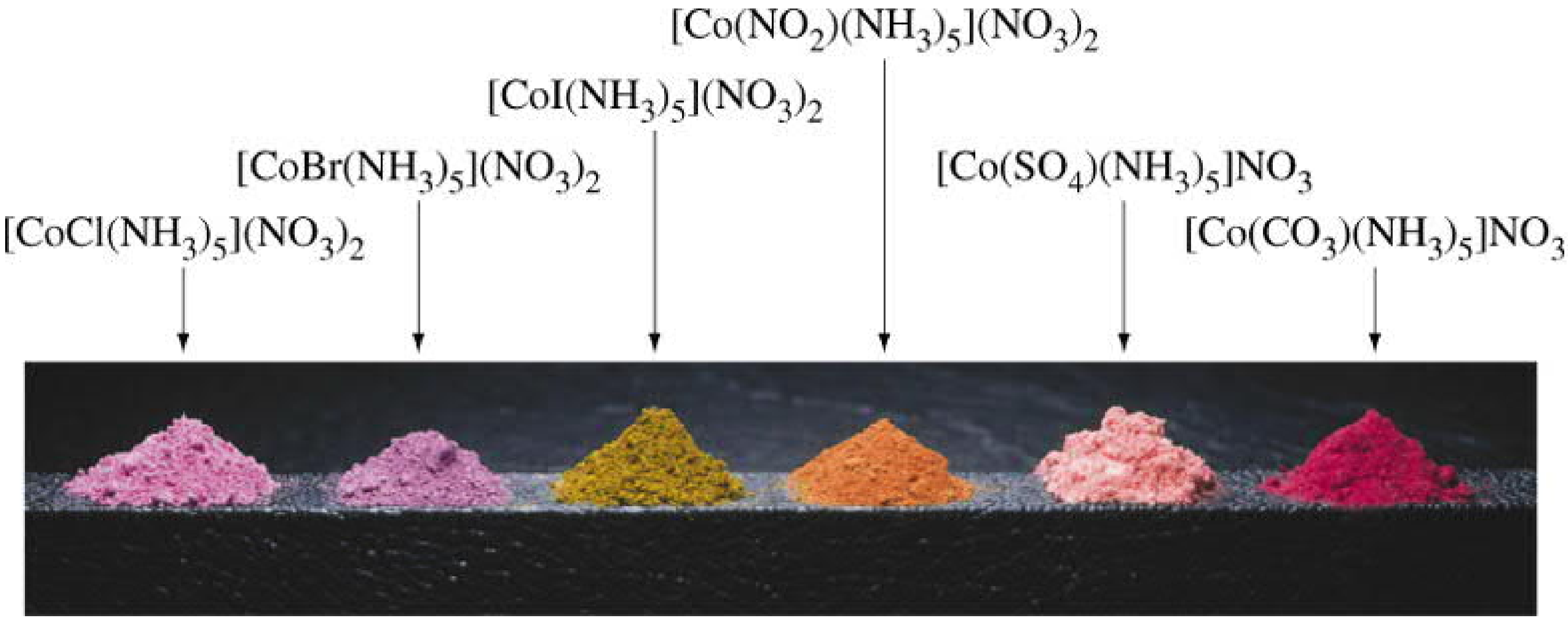
EXAMPLE: Fe^{2+}: d^6

- $[Fe(H_2O)_6]^{2+}$: high-spin → paramagnetic
- $[Fe(CN)_6]^{4-}$: low-spin → diamagnetic



Δ_o varies with the ligand, thus absorption energy and colour also vary with the ligand





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

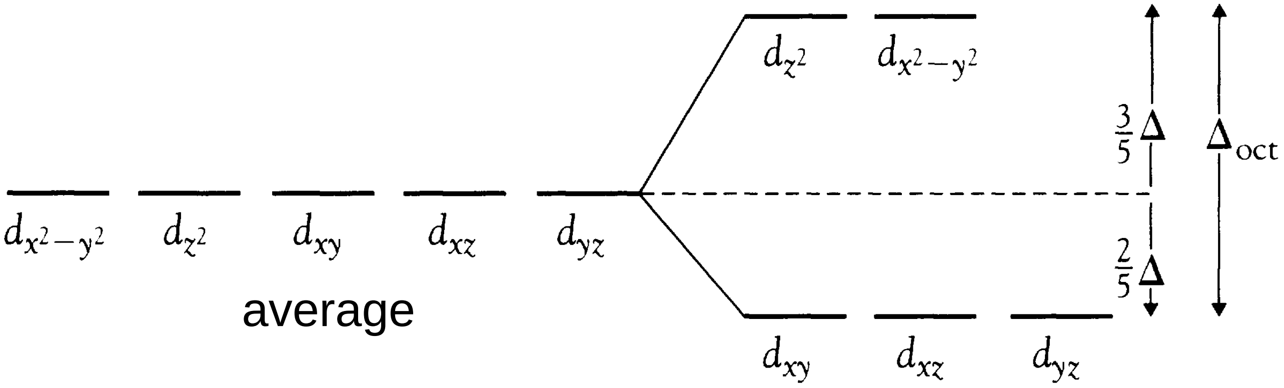
(3) Number of anions/ligands

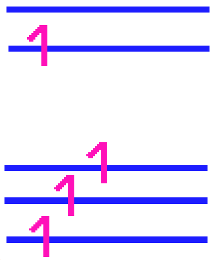
- The more ligands the larger Δ : $\Delta_{tet} \approx 4/9 \times \Delta_{oct}$

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**

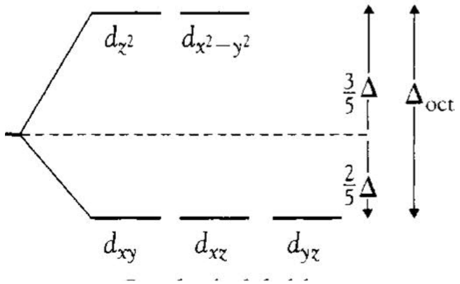


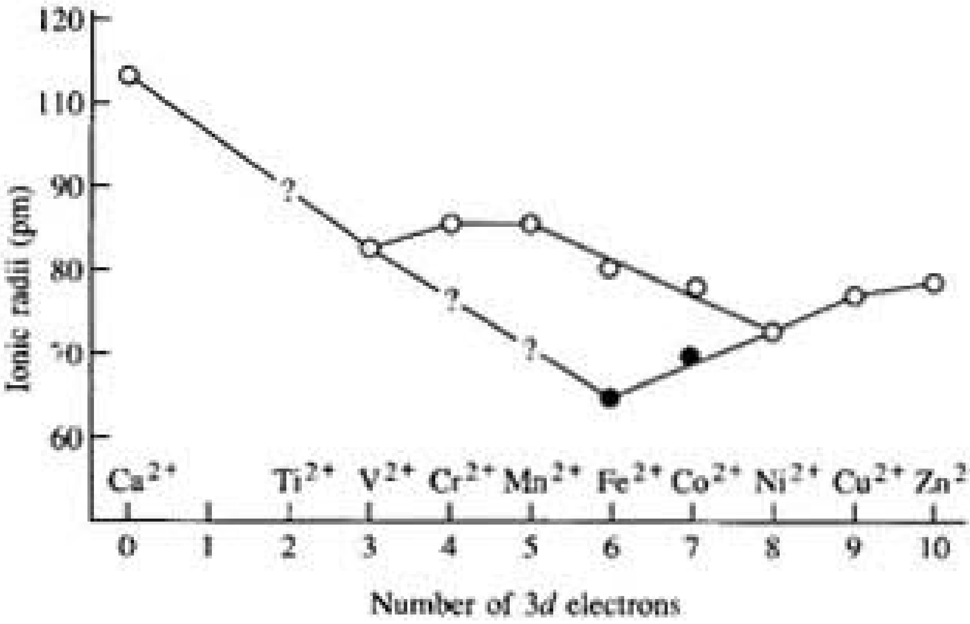


CFSE = [3 x (-2/5) + 1 x (3/5)]Δo = - 3/5 Δo

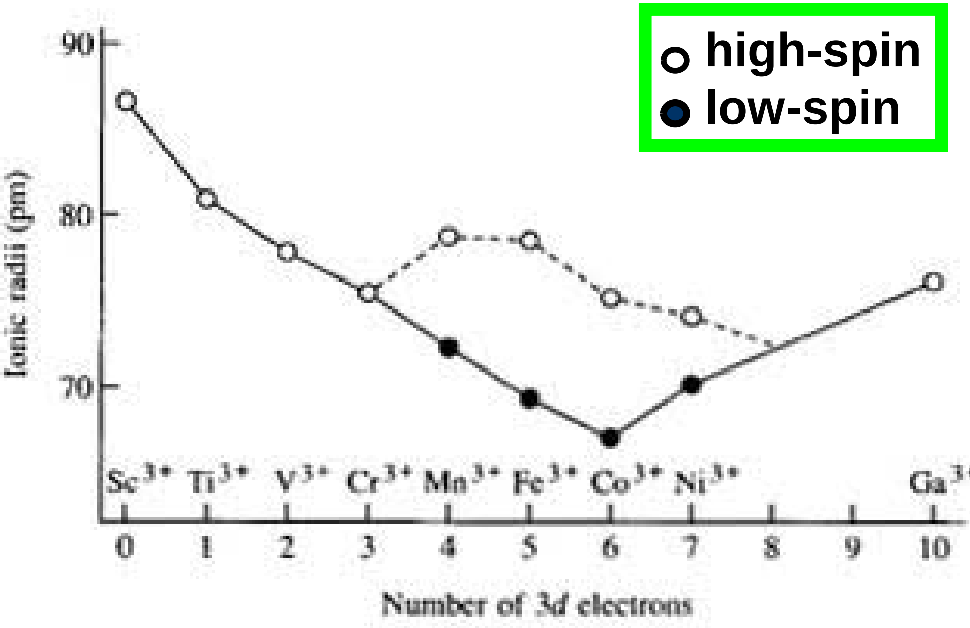
How CFSE is seen in ionic radius

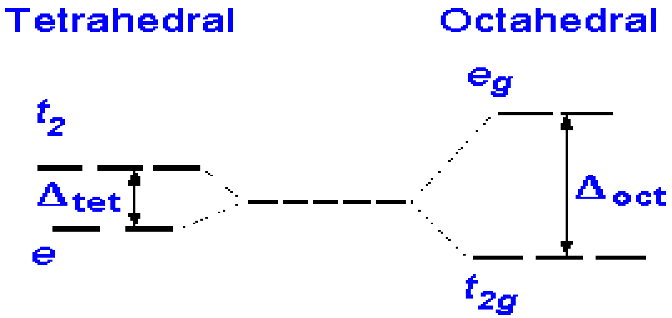
- **FOR EXAMPLE: 3d metals in octahedral coordination**
- **At a fixed oxidation state, ionic radius decreases from left to right**
- **HOWEVER: each electron in e_g orbital increases the ionic radii**
- **Ionic radius depends on spin state !**

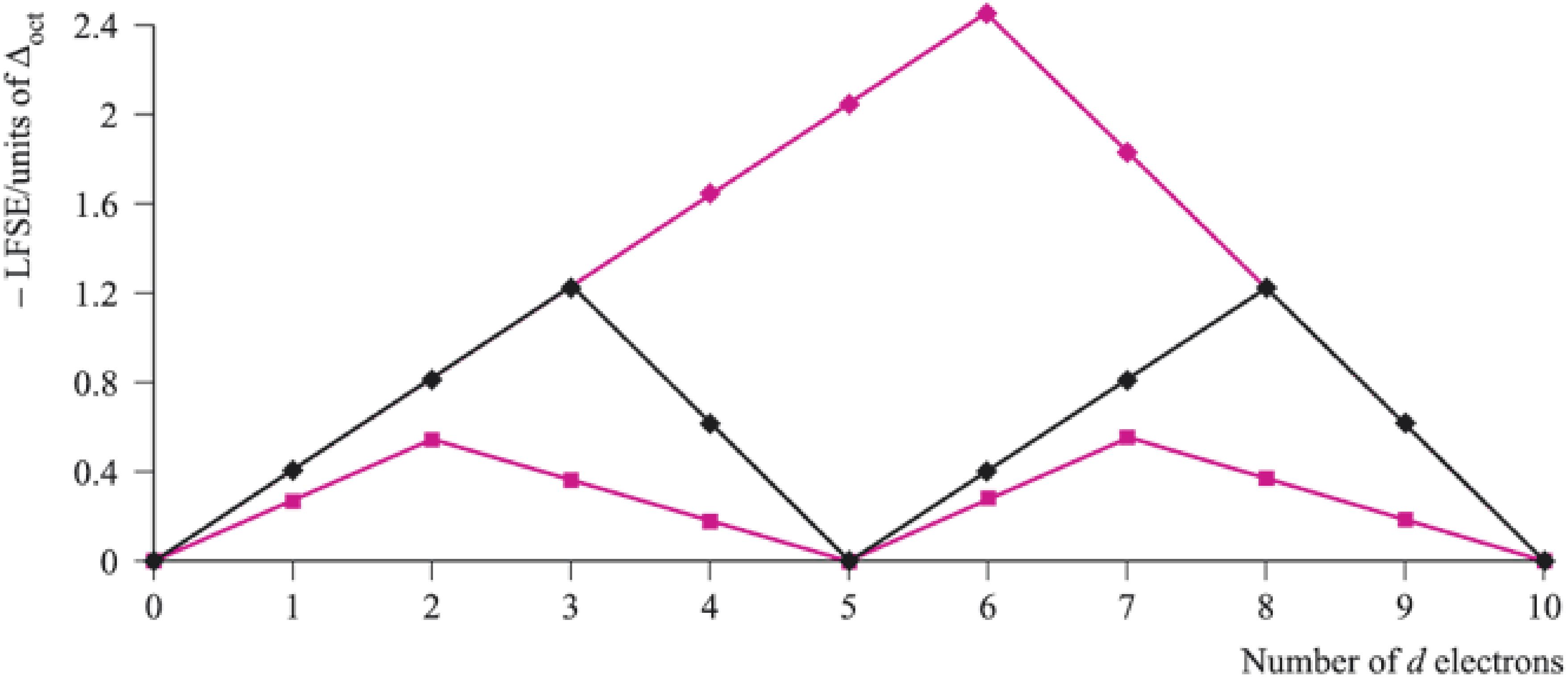




○ **high-spin**
● **low-spin**




Tetrahedral
Octahedral
t_2
Δ_{tet}
e
e_g
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