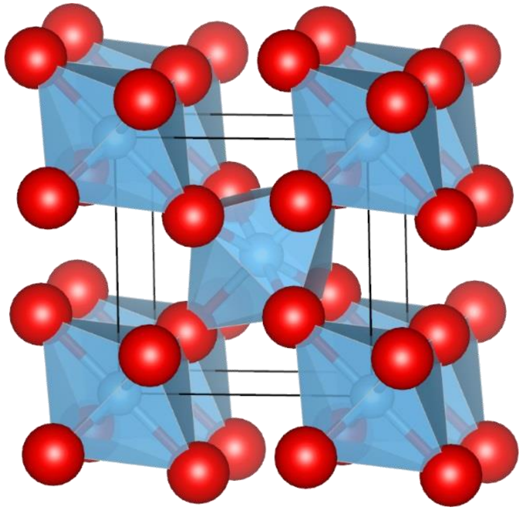
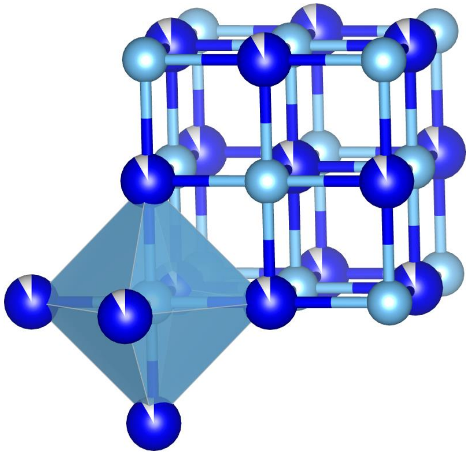
Lecture 12: Magnetism and *d*-block compounds

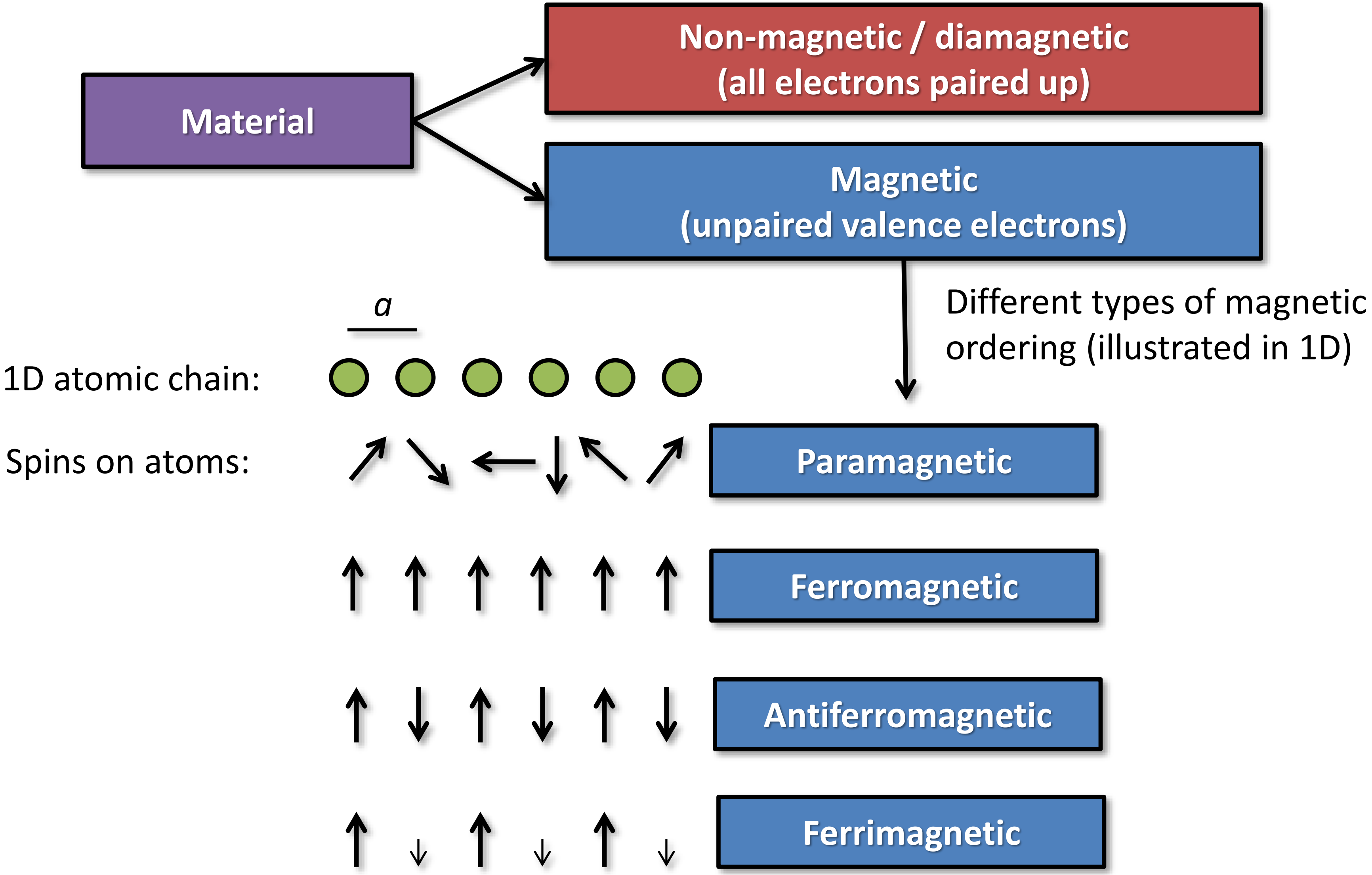
- Magnetism
  - Magnetic susceptibility
  - Various magnetic configurations
  - Temperature dependence
- *d*-block metal oxides
  - Bonding
  - Important structural types
  - Functionalities
- Other compounds of *d*-block elements





Figures: AJK

Spin-based magnetism



Material

Non-magnetic / diamagnetic (all electrons paired up)

Magnetic (unpaired valence electrons)

Different types of magnetic ordering (illustrated in 1D)

Paramagnetic

Ferromagnetic

Antiferromagnetic

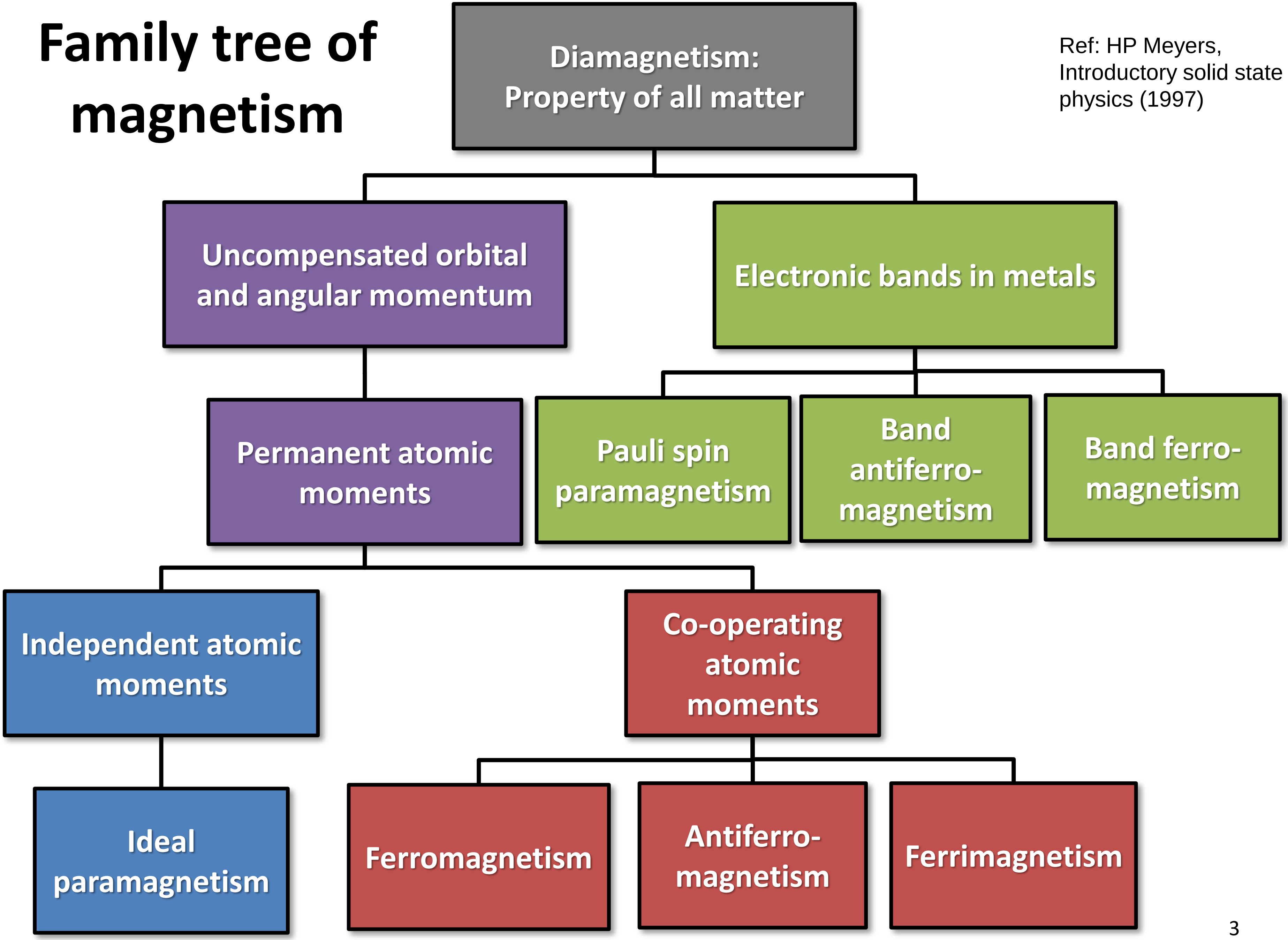
Ferrimagnetic

Ref: West p. 445-446

Figure: AJK

Family tree of magnetism

Ref: HP Meyers,
Introductory solid state
physics (1997)



- Diamagnetism: Property of all matter
  - Uncompensated orbital and angular momentum
    - Permanent atomic moments
      - Independent atomic moments
        - Ideal paramagnetism
      - Co-operating atomic moments
        - Ferromagnetism
        - Antiferro-magnetism
        - Ferrimagnetism
  - Electronic bands in metals
    - Pauli spin paramagnetism
    - Band antiferro-magnetism
    - Band ferro-magnetism

Magnetic susceptibility

- When a substance is placed in a magnetic field H (units A m^{-1}), the magnetic induction B (units T, tesla) is

$$B = \mu H = \mu_0 H + \mu_0 M,$$

where μ is *permeability*, μ_0 is the permeability of free space (4π * 10^{-7} H m^{-1}, H = henry) and M is the magnetic moment or **magnetization** of the sample

- Magnetization = **magnetic moment per unit volume or mass**
- $\mu_0 H$ is the induction generated by the field alone and $\mu_0 M$ is the additional induction contributed by the sample
- The magnetic susceptibility, χ, is defined as the ratio of magnetization M to field H:

$$\chi = \frac{M}{H}$$

- In other words: **high magnetization** M means **high susceptibility** χ
- Susceptibility χ is the most important measurable quantity for the characterization of magnetic properties
  - Provides a measure of the **response of a sample to an applied magnetic field**
  - Somewhat analogous to polarizability (response to an applied electric field)

Ref: West p. 446

Classification based on susceptibility χ

- The different kinds of magnetic behavior may be distinguished by the values of χ
  - In *diamagnetic* materials, χ is very small and slightly negative
  - In *paramagnetic* materials, χ is small and positive
  - In *ferromagnetic* materials, $\chi > 1$ and such materials are strongly attracted to a magnetic field.
  - In *antiferromagnetic* materials, χ is positive and comparable to paramagnetic substances (or somewhat smaller).

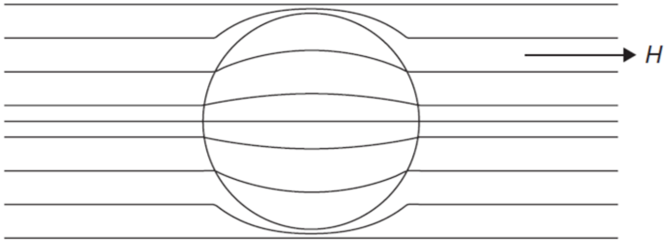
Behavior	**Typical χ values**	**Change of χ with increase in temperature**	**Field dependent**
Diamagnetism	-8×10^{-6} for Cu -1 for superconductors	None	No
Paramagnetism	0.1–0.001 for *d*-metal compounds	Decreases	No
Pauli paramagnetism	8.3×10^{-4} for Mn	None	Yes
Ferromagnetism	5×10^{3} for Fe	Decreases	Yes
Antiferromagnetism	$0–10^{-2}$	Increases	(Yes)

Ref: West p. 447

Dia- and paramagnetism

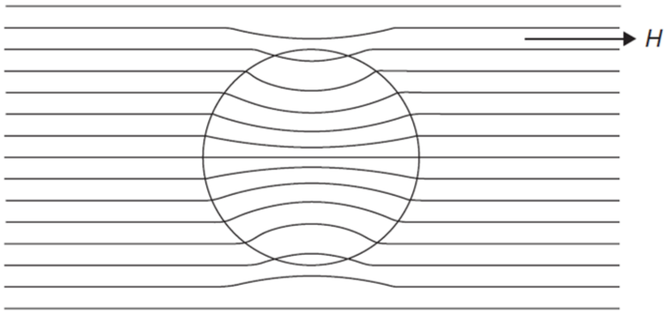
- Diamagnetism is a property of all materials
- When diamagnetism dominates, there is a slight repulsion by a magnetic field
  - Diamagnetism is associated with orbital motion of electrons in atoms.
  - This orbital motion generates a small electric field
  - In the presence of an external field, the orbital motion is modified slightly to give a magnetic moment that opposes the applied field leading to a slight repulsion effect which is explained by Lenz’s law of electromagnetism.
  - Superconductors represent a special, extreme type of diamagnetism since they repel magnetic fields completely, leading in magnetic levitation
- Paramagnetic materials are attracted by a magnetic field

Diamagnetic



(a)

Paramagnetic



(b)

Temperature dependence of magnetism

- Ordered magnetic structures lose their ordered structures above a certain temperature
  - ***Curie temperature***, T_c for ferromagnets and ferrimagnets
  - ***Néel temperature***, T_N for antiferromagnets
- The spins become disordered and the materials become paramagnetic

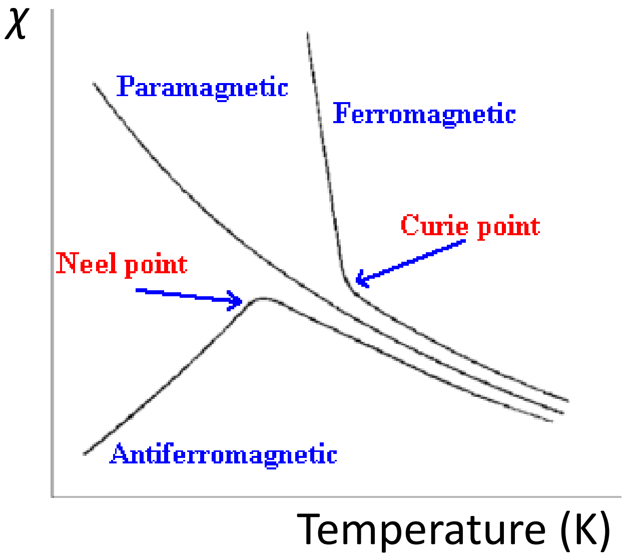


Figure: Robert John Lancashire

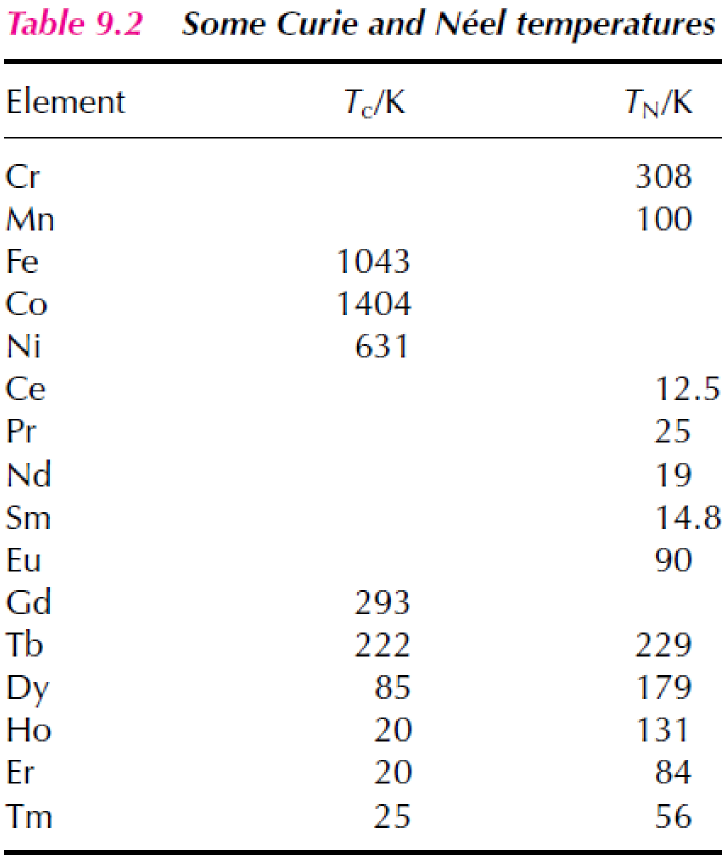
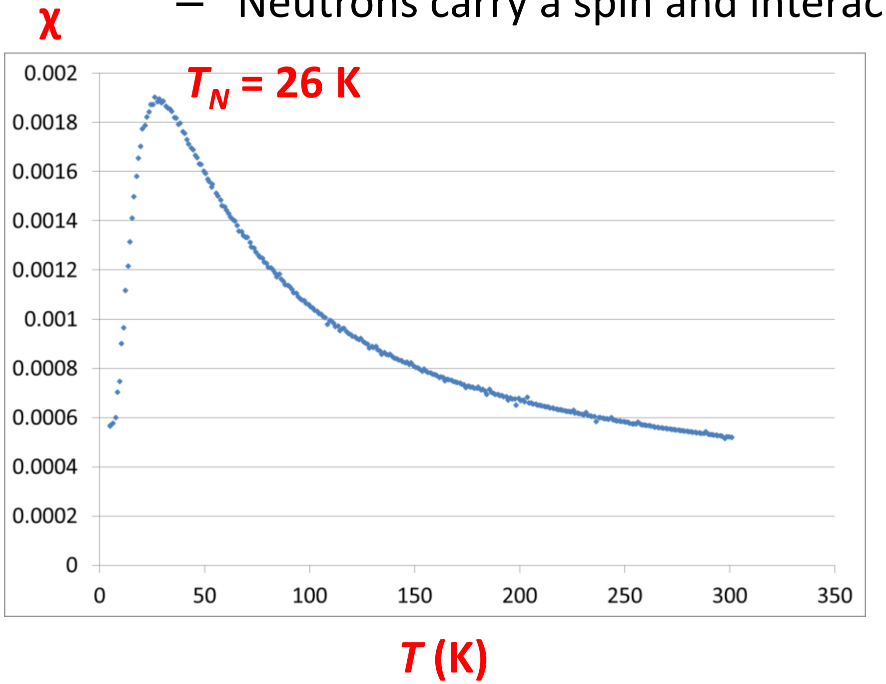


Table 9.2 *Some Curie and Néel temperatures*

Element	T_c/K	T_N/K
Cr		308
Mn		100
Fe	1043	
Co	1404	
Ni	631	
Ce		12.5
Pr		25
Nd		19
Sm		14.8
Eu		90
Gd	293	
Tb	222	229
Dy	85	179
Ho	20	131
Er	20	84
Tm	25	56

Experimental characterization of the magnetic ground state

- SQUID (Superconducting Quantum Interference Device)
  - Very sensitive magnetometer (measure susceptibility as a function of *T*)
- Neutron diffraction
  - Neutrons carry a spin and interact with magnetic moments



SQUID data for antiferromagnetic SrU_2F_{12} (Otto Mustonen / Aalto)

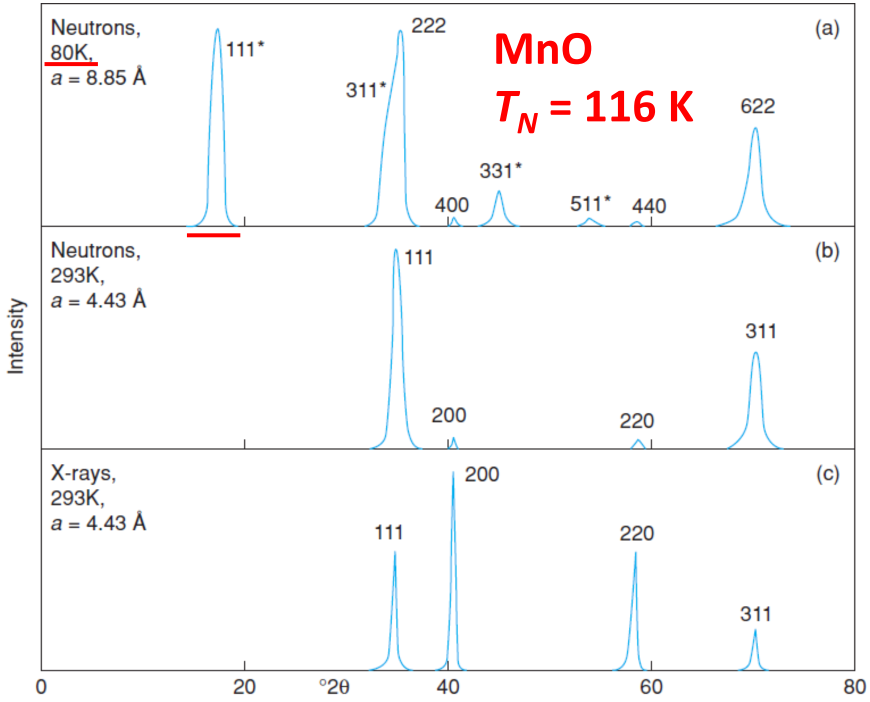
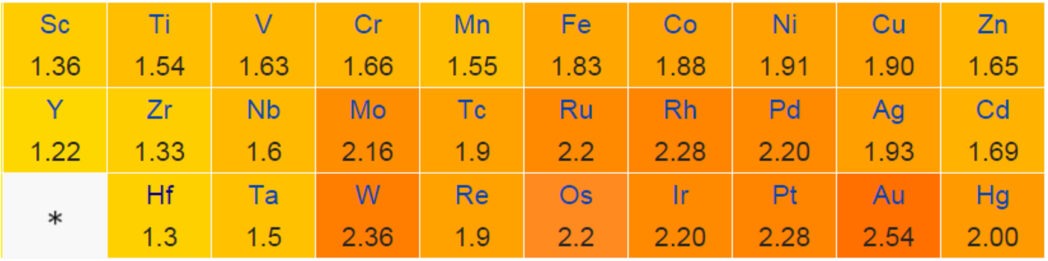


Figure 5.26 Schematic neutron and powder XRD patterns for MnO for λ = 1.542 Å. Peaks are assigned Miller indices for the cubic unit cells given. Neutron data adapted from Shull, Strauser and Wollan, Phys. Rev., 83, *333, © 1951 American Physical Society.*

d-block metal oxides

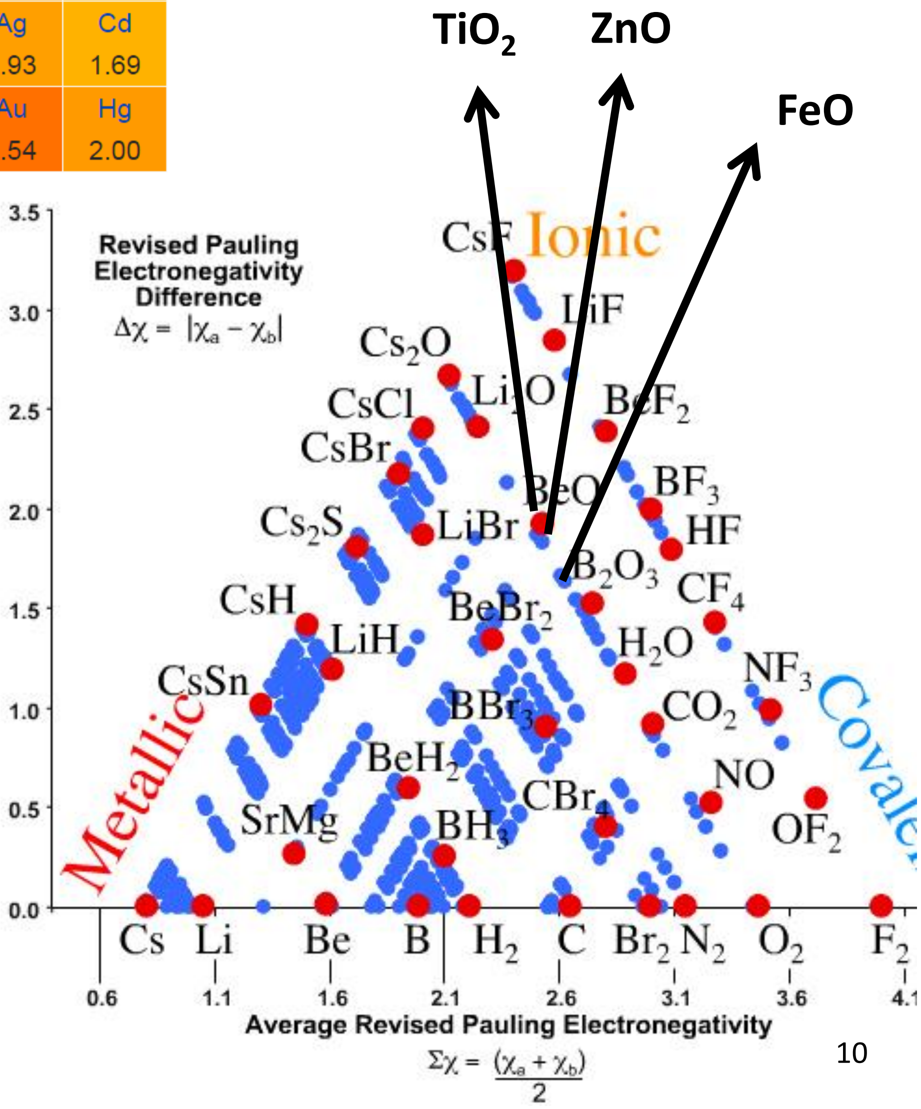
d-block metal oxides

Pauling electronegativities



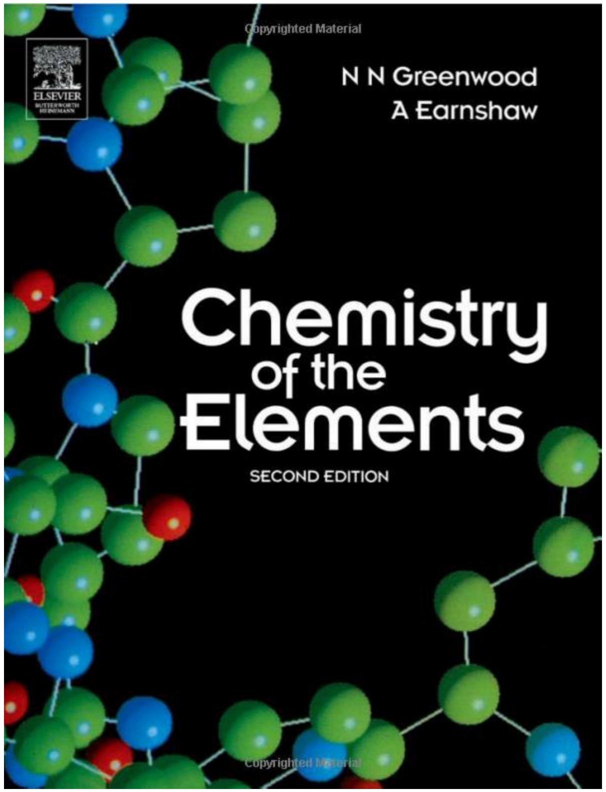
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
1.36	1.54	1.63	1.66	1.55	1.83	1.88	1.91	1.90	1.65
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
1.22	1.33	1.6	2.16	1.9	2.2	2.28	2.20	1.93	1.69
*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
	1.3	1.5	2.36	1.9	2.2	2.20	2.28	2.54	2.00

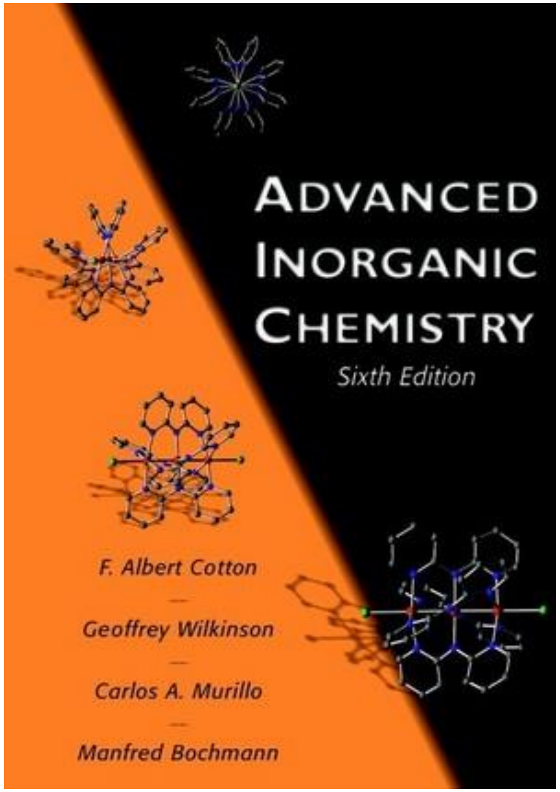
- Pauling electronegativity (EN) of oxygen is 3.44
- EN differences (EN average):
  - FeO = 1.61 (2.63)
  - ZnO = 1.79 (2.55)
  - TiO_2 = 1.9 (2.49)
- ***Mixed ionic-covalent*** bonding, typically insulating or semiconducting materials
- Due to band structure features:
  - Some *d*-metal oxides are metallic (e.g. RuO_2)
  - Some *d*-metal oxides are half-metals (e.g. CrO_2)

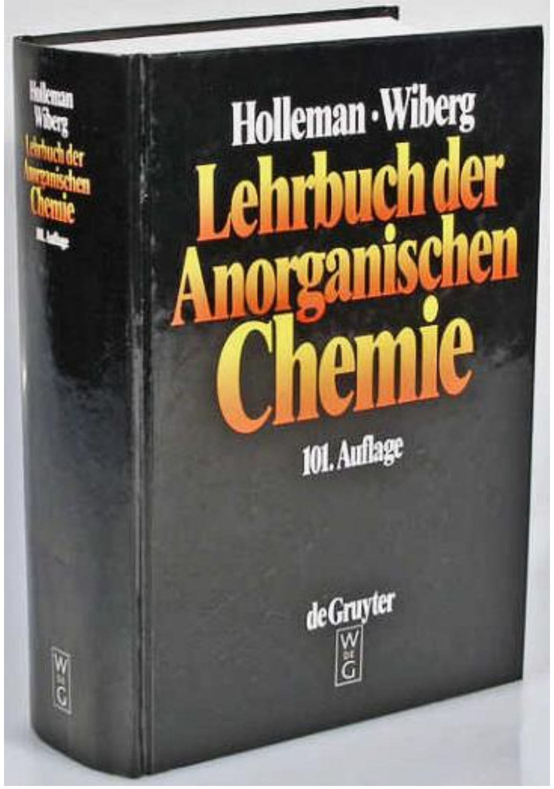


Literature

- The amount of known *d*-metal oxides is vast
  - Over 100 binary *d*-metal oxides are known at ambient pressure (TiO_2, ZnO, …)
  - Hundreds of ternary *d*-metal oxides are known (Fe_2TiO_4, $NiCo_2O_4$, …)
  - Even for one class of $A_2B'B''O_6$ ”double perovskites”, > 1000 structures are known







d-metal oxides as functional materials

- Li-ion battery materials ($LiNi_xMn_yCo_zO_2$, $LiMn_2O_4$, $LiFePO_4$, $Li_4Ti_5O_{12}$, etc.)
- High-temperature superconductors ($YBa_2Cu_3O_{7-x}$, etc.)
- Ferro/ferrimagnets (magnetite Fe_3O_4, maghemite γ-Fe_2O_3, magnetic storage)
- Catalysts (PdO, PtO_2, etc.)
- Solid oxide fuel cells (YSZ = ZrO_2-Y_2O_3 etc.)
- Thermal barrier coatings (e.g. YSZ)
- High-temperature thermoelectrics ($NaCo_2O_4$, ZnO, etc.)
- Protective coatings (e.g. Al_2O_3 coatings fabricated with ALD)

Discussed in CHEM-E4215 Functional Inorganic Materials

Some everyday metal oxides

Inert, non-toxic, abundant

TiO_2 (sunscreen, white pigment)

ZnO (pigment, food additive, medicine, …)

Rust contains $\alpha\text{-}Fe_2O_3 \cdot nH_2O$

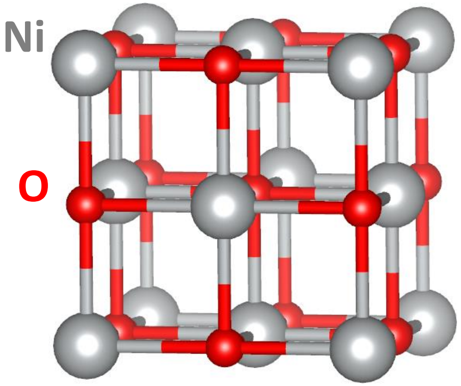
Native oxides on the surface of metals (here Al_2O_3)

CuO (dietary supplement for animals, colourful pigments)

Important structure types for *d*-metal oxides

”Non-oxide” structure types

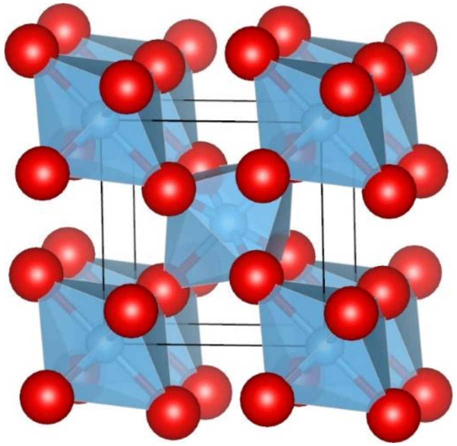
- NaCl (rocksalt): TiO, MnO, FeO, CoO, NiO
- ZnS (wurtzite): ZnO
- Not important for oxides:
  - CsCl, ZnS (sphalerite), NiAs



NiO (*Fm*-3*m*)

”Oxide” structure types

- Rutile (TiO_2)
- Perovskite ($CaTiO_3$)
- Spinel ($MgAl_2O_4$)
- Corundum (Al_2O_3)
- Olivine $(Mg, Fe)_2SiO_4$

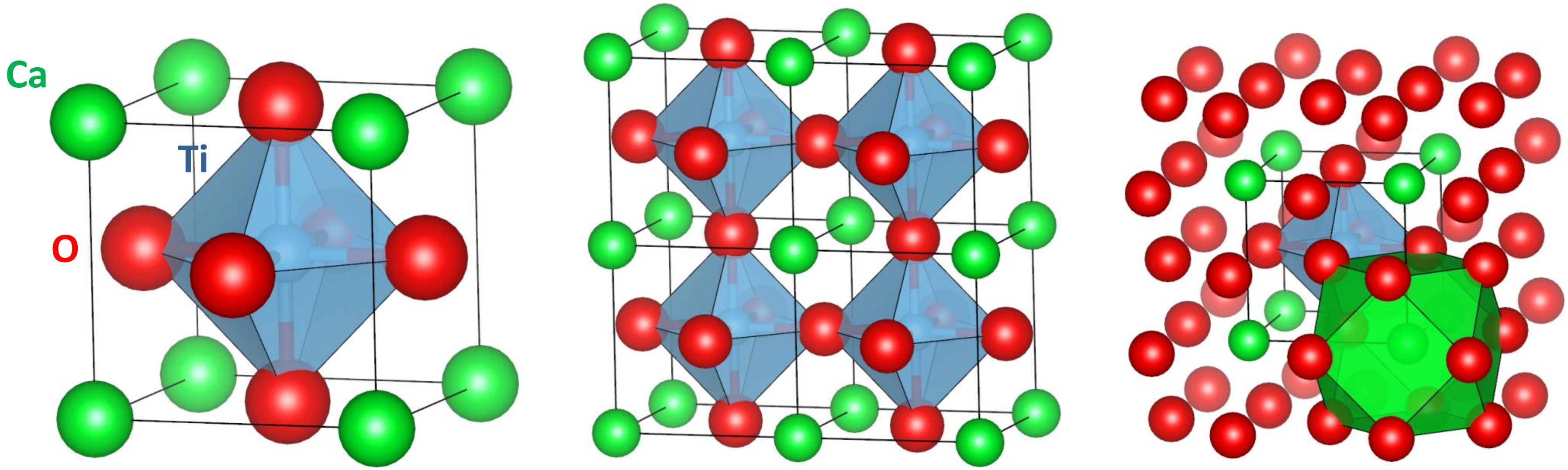


TiO_2 rutile ($P4_2/mnm$)

See Solid State Chemistry Wiki for structure types.
Here only perovskites are discussed in detail.

Figures: AJK

$CaTiO_3$ perovskite (*Pm*-3*m*)



Figures: AJK

- General formula ABX_3, where A and B are cations and X is anion
  - *ccp* anion array, B cations at octahedral sites
- In oxides: **ABO_3**, for example $A^{2+}B^{4+}O_3$ in $CaTiO_3$
- Non-oxide example: Fluoroperovskite $TlMnF_3$ with $Tl^{1+}Mn^{2+}F_3$
- Cubic $CaTiO_3$ perovskite is a high-temperature phase!
  - At lower temperatures, numerous perovskites crystallize at lower symmetry crystal systems (tetragonal, orthorhombic, monoclinic)

Much more information on perovskites in Solid State Chemistry Wiki.

Perovskites as functional materials

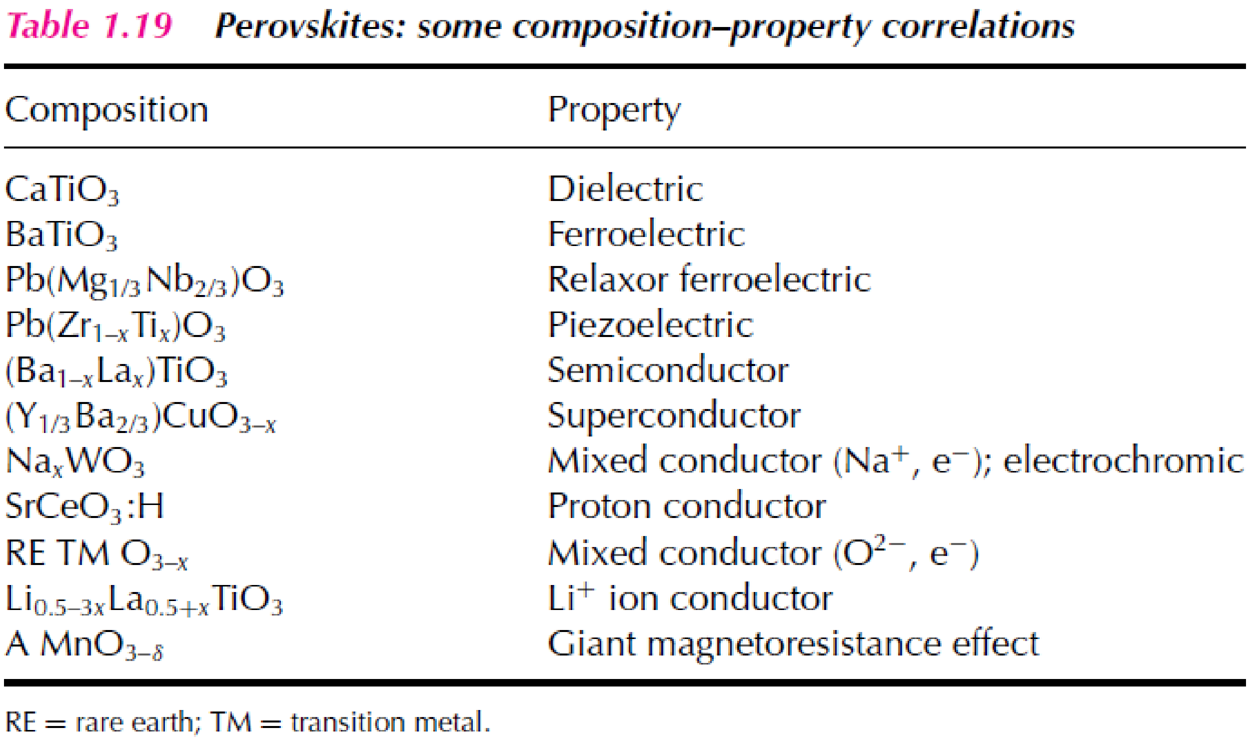


Table 1.19 *Perovskites: some composition–property correlations*

Composition	Property
$CaTiO_3$	Dielectric
$BaTiO_3$	Ferroelectric
$Pb(Mg_{1/3}Nb_{2/3})O_3$	Relaxor ferroelectric
$Pb(Zr_{1-x}Ti_x)O_3$	Piezoelectric
$(Ba_{1-x}La_x)TiO_3$	Semiconductor
$(Y_{1/3}Ba_{2/3})CuO_{3-x}$	Superconductor
Na_xWO_3	Mixed conductor (Na^+, e^-); electrochromic
$SrCeO_3$:H	Proton conductor
RE TM O_{3-x}	Mixed conductor (O^{2-}, e^-)
$Li_{0.5-3x}La_{0.5+x}TiO_3$	Li^+ ion conductor
A $MnO_{3-\delta}$	Giant magnetoresistance effect

RE = rare earth; TM = transition metal.

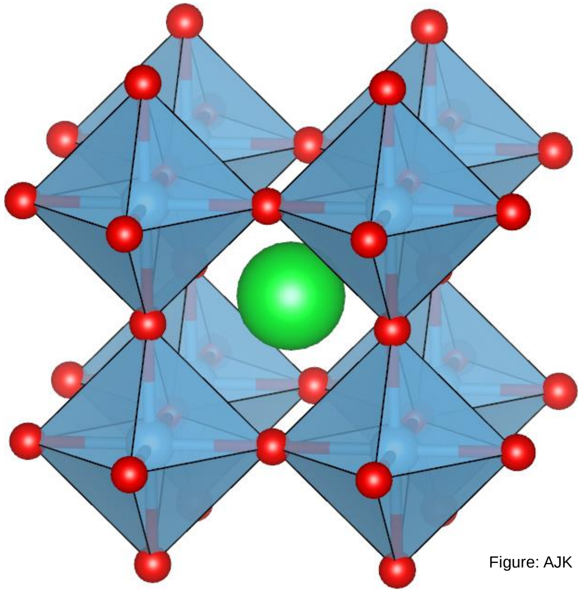
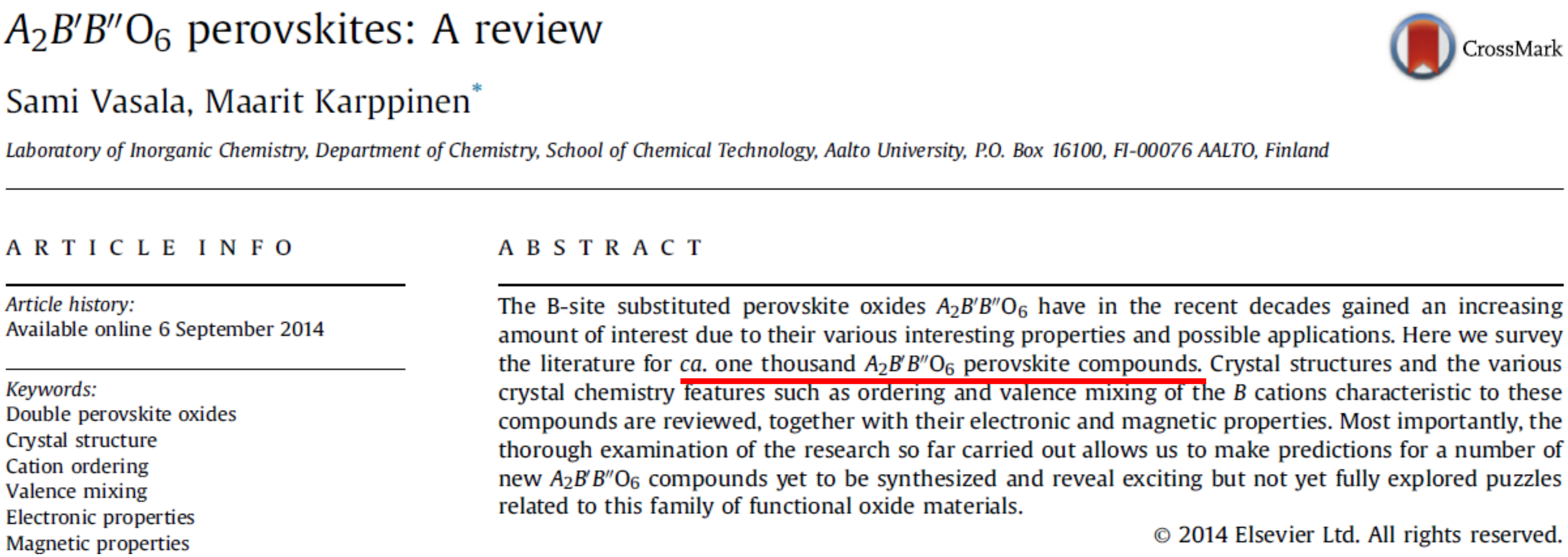


Figure: AJK

Discussed in CHEM-E4215 Functional Inorganic Materials

$A_2B'B''O_6$ double perovskites (1)

- Several classes of perovskite derivatives have been studied extensively
- Widely studied $A_2B'B''O_6$ perovskites are also known as ”Double perovskites”
- Lots of ongoing materials research for example in the field of *spintronics*
  - Spin-liquid-like state in a spin-1/2 square-lattice antiferromagnet perovskite (DOI), O. Mustonen, et al. *Nature Commun.* **2018**, *9*, 1085.



$A_2B'B''O_6$ perovskites: A review

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A R T I C L E   I N F O

Article history:
Available online 6 September 2014

Keywords:
Double perovskite oxides
Crystal structure
Cation ordering
Valence mixing
Electronic properties
Magnetic properties

A B S T R A C T

The B-site substituted perovskite oxides $A_2B'B''O_6$ have in the recent decades gained an increasing amount of interest due to their various interesting properties and possible applications. Here we survey the literature for *ca.* one thousand $A_2B'B''O_6$ perovskite compounds. Crystal structures and the various crystal chemistry features such as ordering and valence mixing of the *B* cations characteristic to these compounds are reviewed, together with their electronic and magnetic properties. Most importantly, the thorough examination of the research so far carried out allows us to make predictions for a number of new $A_2B'B''O_6$ compounds yet to be synthesized and reveal exciting but not yet fully explored puzzles related to this family of functional oxide materials.

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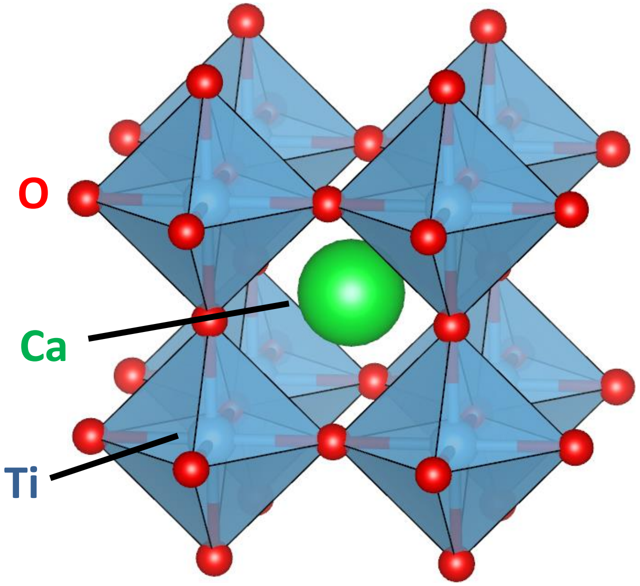
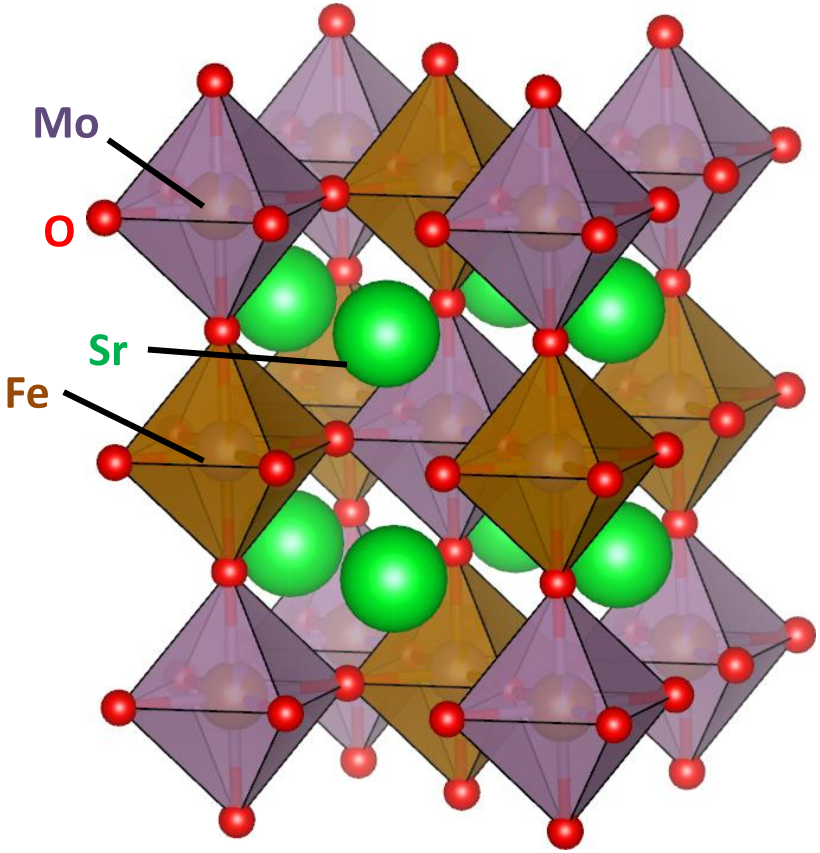
S. Vasala, M. Karppinen, *Progress in Solid State Chemistry*, **2015**, *43*, 1–36 (DOI).

$A_2B'B''O_6$ double perovskites (2)



Perovskite $CaTiO_3$ (*Pm*-3*m*)



Sr_2FeMoO_6 (*I*4/*mmm*)
Rocksalt-like ordering of FeO_6 and MoO_6 polyhedra

Figures: AJK

$A_2B'B''O_6$ double perovskites (3)

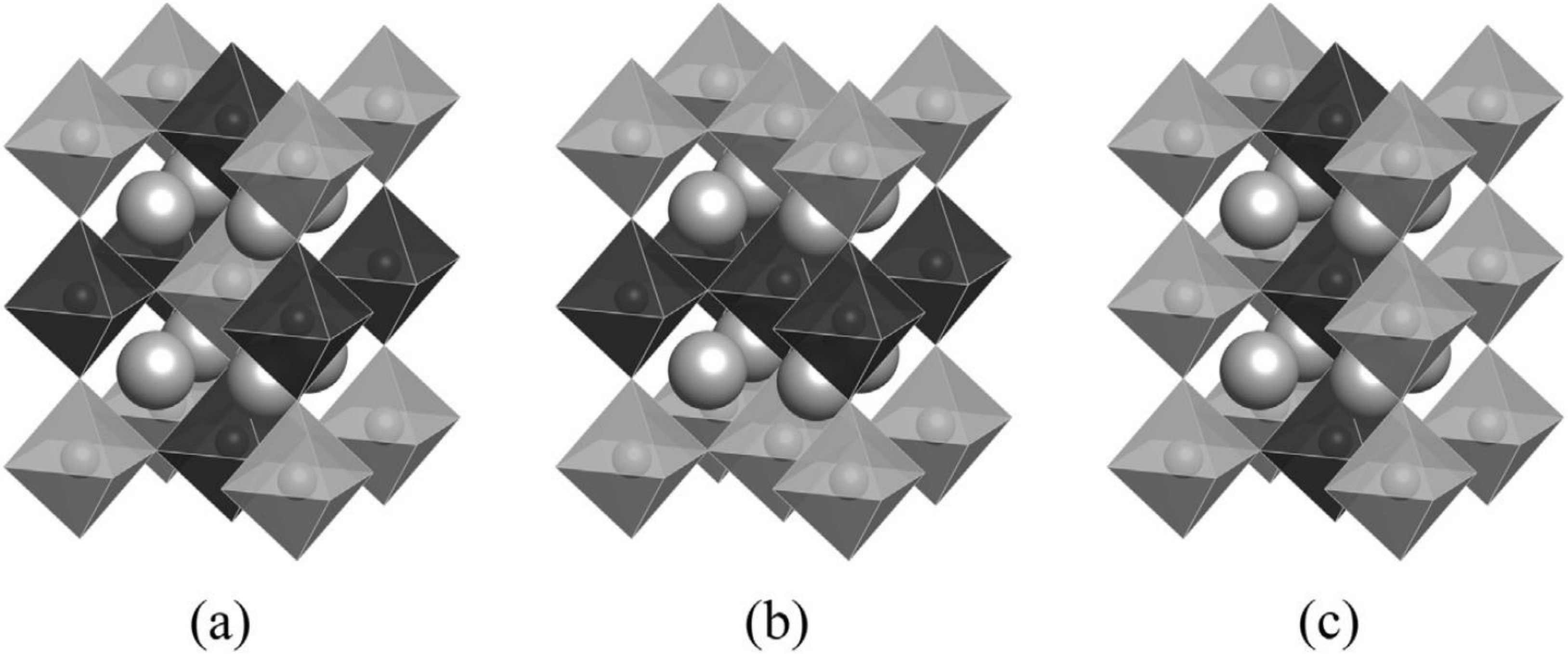

(a) (b) (c)

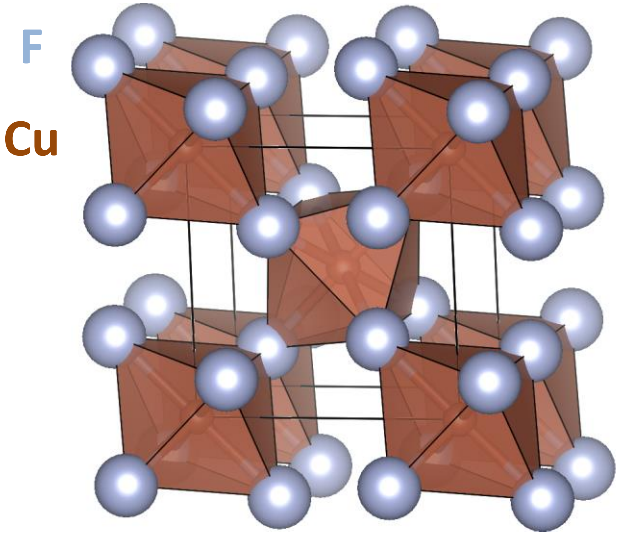
Fig. 1. Different *B*-site cation orderings found in $A_2B'B''O_6$ perovskites: (a) rock-salt, (b) layered and (c) columnar order.

S. Vasala, M. Karppinen, *Progress in Solid State Chemistry*, **2015**, *43*, 1–36.

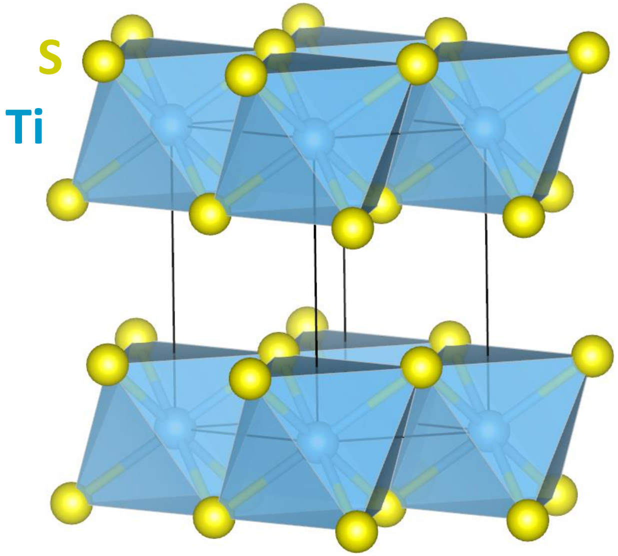
Non-oxide *d*-block compounds

d-block + *p*-block compounds (1)

- *d*-block + group 17 (F, Cl, Br, I)
  - All *d*-metals form halides with group 17 elements
  - Many are molecular, but numerous polymeric / 3D structures are also known
- *d*-block + group 16 (O, S, Se, Te)
  - Oxides typically form 3D networks, but some are molecular (e.g. CrO_3)
  - S, Se, Te compounds often show 2D sheets (like TiS_2, MoS_2, WS_2, …)



CuF_2 ($P2_1/n$)

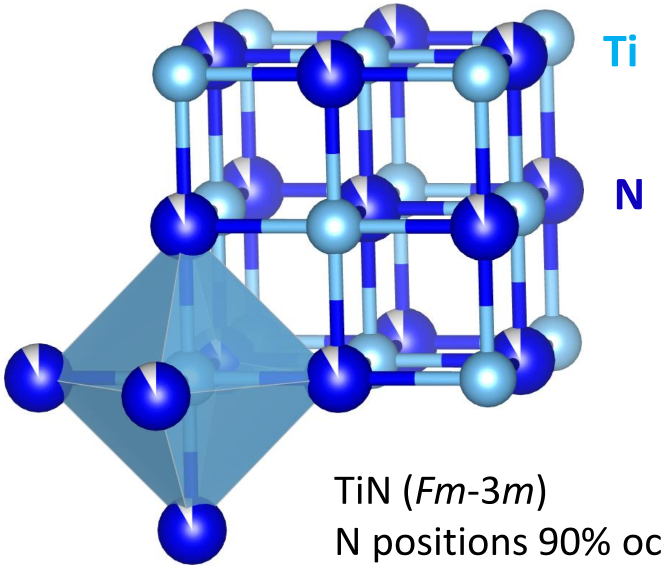


TiS_2 (P-$3m$)

Figures: AJK

d-block + *p*-block compounds (2)

- *d*-block + group 15 (N, P, As, Sb, Bi)
  - Many nitrides are particularly important due to their hardness (coatings)
  - For example: TiN (see figure below)
  - Numerous phosphides, arsenides, and antimonides are known. Bismuth is already so metallic that it rather forms alloys
  - Phosphides show various different phosphorus anions and anion networks (e.g. P_2^{4-}, isoelectronic to Cl_2)



TiN (*Fm*-3*m*)
N positions 90% occupied

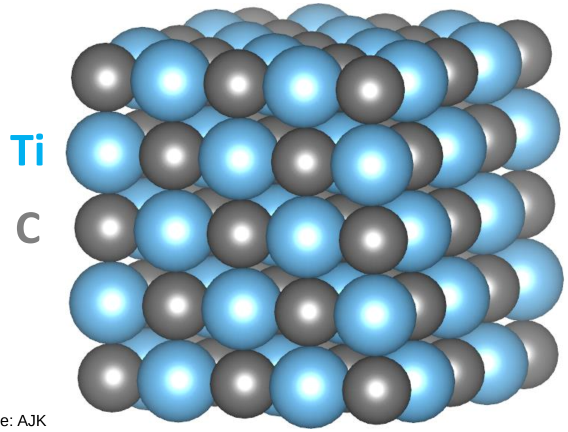
Figure: AJK

TiN coatings have gold-like appearance

Figure: Wikipedia

d-block + *p*-block compounds (3)

- *d*-block + group 14 (C, Si, Ge, Sn, Pb)
  - Many carbides are technologically highly relevant
  - For example, cementite Fe_3C is present in most steels.
  - Some carbides such as TiC and WC are extremely hard (Mohs hardness ~ 9)
  - **Organometallic chemistry** (compounds with M-C bonds) is a huge branch of chemistry, but since it mainly deals with molecular species, not discussed here
  - Many silicides and germanides are well-known, but tin and lead are metallic and rather form alloys (e.g. Cu + Sn = **bronze**, typically ~90% Cu)
- *d*-block + group 13 (B, Al, Ga, In, Tl)
  - Many borides are hard materials, *e.g.* OsB_2, WB_4, and ReB_2
  - Al, Ga, In, Tl -> metallic, rather form alloys and **intermetallic compounds**



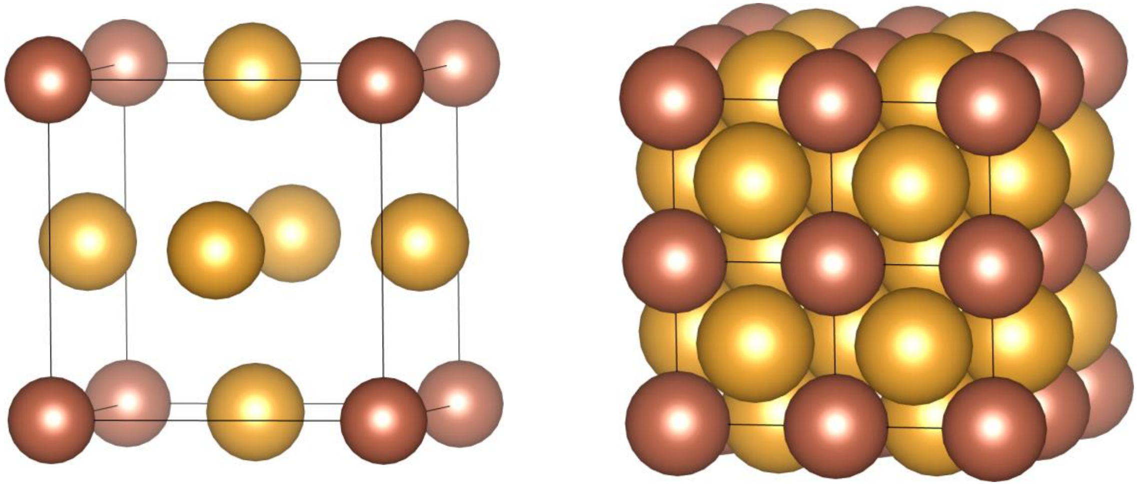
TiC (*Fm*-3*m*)

Figure: AJK

Intermetallic compounds

- Intermetallics are solid-state compounds exhibiting
  - Metallic bonding (metal-metal bonds)
  - Defined stoichiometry
  - **Ordered** crystal structure (different from **metal alloys**)
- Definition normally includes also *s*- and *p*-block metals (Na, Mg, Al, *etc.*)
  - For example, Cu_3Al, NiAl, Ni_3Al, Cu_3Sn… (ordered structures!)
- Often offer a compromise between ceramic and metallic properties
- Can also display desirable magnetic, superconducting, and chemical properties, due to mixed metallic and covalent/ionic bonding
- **Heusler compounds** discussed here as examples, Laves phases as extra material

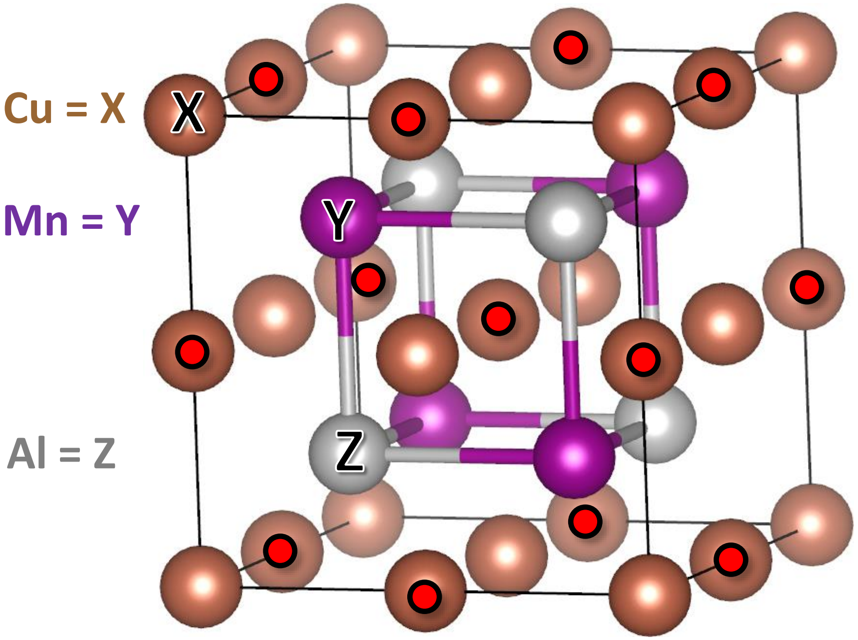
Au_3Cu (*Pm*-3*m*)



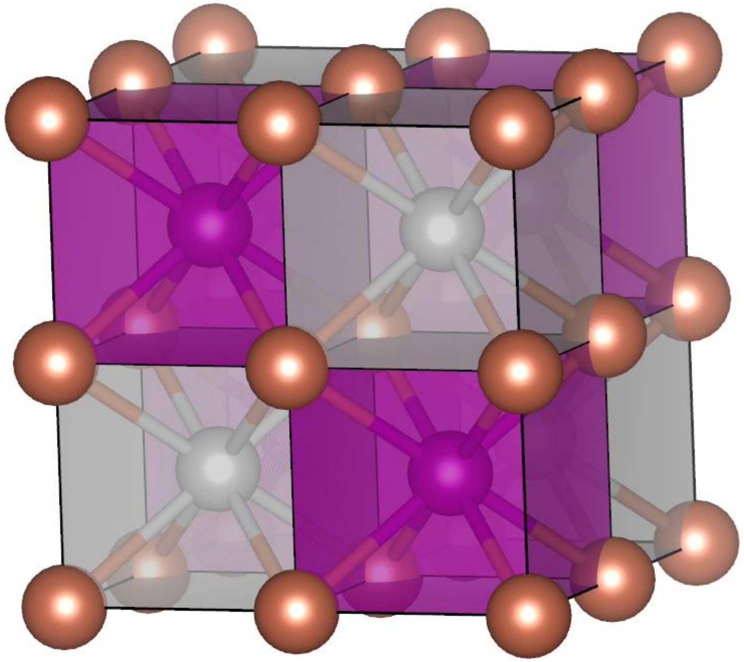
Ref: Wikipedia

Heusler alloys

- Intermetallics with composition X_2YZ and face-centered cubic crystal structure
- For example, Cu_2MnAl, Ni_2TiSn, Co_2MnSi, …
- Removing half of the X atoms, the second fcc sublattice marked with red dots, lowers the symmetry to *F*-43*m* and gives rise to **Half-Heusler phases**



Cu_2MnAl (F*m*-3*m*)
Cu = **X**; Mn = **Y**, Al = **Z**
Mn-Al contacts drawn for clarity, not bonds
Metallic, ferromagnetic

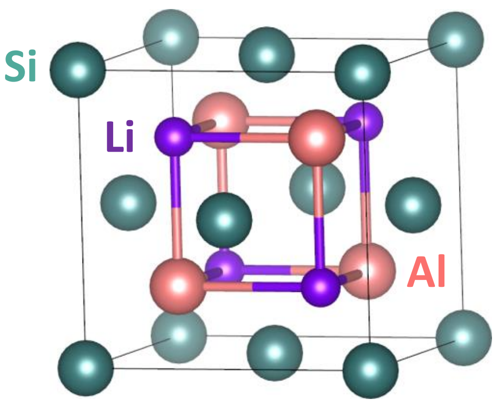


Another view: all metal atoms are 8-coordinated

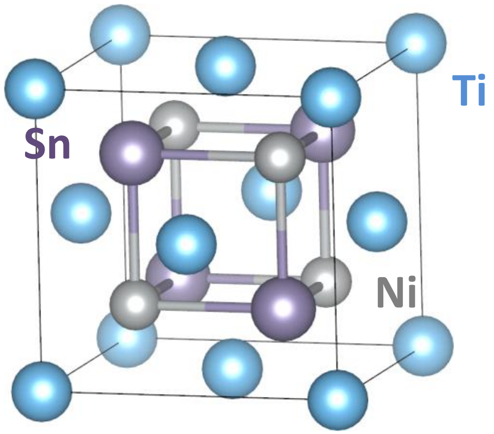
Figures: AJK

Half-Heusler phases

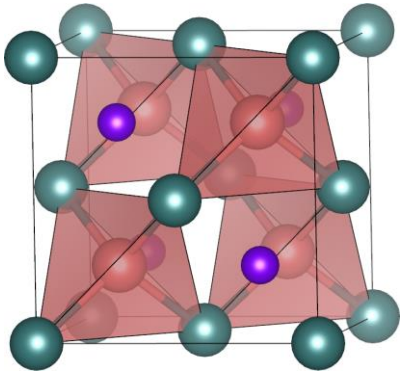
- Half-Heusler: XYZ (e.g. NiTiSn, CoTiSb, LiAlSi)
- Semiconductors, when **8** or **18** valence electrons (VE)
- Studied for example because of their thermoelectric properties



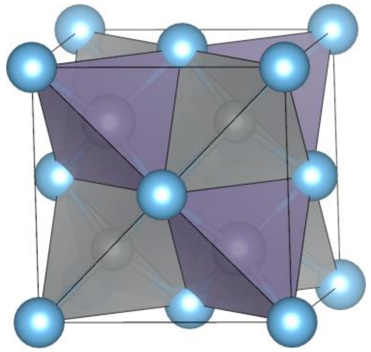
LiAlSi (*F*-43*m*)
Si = **X**; Li = **Y**; Al = **Z**
Semiconductor (8 valence e^-)
Can be considered as a Zintl phase!
Li-Al drawn for clarity, not bonds



TiSnNi (*F*-43*m*)
Ti = **X**; Sn = **Y**; Ni = **Z**
Semiconductor (18 VE)
Sn-Ni contacts drawn for clarity, not bonds



Another view, Si and Al 4-coordinated, Li^+ cations



Figures: AJK

Another view, Sn and Ni 4-coordinated, Ti 8-coord.

Extra slides

“Nice-to-know”-type material that is not
needed for completing the exercises

Pauli paramagnetism

- In addition to the strong ferro- or antiferromagnetic coupling shown by some metals, most metals display a weak *Pauli paramagnetism* in the presence of a magnetic field

Only small number of electrons near E_F contribute to the Pauli paramagnetism

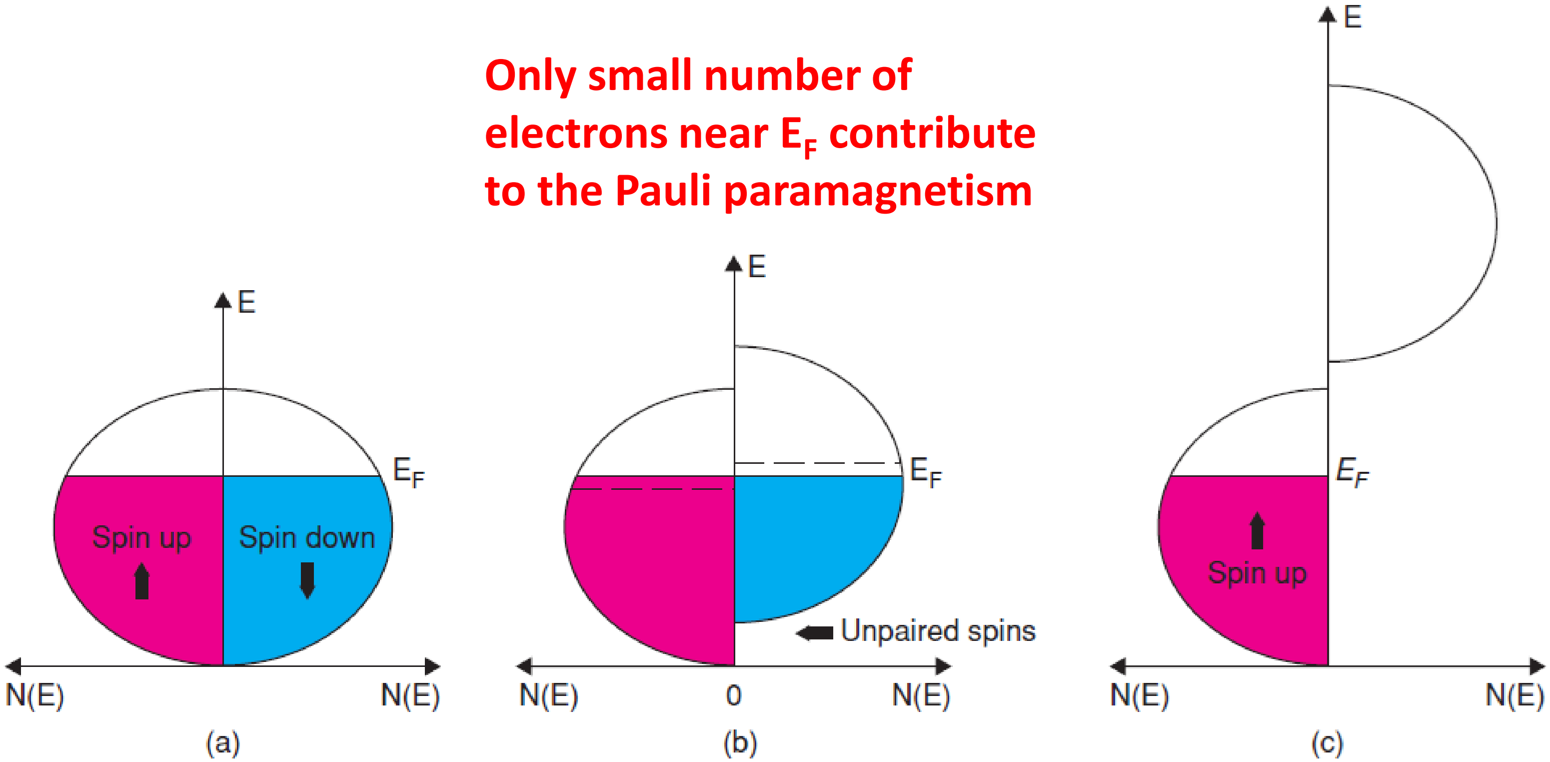


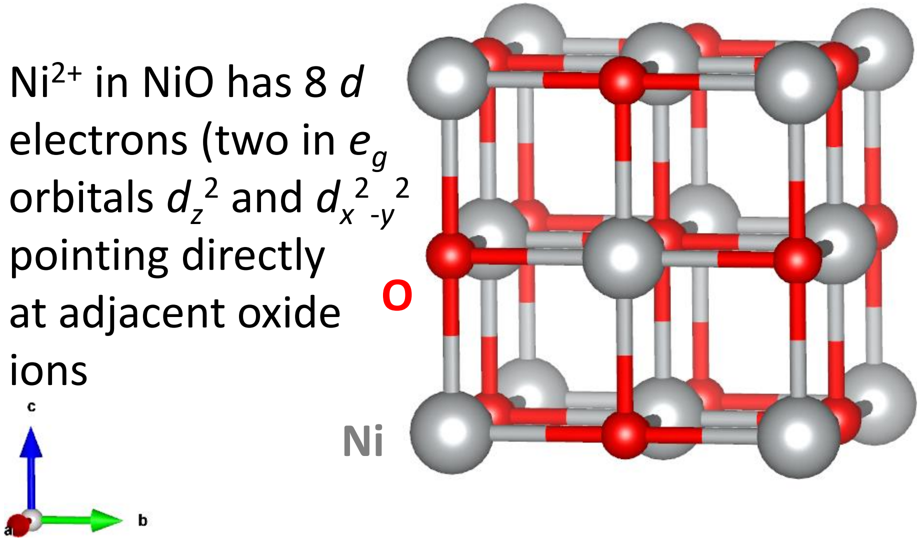
Figure 9.9 Schematic splitting of 3d band into two sub-bands: (a) in the absence of a magnetic field; (b) in Pauli paramagnets, an energy difference develops in a magnetic field; (c) in ferromagnetic transition metals, the splitting occurs spontaneously.

Ref: West p. 458

Antiferromagnetic ordering: superexchange

- Superexchange is the mechanism of antiferromagnetism in, e.g. NiO

Ni^{2+} in NiO has 8 *d* electrons (two in e_g orbitals d_{z^2} and $d_{x^2-y^2}$ pointing directly at adjacent oxide ions



The unpaired electrons in these e_g orbitals couple with electrons in the *p* orbitals of the O^{2-} ions

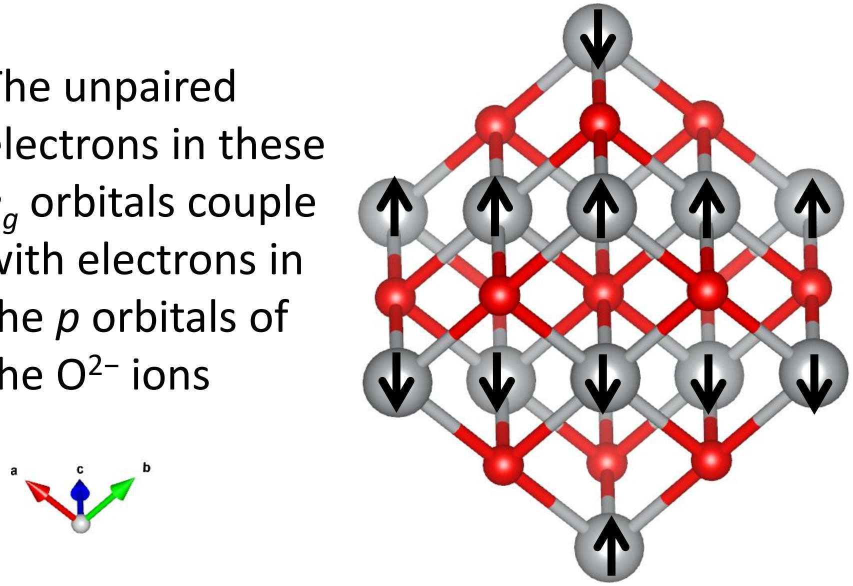


Figure: AJK

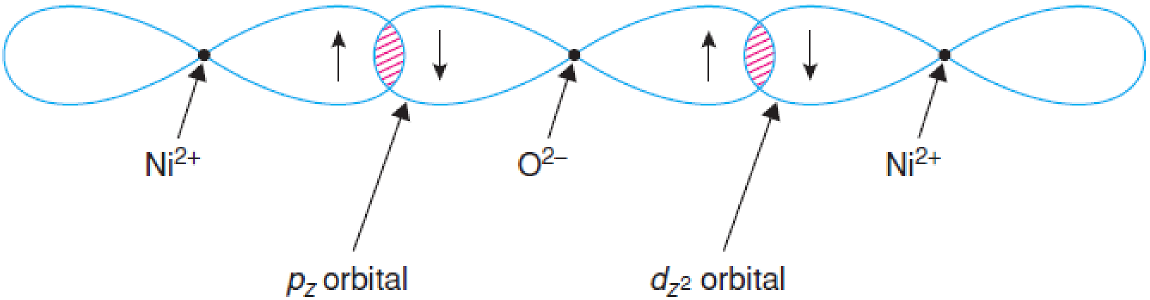
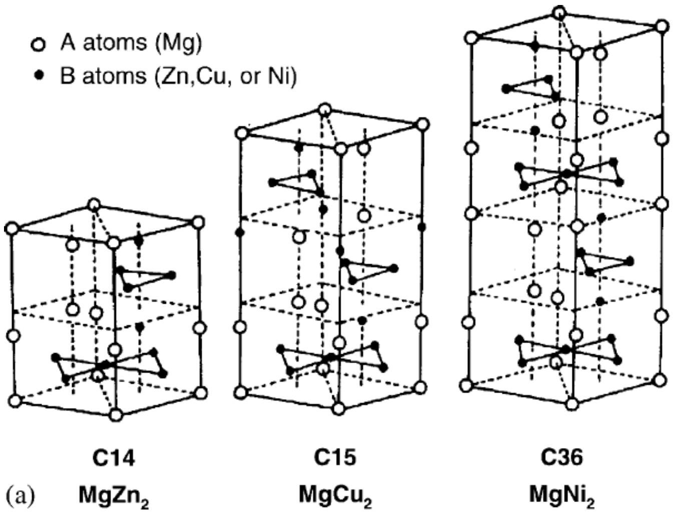


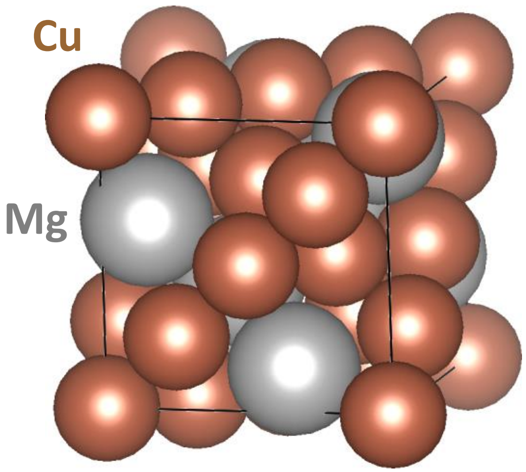
Figure 9.5 Antiferromagnetic coupling of spins of d electrons on Ni^{2+} ions through p electrons of oxide ions.

Laves phases

- Laves phases form the largest group of intermetallic compounds
  - Often also referred to as Friauf-Laves phases
- General composition AB_2 with the larger A atoms in the center of a 16-atom (Frank–Kasper) polyhedron and smaller B atoms in the centers of icosahedra (12-c)
- More than 1400 binary and ternary Laves phases are reported in Pearson’s Handbook of Crystallographic Data for Intermetallic Phases
- Three different polytypes: $MgCu_2$ (cubic), $MgZn_2$ (hex), and $MgNi_2$ (hex).



Ref: Stein, *Intermetallics* **2004**, *12*, 713–720



$MgCu_2$ (*Fd*-3*m*)
Related to diamond structure

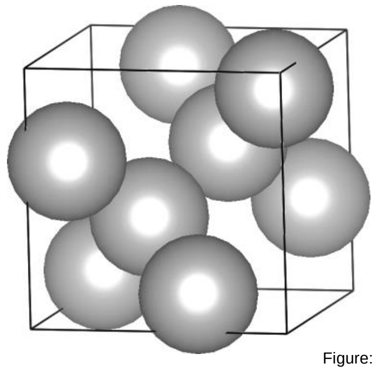


Figure: AJK

Mg sublattice