

LECTURE SCHEDULE

Mon (Ke3) 12.15 – 14.00
Wed (Ke2) 10.15 – 12.00
Fri (Ke5) 10.15 – 12.00

	Date	Topic
1.	Wed 06.09.	Course Introduction & Short Review on Elements & Periodic Table
2.	Fri 08.09.	Short Survey of Main Group Elements
3.	Mon 11.09.	Zn + Ti, Zr, Hf & Atomic Layer Deposition (ALD)
4.	Wed 13.09.	Transition Metals: General Aspects & Pigments
5.	Fri 15.09.	Redox Chemistry (Ke4)
6.	Mon 18.09.	Crystal Field Theory
7.	Wed 20.09.	V, Nb, Ta & Perovskites & Metal Complexes & MOFs & MLD
8.	Mon 25.09.	Cr, Mo, W & 2D materials & Mxenes & Layer-Engineering
9.	Wed 27.09.	Mn, Fe, Co, Ni, Cu
10.	Fri 29.09.	Cu & Magnetism & Superconductivity
11.	Mon 02.10.	Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)
12.	Wed 04.10.	Lanthanoids + Actinoids & Luminescence
13.	Fri 06.10.	Resources of Elements & Rare/Critical Elements & Element Substitutions
14.	Fri 13.10.	Inorganic Materials Chemistry Research

EXAM: Tuesday Oct. 17, 9:00-12:00 in Ke2

PRESENTATION TOPICS/SCHEDULE

Mon	25.09.	Mo:	Maryam Jafarishiad & Saara Siekkinen
Wed	27.09.	Mn:	Naomi Lyle & Sanni Ilmaranta
		Ru:	Miklos Nemeszeghy & Timo de Jonge
Fri	29.09.	Cu:	Koshila Hiruni & Kaushalya Poonanoo
Wed	04.10.	Eu:	Binglu Wang & Mari
		Nd:	Patrich Wiesenfeldt & Tomoki Nakayama
		U:	Miikka Viirto & Ashish Singh
Fri	06.10.	Co:	Gabrielle Laurent & Yan Zheng
		In:	Sonja Alasaukko-oja & Katri Haapalinna
		Te:	Sofia Rantala & Roger Peltonen

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 slides are put up in MyCourses (please email them to maarit.karppinen@aalto.fi by the morning of your presentation)
- Content of the presentation:
 - **ELEMENT:** discovery, origin of name, abundancy, world production, special features if any, etc.
 - **CHEMISTRY:**, electronic configuration, oxidation states, metal and ionic sizes, reactivity, etc., **regarding the position in Periodic Table**
 - **COMPOUNDS:** examples of important compounds, their properties and applications, etc.
 - **SPECIFIC FUNCTIONALITIES/APPLICATIONS:** Two or three examples of exciting functionalities/applications of the element/its compounds. If possible, please discuss the role(importance of the specific element in the selected applications. **You can find in MyCourses one or two possible scientific reference articles and you should search for couple of more (recent) articles to be discussed in the presentation.**

QUESTIONS: Lecture 4

- **Give plausible explanations for the following melting point (°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 colorless or 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?**

1																	18	
H ¹													B ⁵	C ⁶	N ⁷	O ⁸	F ⁹	He ²
Li ³	Be ⁴											Al ¹³	Si ¹⁴	P ¹⁵	S ¹⁶	Cl ¹⁷	Ar ¹⁸	
Na ¹¹	Mg ¹²	3	4	5	6	7	8	9	10	11	12	Ga ³¹	Ge ³²	As ³³	Se ³⁴	Br ³⁵	Kr ³⁶	
K ¹⁹	Ca ²⁰	Sc ²¹	Ti ²²	V ²³	Cr ²⁴	Mn ²⁵	Fe ²⁶	Co ²⁷	Ni ²⁸	Cu ²⁹	Zn ³⁰	In ⁴⁹	Sn ⁵⁰	Sb ⁵¹	Te ⁵²	I ⁵³	Xe ⁵⁴	
Rb ³⁷	Sr ³⁸	Y ³⁹	Zr ⁴⁰	Nb ⁴¹	Mo ⁴²	Tc ⁴³	Ru ⁴⁴	Rh ⁴⁵	Pd ⁴⁶	Ag ⁴⁷	Cd ⁴⁸	Tl ⁸¹	Pb ⁸²	Bi ⁸³	Po ⁸⁴	At ⁸⁵	Rn ⁸⁶	
Cs ⁵⁵	Ba ⁵⁶	La ⁵⁷	Hf ⁷²	Ta ⁷³	W ⁷⁴	Re ⁷⁵	Os ⁷⁶	Ir ⁷⁷	Pt ⁷⁸	Au ⁷⁹	Hg ⁸⁰	Pb ⁸²	Bi ⁸³	Po ⁸⁴	At ⁸⁵	Rn ⁸⁶		
Fr ⁸⁷	Ra ⁸⁸	Ac ⁸⁹	Rf ¹⁰⁴	Db ¹⁰⁵	Sg ¹⁰⁶	Bh ¹⁰⁷	Hs ¹⁰⁸	Mt ¹⁰⁹	Uun ¹¹⁰									

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

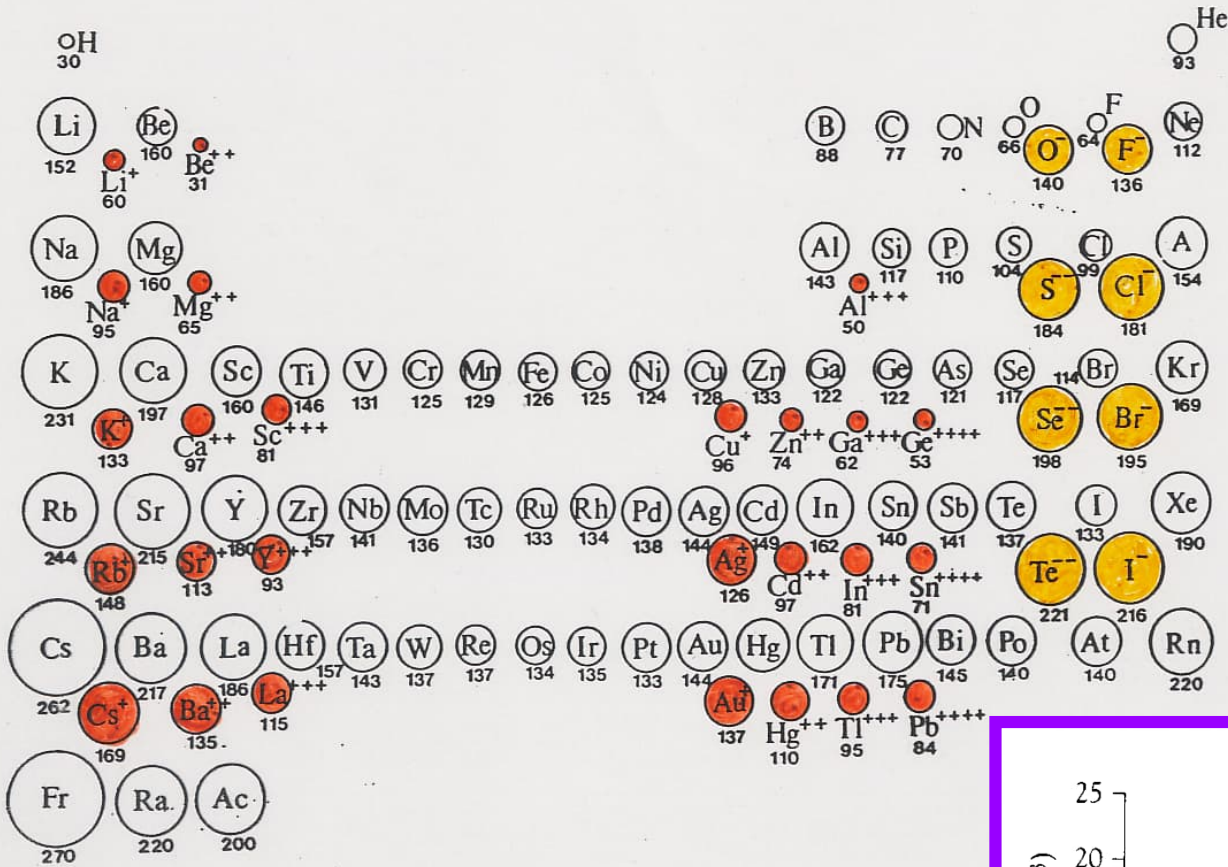
Electron configurations/oxidation states of:
 Zinc, Thallium, Bismuth, Scandium, Lanthanum, Gadolinium,
 Manganese, Copper, ...

d-BLOCK ELEMENTS

GENERAL FEATURES




- All are metals
- Relatively small in size (d electrons shield poorly each other)
- Multiple oxidation states → richness of chemistry
- 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: at low oxidation states positive metal ions, at high oxidation states oxoanions (e.g. Mn^{2+} and MnO_4^-)

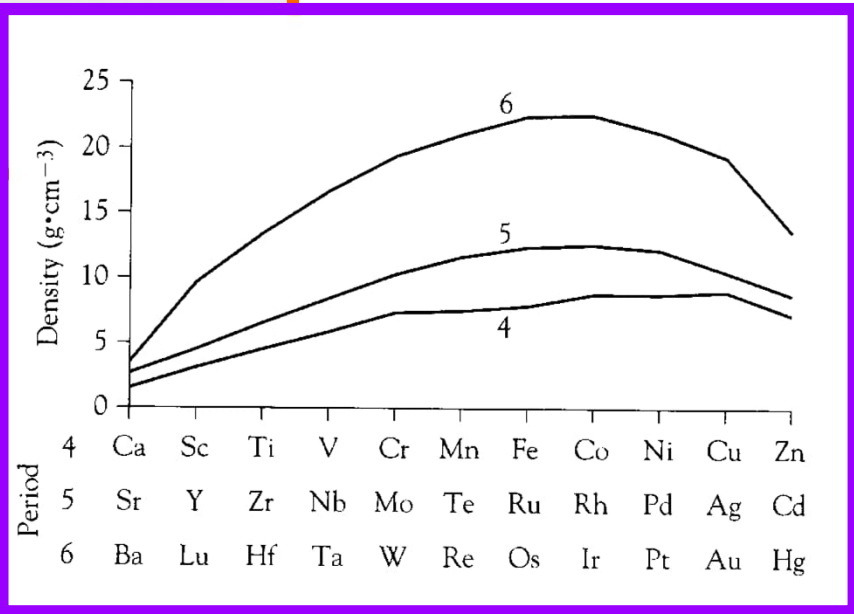
Atomic/ionic radius



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 

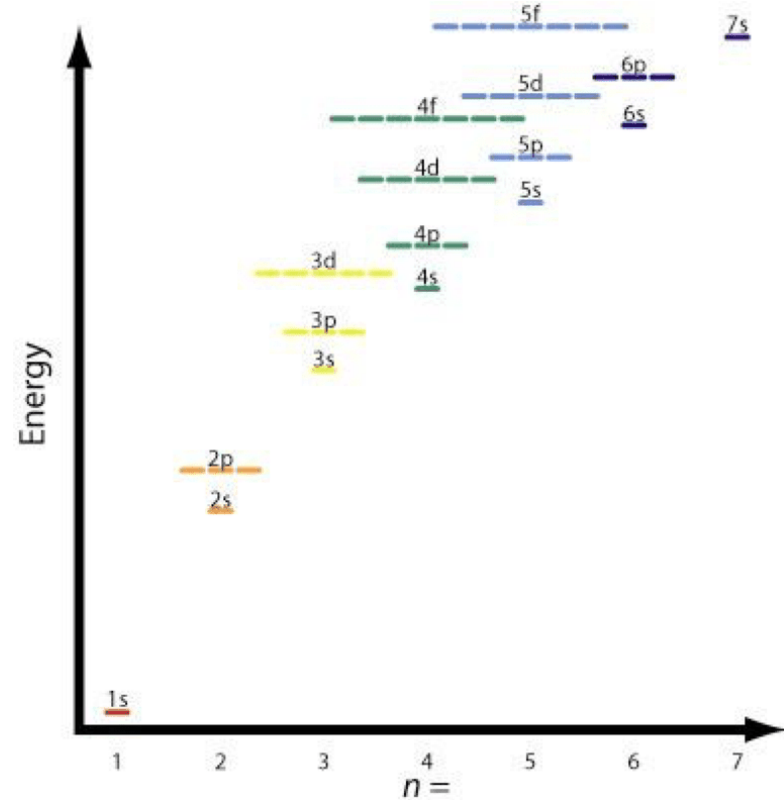
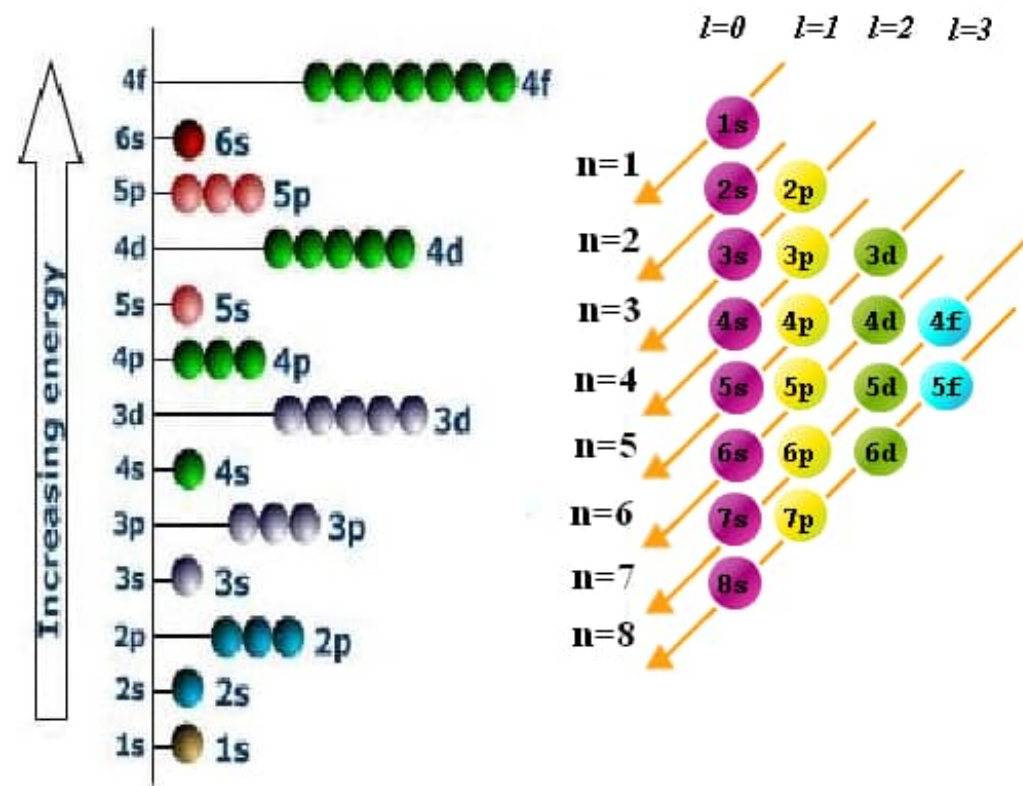


Density

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	-	-



Relative Orbital Energies

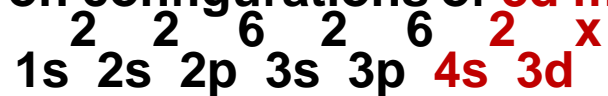
- These diagrams show situation:
 - for empty orbitals
 - in a single isolated atom
- Once an orbital is occupied by electron(s), its relative energy changes
- Once an atom is surrounded by neighbouring atoms, the energies of its (outer) d and f orbitals are splitted (*Crystal Field Splitting*)

s

Period 1	s																2	
	1															He		
Period 2	3	4	d										5	6	7	8	9	10
	Li	Be											B	C	N	O	F	Ne
Period 3	11	12											13	14	15	16	17	18
	Na	Mg											Al	Si	P	S	Cl	Ar
Period 4	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Period 5	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Period 6	55	56	57 to 71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
	Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Period 7	87	88	89 to 103	104	105	106	107	108	109	p								
	Fr	Ra		Rf	Ha	Sg	Ns	Hs	Mt									

Lanthanide series →	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	}	f
	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
Actinide series →	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103		
	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

Electron configurations of 3d metals:

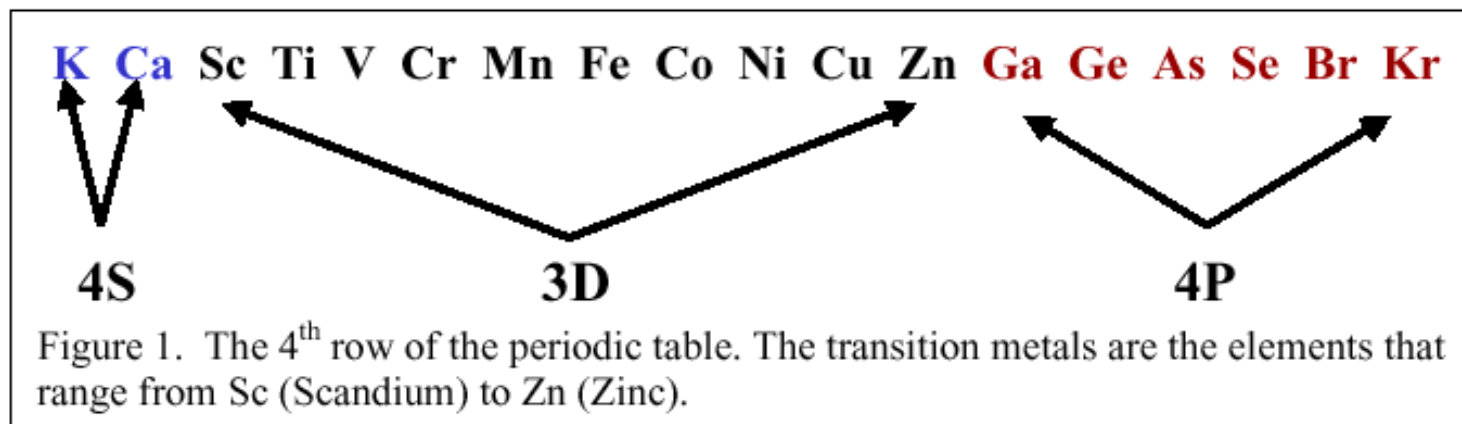


			3d				4s
Scandium (Sc)	↑						↑↓
Titanium (Ti)	↑	↑					↑↓
Vanadium (V)	↑	↑	↑				↑↓
Chromium (Cr)	↑	↑	↑	↑	↑		↑
Manganese (Mn)	↑	↑	↑	↑	↑		↑↓
Iron (Fe)	↑↓	↑	↑	↑	↑		↑↓
Koboltti (Co)	↑↓	↑↓	↑	↑	↑		↑↓
Nikkeli (Ni)	↑↓	↑↓	↑↓	↑	↑		↑↓
Kupari (Cu)	↑↓	↑↓	↑↓	↑↓	↑↓		↑
[Sinkki (Zn)]	↑↓	↑↓	↑↓	↑↓	↑↓		↑↓

OXIDATION STATES

Element	Symbol	Electronic Configuration
Scandium	Sc	$[\text{Ar}]3d^14s^2$
Titanium	Ti	$[\text{Ar}]3d^24s^2$
Vanadium	V	$[\text{Ar}]3d^34s^2$
Chromium	Cr	$[\text{Ar}]3d^54s^1$
Manganese	Mn	$[\text{Ar}]3d^54s^2$
Iron	Fe	$[\text{Ar}]3d^64s^2$
Cobalt	Co	$[\text{Ar}]3d^74s^2$
Nickel	Ni	$[\text{Ar}]3d^84s^2$
Copper	Cu	$[\text{Ar}]3d^{10}4s^1$
Zinc	Zn	$[\text{Ar}]3d^{10}4s^2$

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					



	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	(Zn)
+VIII										
+VII					•					
+VI				•	0	0				
+V			•		•					
+IV		•	0		0			0		
+III	•	•	•	•	0	•	•			
+II		0	0	0	•	•	•	•	•	•
+I									•	
	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	(Cd)
+VIII						0				
+VII					•					
+VI				•	0	0				
+V			•	0						
+IV		•	0	0	0	•	0	0		
+III	•	0	0	0	0	0	•		0	
+II			0	0		0	0	•		•
+I						0	0		•	
	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	(Hg)
+VIII						•				
+VII					•					
+VI				•	0	•				
+V			•	0	0					
+IV		•	0	0	0	0	•	•		
+III	•		0	0	0		•		•	
+II			0	0				•		•
+I									0	•



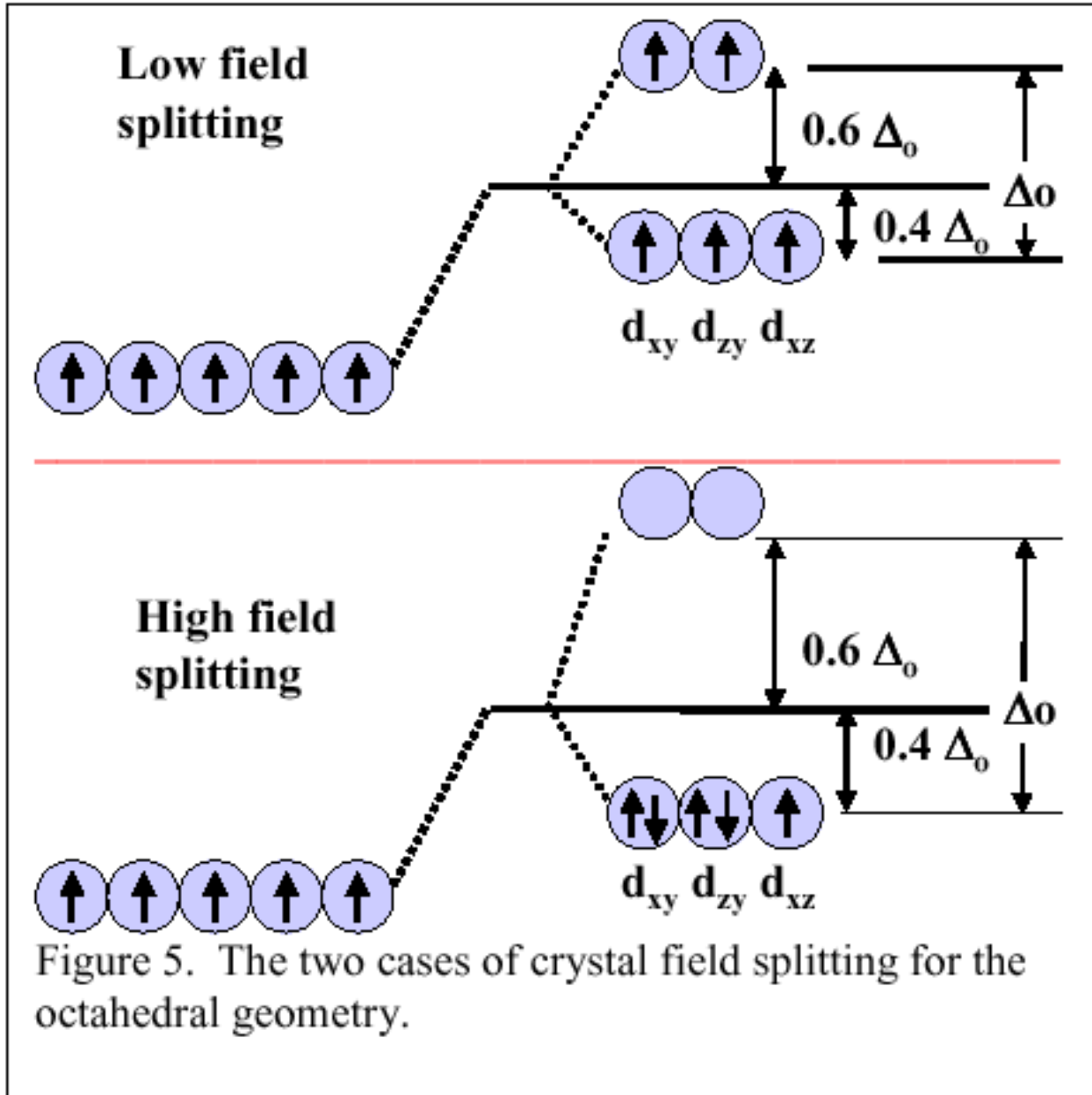
• : most stable
0 : possible

MELTING POINTS (°C)

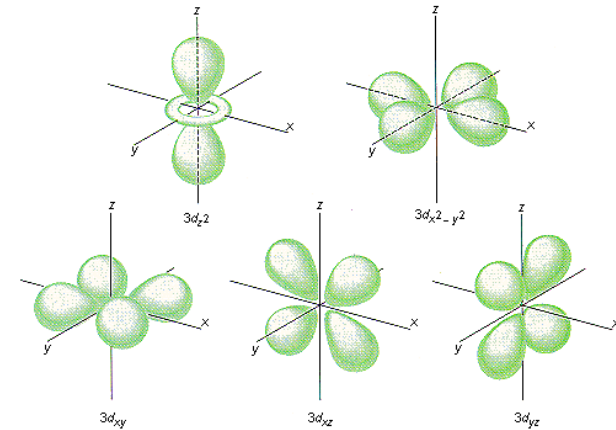
Ti	1668	Zr	1852	Hf	2220
V	1890	Nb	1470	Ta	3000
Cr	1860	Mo	2620	W	3410
Mn	1245	Tc	2140	Re	3180
Fe	1535	Ru	2282	Os	3045
Co	1492	Rh	1960	Ir	2443
Ni	1452	Pd	1552	Pt	1769
Cu	1083	Ag	961	Au	1063

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

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



d-orbital energies



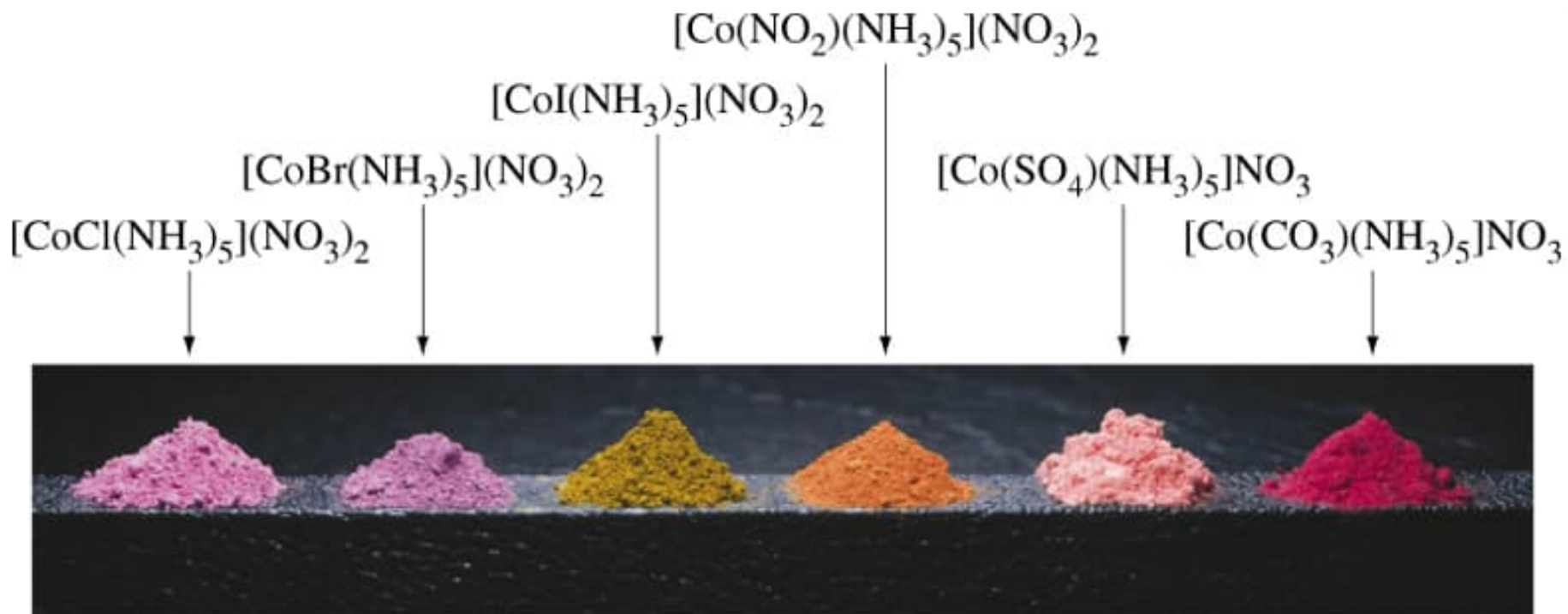
In an isolated atom the different *d*-orbitals of the same shell all have the same energy (but different shapes & orientations)

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 colorless
- ions with half-filled orbitals (d^5) are colourless or faintly coloured

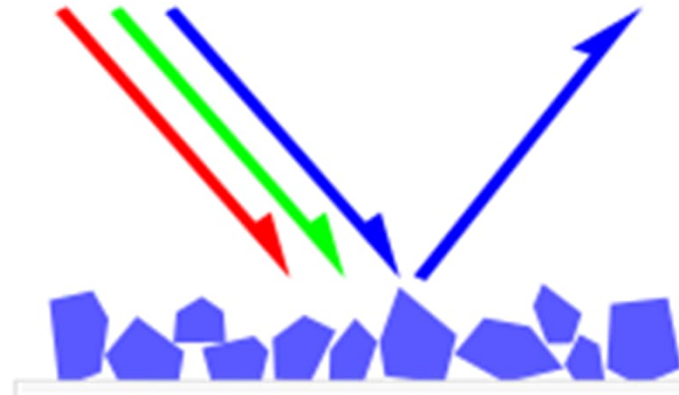


Co³⁺



PIGMENTS

- Pigment: material with **wavelength-selective absorption**
- Practically usable pigment:
 - high tinting strength
 - stable in light and heat
 - insoluble in binder (or water) → suspension (compare to dyes: dissolved in solvent)
 - nonpoisonous, etc.
- Application fields: paints, inks, arts, plastics, fabrics, cosmetics, food, etc.
- Many 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



- **INORGANIC PIGMENTS** more stable than organic pigments
- **Different absorption processes**
 - Conjugated organic 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:** spectrum of the incident light affects the colour of the pigment, as different wavelength ranges are left to be reflected or scattered

Inorganic BLUE PIGMENTS

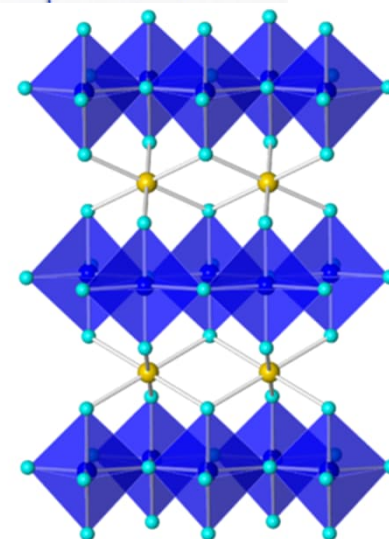
- Very rare in nature/unstable/poisonous
- **6 000 years ago, *Ultramarine*: expensive !!**
“beyond the sea” made from *lapis lazuli*
(= semiprecious gemstone mined in Afghanistan)
- **4 000 years ago, *Egyptian Blue*:**
“turquoise”, $\text{CaCuSi}_4\text{O}_{10}$
first synthetic pigment: sand & Cu mineral & heat
- **2 000 years ago, Chinese Han Blue:**
 $\text{BaCuSi}_4\text{O}_{10}$
- **1826 *French Ultramarine*:** synthetic
- **1704 *Prussian Blue*:** $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$
(also called: Berlin, Turnbull or midnight blue)
- **1802 *Cobalt Blue*:** CoAl_2O_4
- **2009 *Mas Blue*:** $\text{Y}(\text{In},\text{Mn})\text{O}_3$



Vermeer 1665

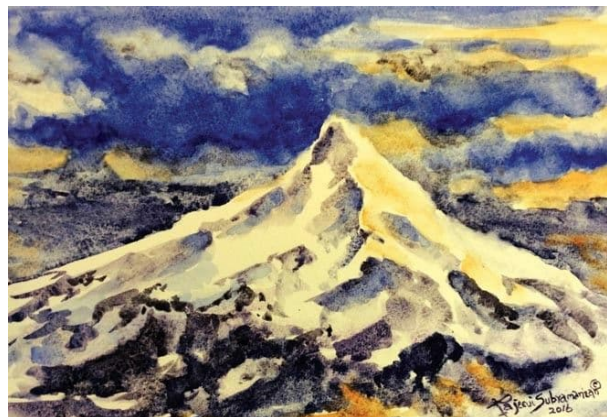


- **Prof. Mas Subramanian** received 2008 National Science Foundation grant to explore **novel materials for electronics applications**
- Research aim: **multiferroic (FM + FE)** materials
- He directed his PhD student Andrew Smith to synthesize a mixture of two oxides:
 YInO_3 (ferroelectric; white)
 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 (**Crystal Field Engineering**):
 $\text{Y}(\text{In}_{0.8}\text{Mn}_{0.2})\text{O}_3$ strongest
- **Huge Public interest:**
 - industry: Nike, Crayola, etc.
 - media: New York Times, Time Magazine, National Geographic, Businessweek, etc.
 - arts: Harvard Art Museum, etc.

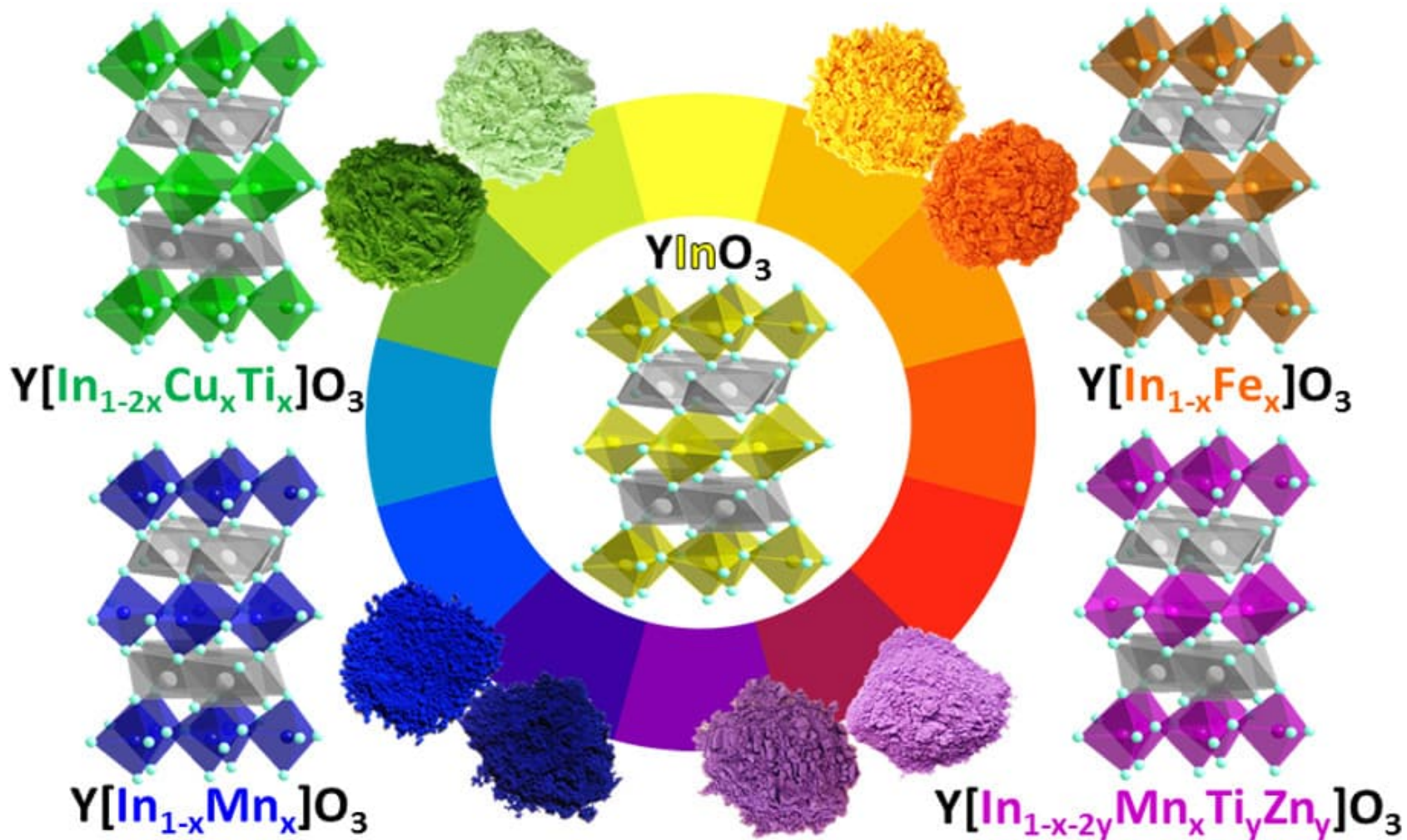


Mas Subramanian

- Born: 1954, Chennai, India
- MSc. 1977 (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: **(Y,In)MnO₃** or **“Mas Blue”**



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

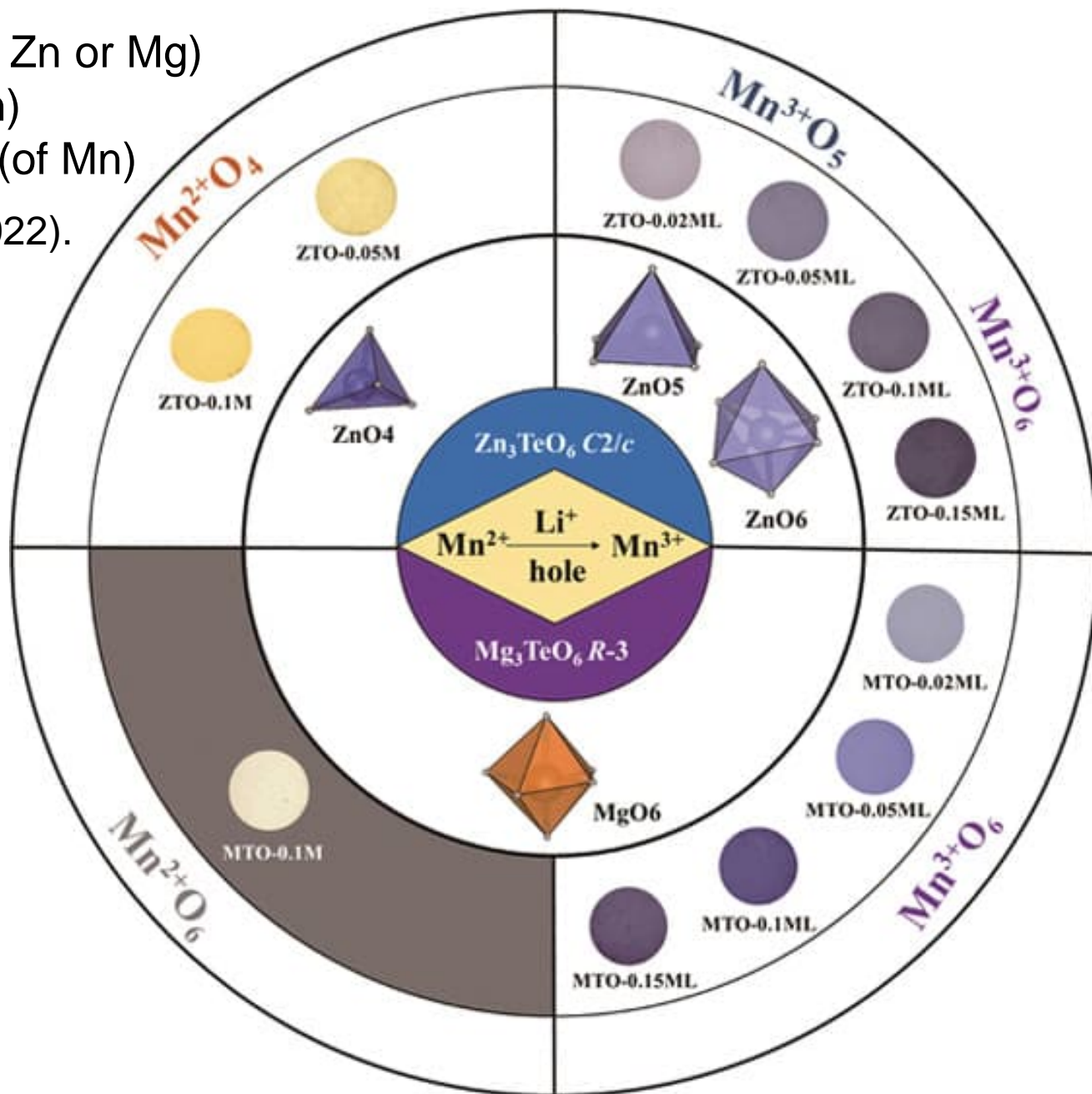


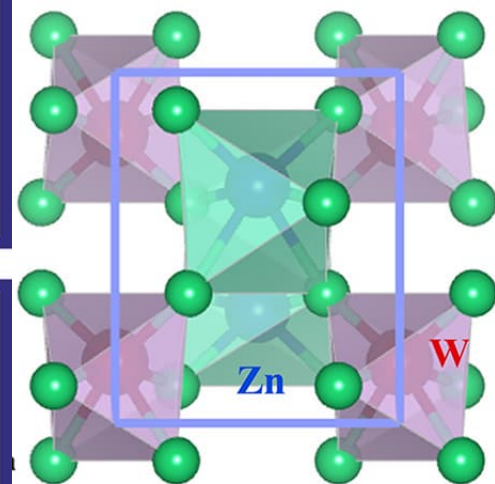
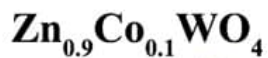
J. Li, S. Lorget, J.K. Stalick, A.W. Sleight & M.A. Subramanian,
 From serendipity to rational design: tuning the blue **trigonal bipyramidal Mn⁺³**
 chromophore to violet and purple through application of **chemical pressure**,
Inorganic Chemistry 55, 9798 (2016).

RATIONAL DESIGN of INORGANIC PIGMENTS

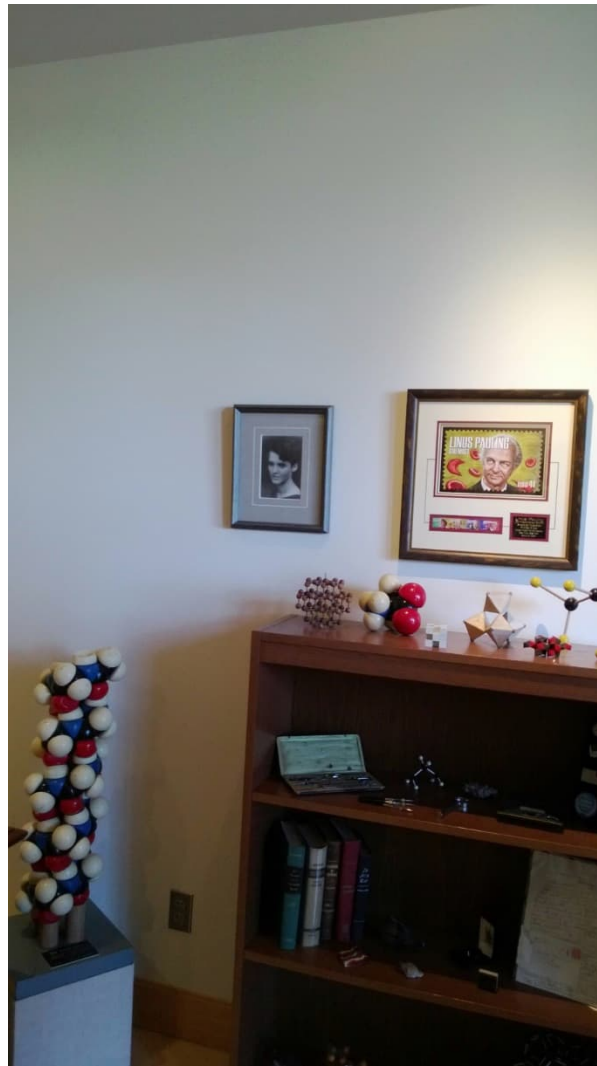
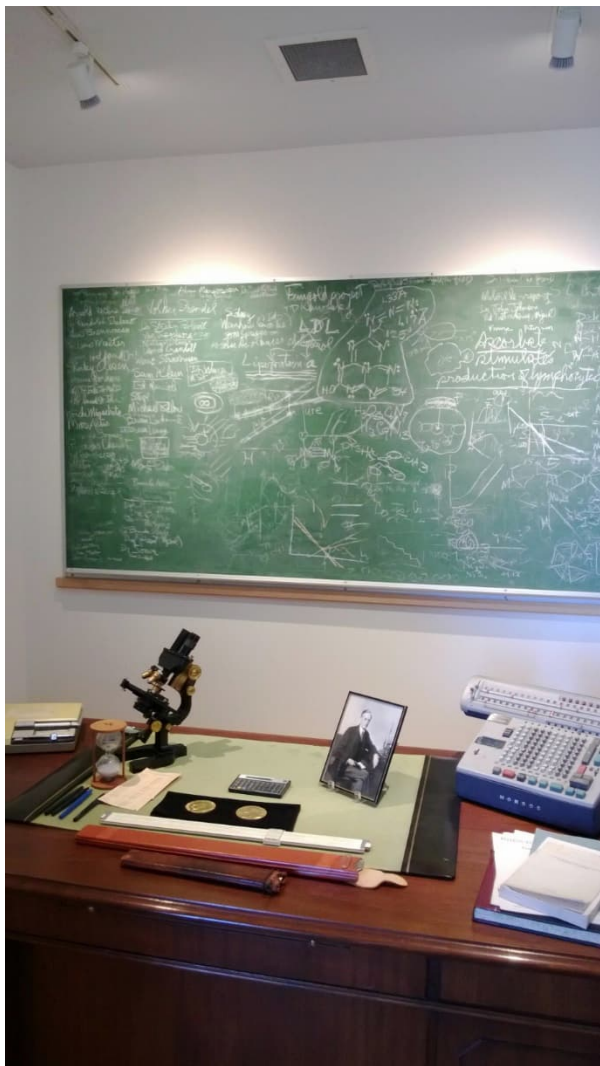
- $(A, \text{Mn}, \text{Li})_3\text{TeO}_6$ ($A = \text{Zn}$ or Mg)
- Ionic valence (of Mn)
- Local surroundings (of Mn)

Inorg. Chem. 61, 693 (2022).





W. Zhou, J. Ye, Z. Liu, L. Wang, L. Chen, S. Zhuo, Y. Liu & W. Chen,
High near-infrared reflective $\text{Zn}_{1-x}\text{A}_x\text{WO}_4$ pigments with various hues facily fabricated by tuning doped transition metal ions ($\text{A} = \text{Co}, \text{Mn}, \text{and Fe}$),
Inorganic Chemistry 61, 693 (2022).



Linus Pauling (1901–1994)

- American chemist, biochemist and peace activist, graduated from **Oregon State University**
- One of the founders of quantum chemistry: contributions to chemical bonding, electronegativity, orbital hybridization, molecular biology, protein structure, X-ray crystallography
- **Nobel Prize in Chemistry in 1954, Nobel Peace Prize in 1962**