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:	
Fri	08.10.	Mo:	Ahmed, Shamshad, Svinhufvud
Mon	11.10.	Mn:	Majaniemi, Thakur, Ahkiola
		Ru:	Ichanson, Locqueville
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

QUESTIONS: Lecture 5

- Give plausible explanations for the following melting point (^{o}C) comparisons:

  Cu 1083 & Zn 420

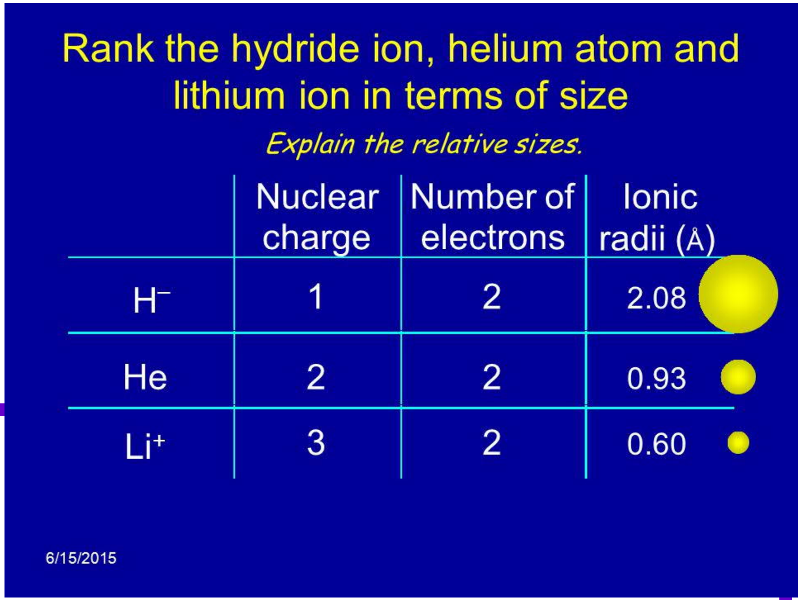
  Cr 1860 & Mn 1245 & Fe 1535

  Fe 1535 & Ru 2282 & Os 3045

- Select among the following ions those which you assume would be color-less or very weakly colored: Ti^{4+}, Ti^{3+}, Mn^{4+}, Mn^{3+}, Mn^{2+}, Fe^{3+}, Fe^{2+}, Co^{2+}, Cu^{2+}, Cu^{+}. Most importantly, motivate your answer with short explanations.

- Why pigments may appear different under sunlight and under fluorescent lighting?

d-BLOCK ELEMENTS


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

Explain the relative sizes.

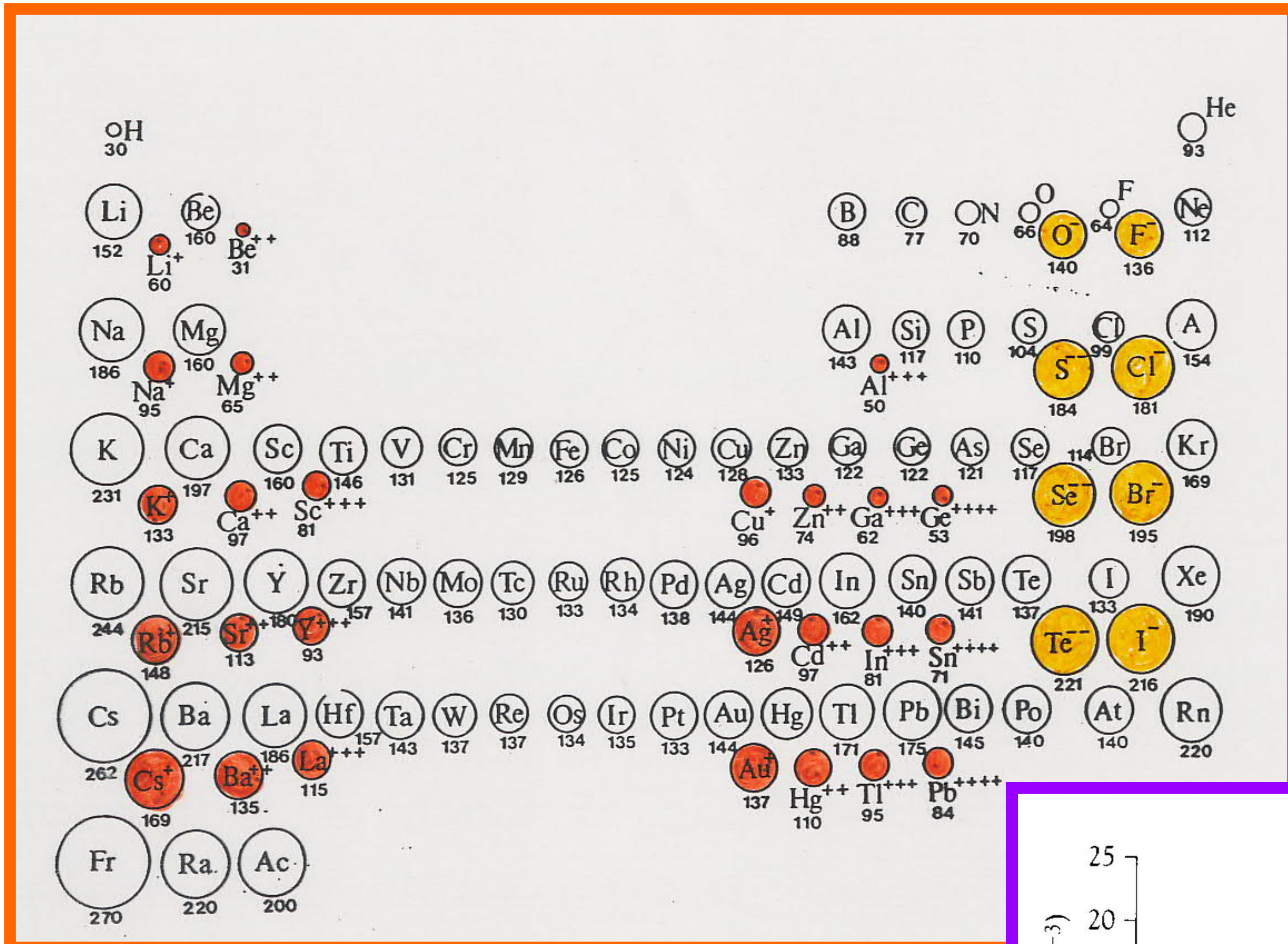
	Nuclear charge	Number of electrons	Ionic radii (Å)
H^-	1	2	2.08
He	2	2	0.93
Li^+	3	2	0.60

6/15/2015

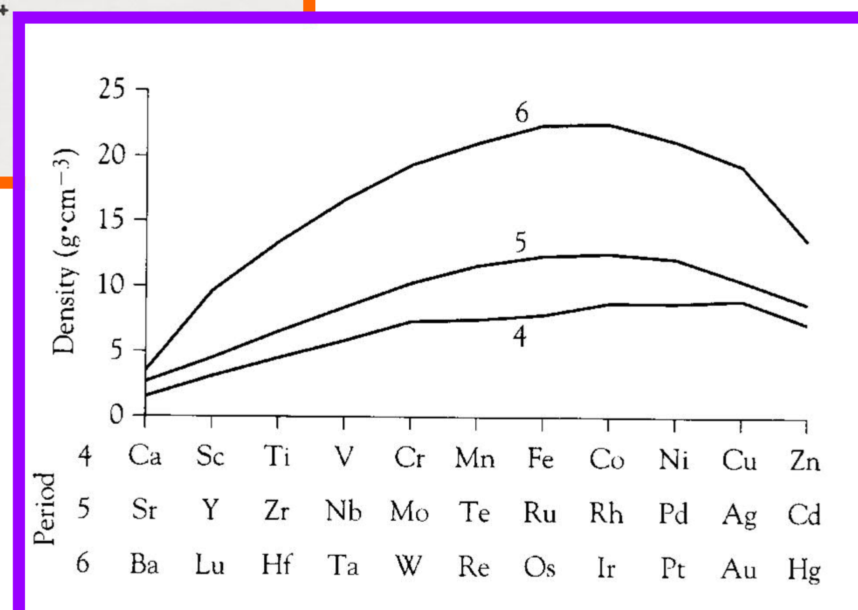
GENERAL FEATURES

- **All are metals**
- **Relatively small in size (d electrons shield poorly each other)**
- **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 (behaves more like a metal)**
- **General rule: positive metal ions at low oxidation state, oxoanions at high oxidation states (e.g. Mn^{2+} and MnO_4^-)**

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	-	-

OXIDATION STATES

Element	Symbol	Electronic Configuration
Scandium	Sc	$[Ar]3d^1 4s^2$
Titanium	Ti	$[Ar]3d^2 4s^2$
Vanadium	V	$[Ar]3d^3 4s^2$
Chromium	Cr	$[Ar]3d^5 4s^1$
Manganese	Mn	$[Ar]3d^5 4s^2$
Iron	Fe	$[Ar]3d^6 4s^2$
Cobalt	Co	$[Ar]3d^7 4s^2$
Nickel	Ni	$[Ar]3d^8 4s^2$
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**					

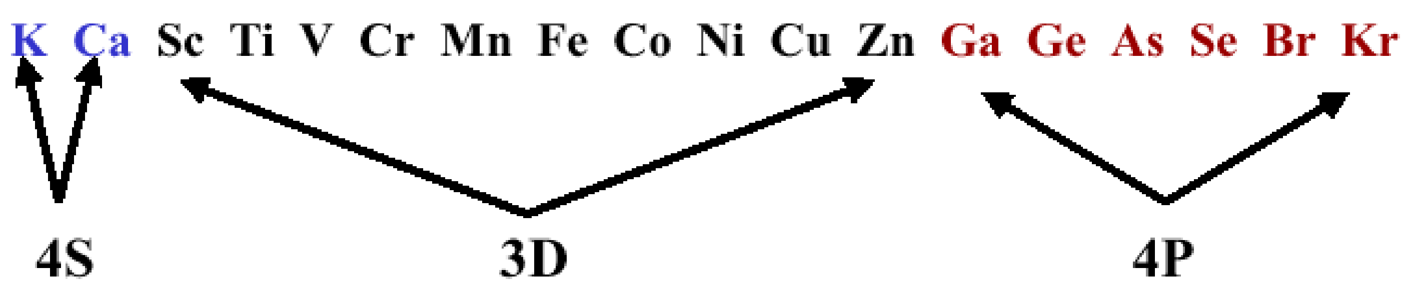


Figure 1. The 4th row of the periodic table. The transition metals are the elements that range from Sc (Scandium) to Zn (Zinc).

	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

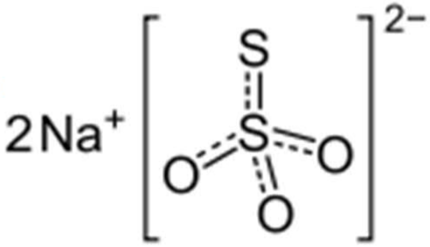
  → high melting points

  → hard

MIXED-VALENCY → electrical conductivity

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

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

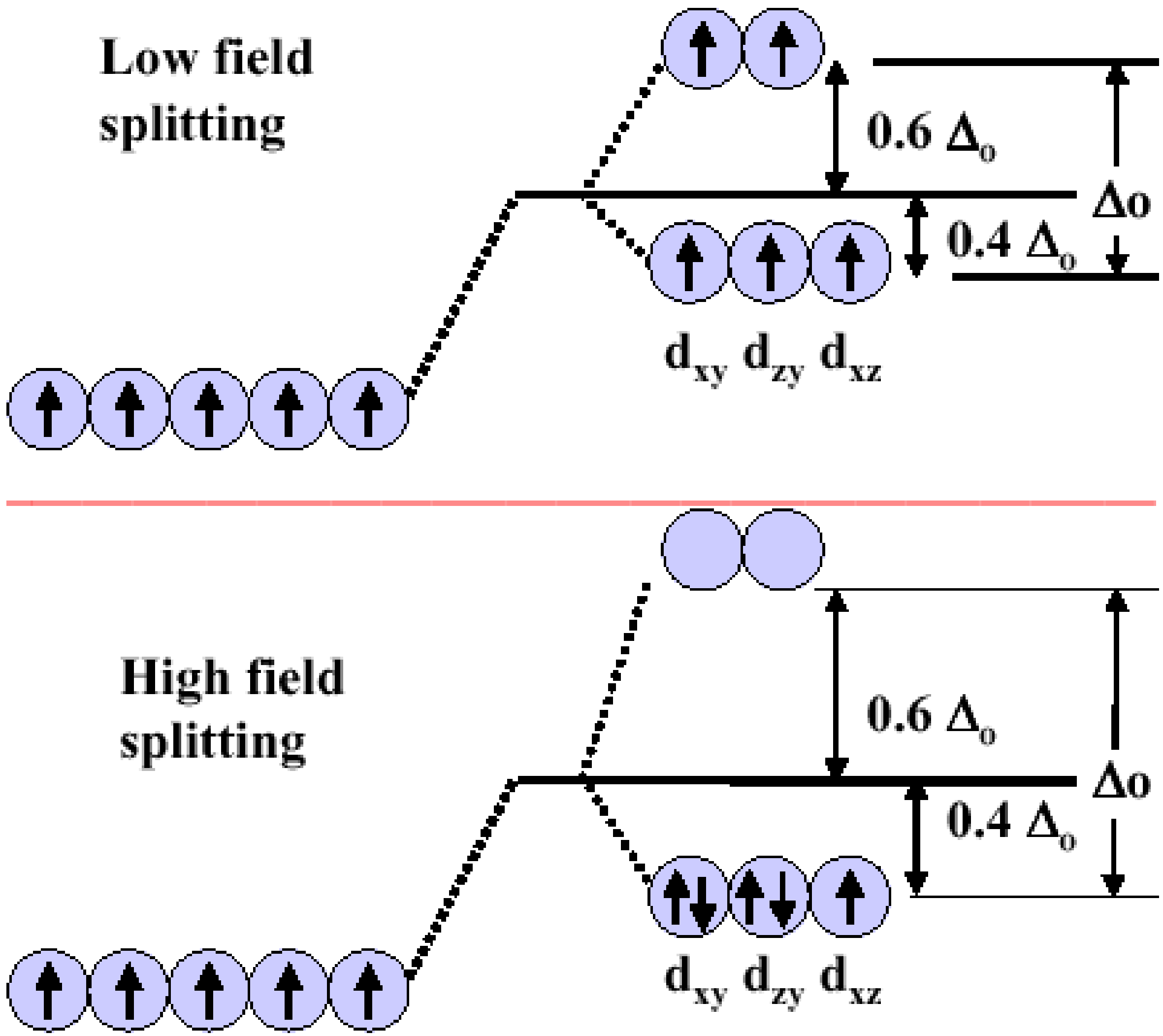
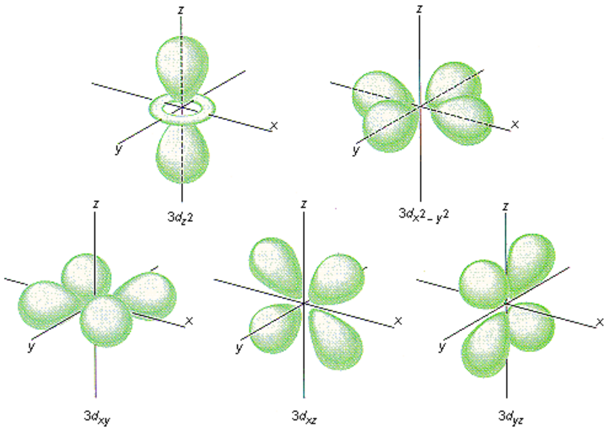


Figure 5. The two cases of crystal field splitting for the octahedral geometry.

d-orbital energies

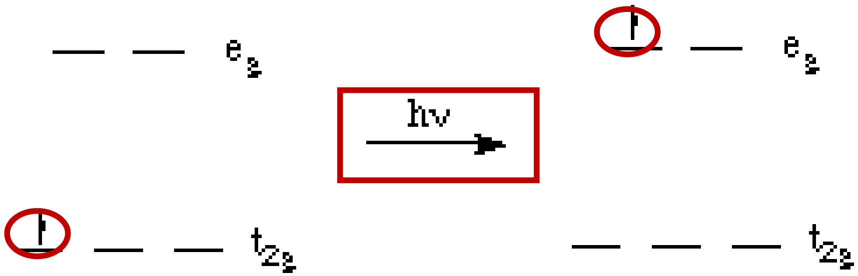


In an isolated atom the different *d*-orbitals of the same shell all have the same energy (but different shapes & orientations)

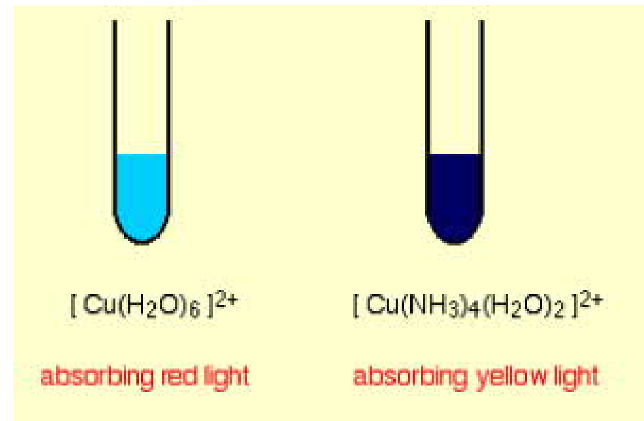
COLOURS

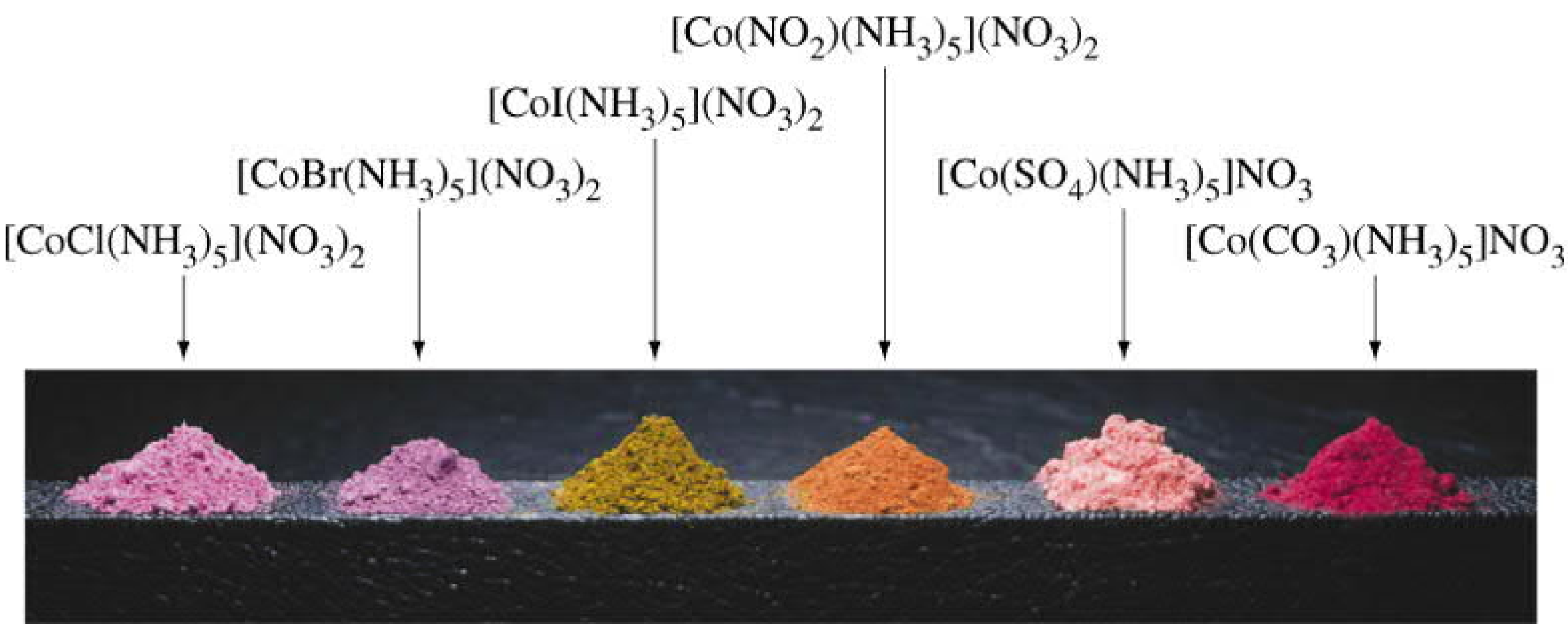
- **partly filled *d*-orbitals**
- **electrons can transfer from one *d*-orbital to another**
- **energy needed for the transfer is small**
- **corresponds to visible light wavelengths**
- **ions absorb certain wavelengths within the visible light spectrum**
- **if ion absorbs certain colour (e.g. red)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

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



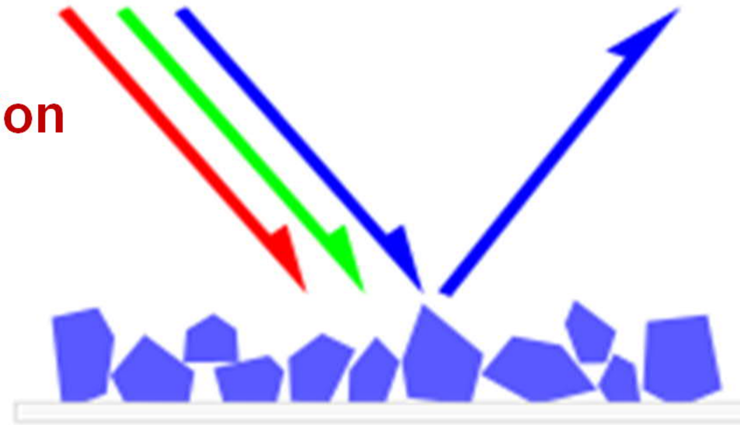
Δ_o varies with the ligand, thus absorption energy and colour also vary with the ligand





PIGMENT

- Material with wavelength-selective absorption
- Practically usable pigment:
  - high tinting strength
  - stable in light and heat
  - Particulate and insoluble in the binder (pigment *versus* dye)
  - insoluble in water
  - nonpoisonous, etc.
- Application fields: paints, inks, plastics, fabrics, cosmetics, food, etc.
- Natural pigments (carbon black, iron-oxide based ochres, etc.) have been used as colorants since prehistoric times
- April 2018 by *Bloomberg Businessweek*:
  - global value of pigment industry $30 billion
  - TiO_2 (white) has the largest share



- **Different absorption processes**

  - Conjugated organics molecules: double bonds absorb light
  - Inorganic pigments: different electron transfer processes

- **Note:** pigments are different from luminescent materials (discussed later on in this course)

- **Note:** the spectrum of the incident light affects the appearance of the pigment, as different wavelength ranges are left to be reflected or scattered

<u>Inorganic</u> BLUE PIGMENTS

- **6 000 years ago, *Ultramarine*:** "true blue" made from semiprecious gemstone *lapis lazuli* mined in e.g. Afghanistan



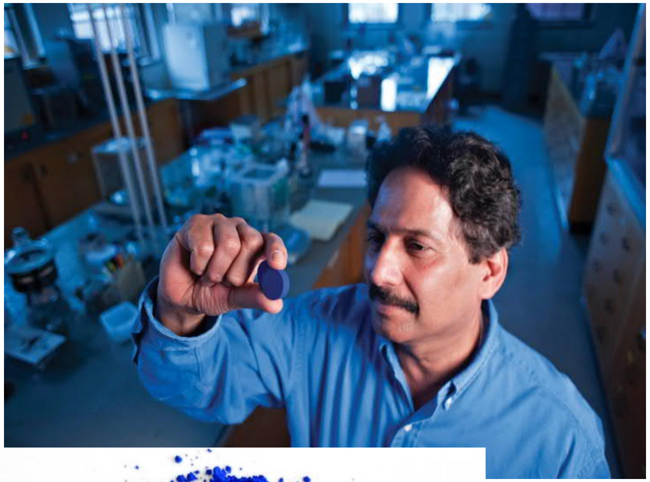
- **1826 *French Ultramarine*:** synthetic ultramarine

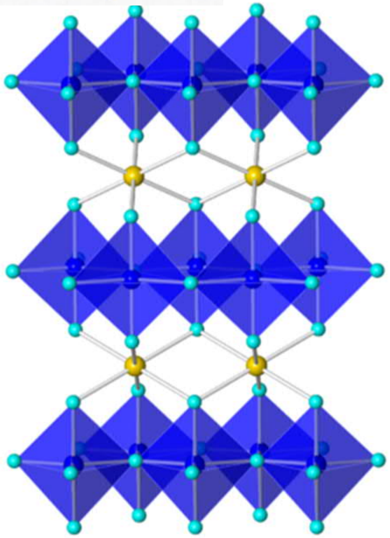
- **4 000 years ago, *Egyptian Blue*:** "turquoise", first synthetic pigment (calcium copper tetrasilicate) made by heating sand and copper together


- **1704 *Prussian Blue*:** $Fe_4[Fe(CN)_6]_3$ (other names: e.g. Berlin, Turnbull, midnight blue)
- **1802 *Cobalt Blue*:** $CoAl_2O_4$ (poisonous)

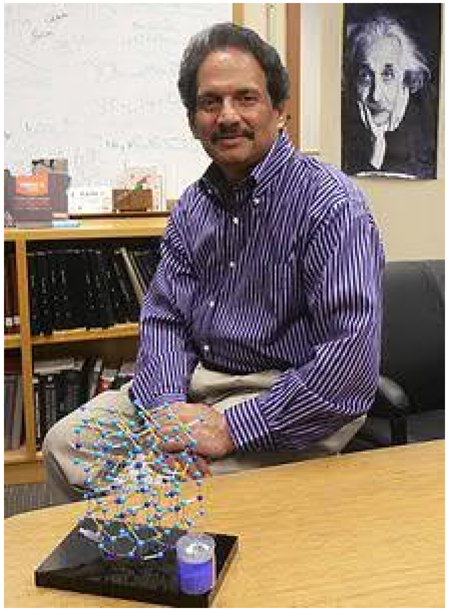

- **2009 *Mas Blue*:** $Y(In,Mn)O_3$

- **Prof. Mas Subramanian** received 2008 National Science Foundation grant to explore **novel materials for electronics applications**
- Main aim: **multiferroic (FM + FE)** materials
- He directed his PhD student Andrew Smith to synthesize a mixture of two oxides:
  $YInO_3$ (ferroelectric; white)
  $YMnO_3$ (antiferromagnetic; black)
- The result was NOT multiferroics, but blue material
- Subramanian has experience in chemical industry (DuPont) and recognized the value of the new **blue pigment** (filed a patent)
- Color adjusted by In/Mn ratio: $Y(In_{0.8}Mn_{0.2})O_3$ strongest
- First blue pigment discovered since 1802 (cobalt blue)
- **Huge interest:**
  - industry: Nike, Crayola, etc.
  - media: New York Times, Time Magazine, National Geographic, Businessweek, etc.
  - arts: Harward Art Museum, etc.

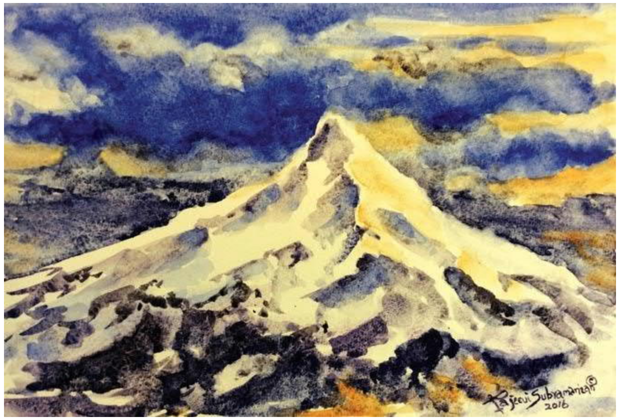




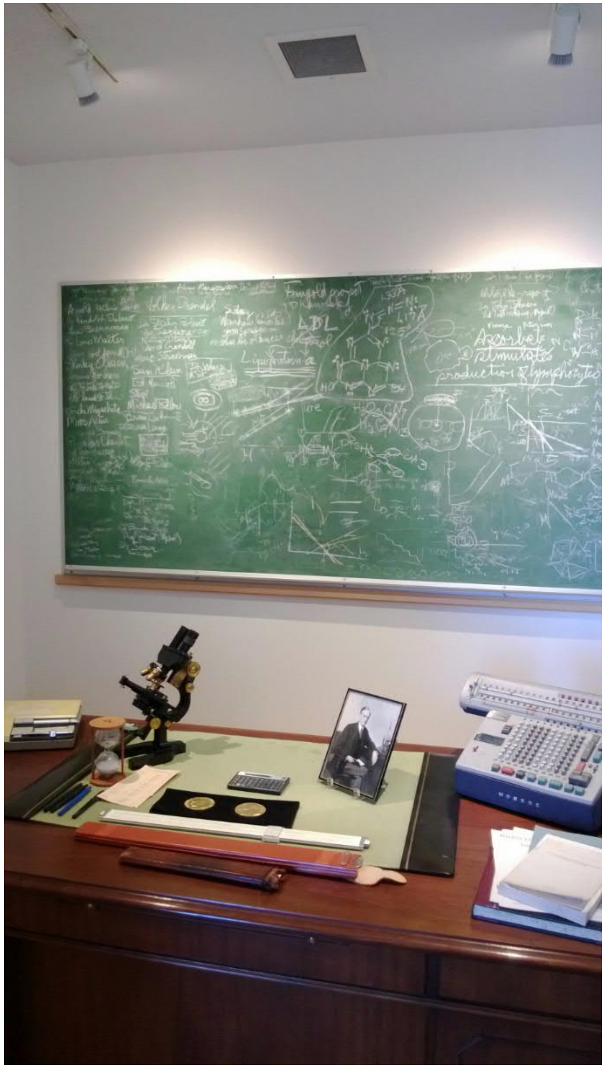
Mas Subramanian

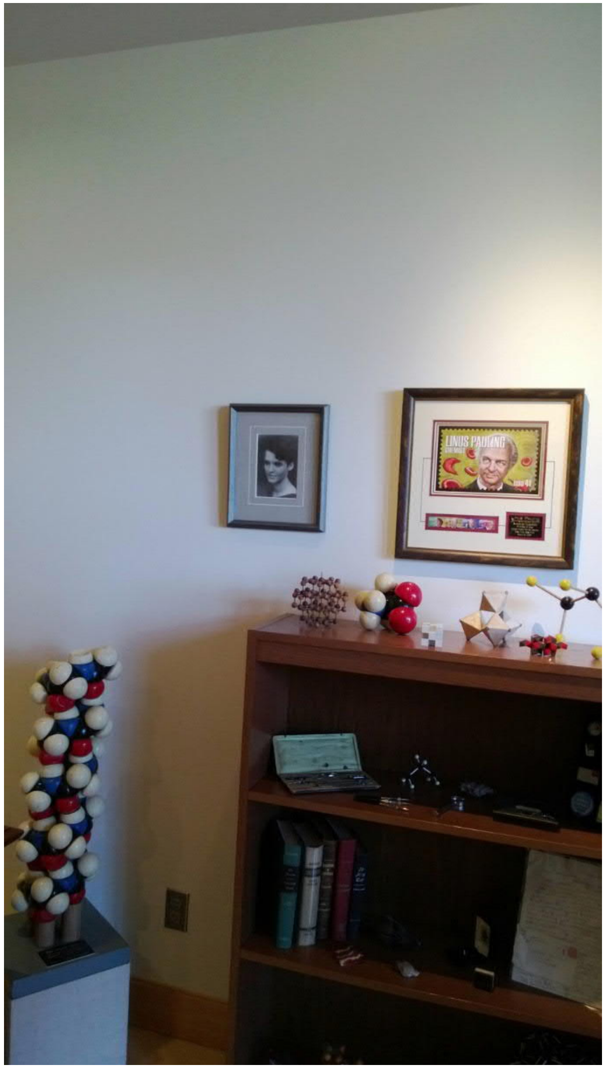


- Born: 1954, Chennai, India
- MSc. I1977 (Inorganic Chemistry: clays and minerals) University of Madras 1977
- PhD 1982 (Solid State Chemistry: pyrochlore oxides) Indian Institute of Technology, Madras
- 1982-1984 PostDoc, Texas A&M University, USA
- 1984-2006 DuPont, USA:
  - ceramics, superconductors, dielectrics, catalysis, thermoelectrics, multiferroics, ionic conductors, etc.
- 2006-now Professor at Oregon State University:
  design and synthesis of novel functional materials for emerging applications in energy, environment & electronics
- 2009: novel durable blue pigment: **YInMn Blue**



Mount Hood (Oregon)
by Aquarelles de Mas Blue
by Ms. Rajeevi Subramanian





Linus Carl Pauling (1901–1994) was an American chemist, biochemist, peace activist, author, and educator, graduated at Oregon State University. He published more than 1200 papers and books, 850 on scientific topics.
New Scientist rated him in 2000 the 16th most important scientist in history.
Pauling was one of the founders of the fields of quantum chemistry and molecular biology.
For his scientific work, Pauling was awarded the Nobel Prize in Chemistry in 1954.
In 1962, for his peace activism, he was awarded the Nobel Peace Prize.
Pauling is one of only two people who have received Nobel Prizes in different fields, the other being Marie Curie.