

Yonsei University Graduate Class

Energy Materials: Design, Discovery and Data Semiconductor Chemistry and Physics

Prof. Aron Walsh

Department of Materials
Imperial College London

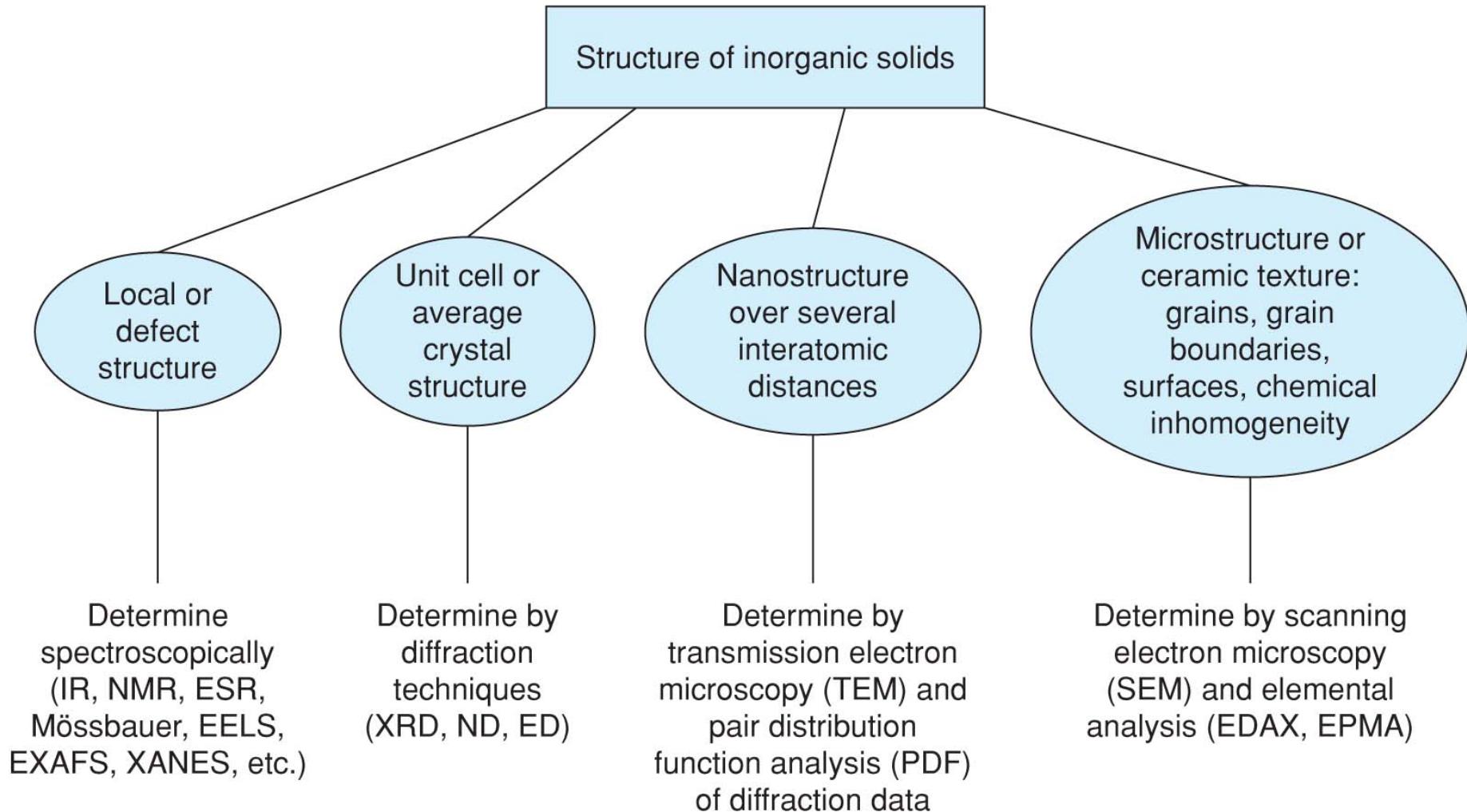


<https://wmd-group.github.io>

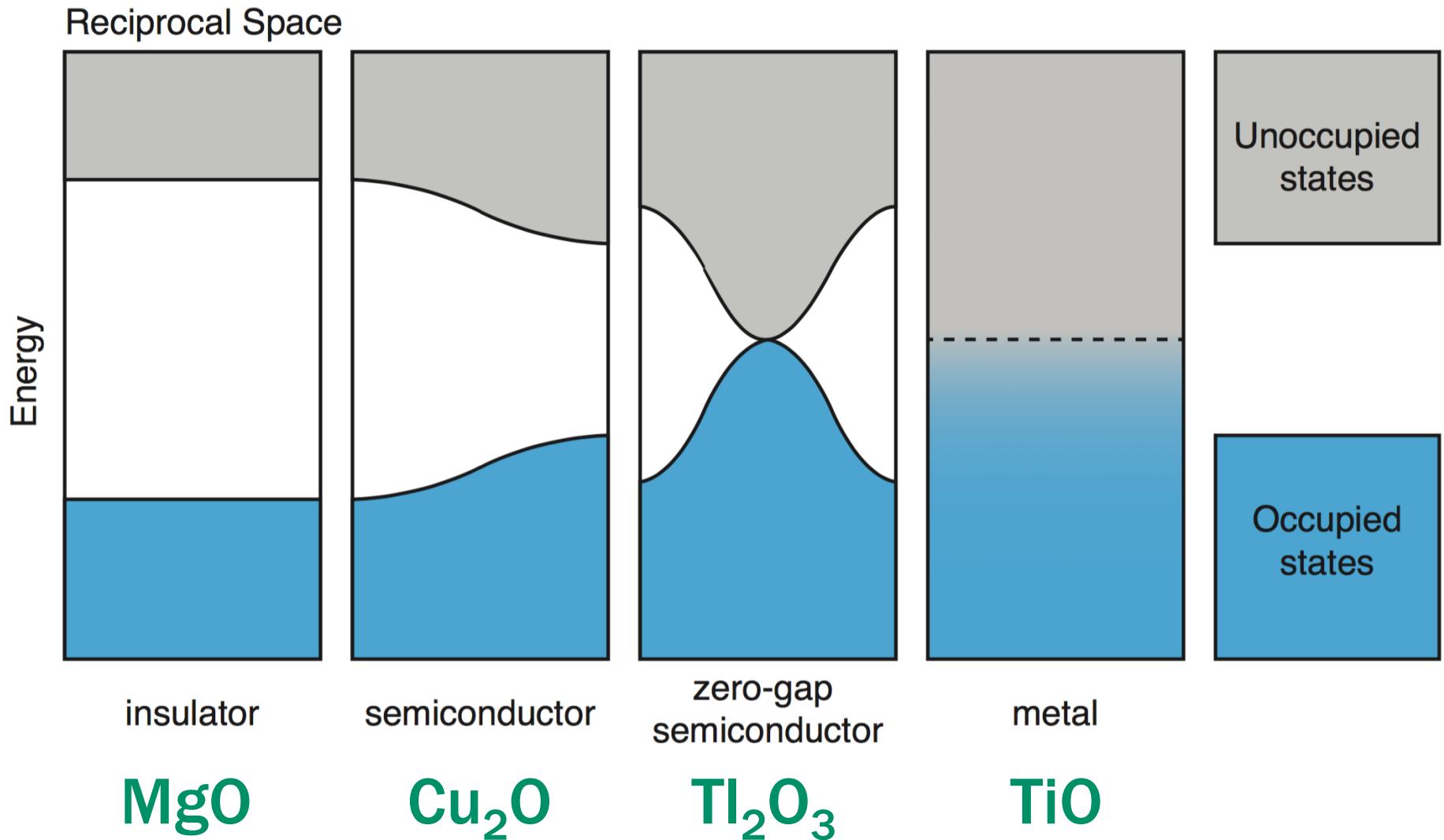


@lonepair

Crystal Structure of Solids (Refresh)

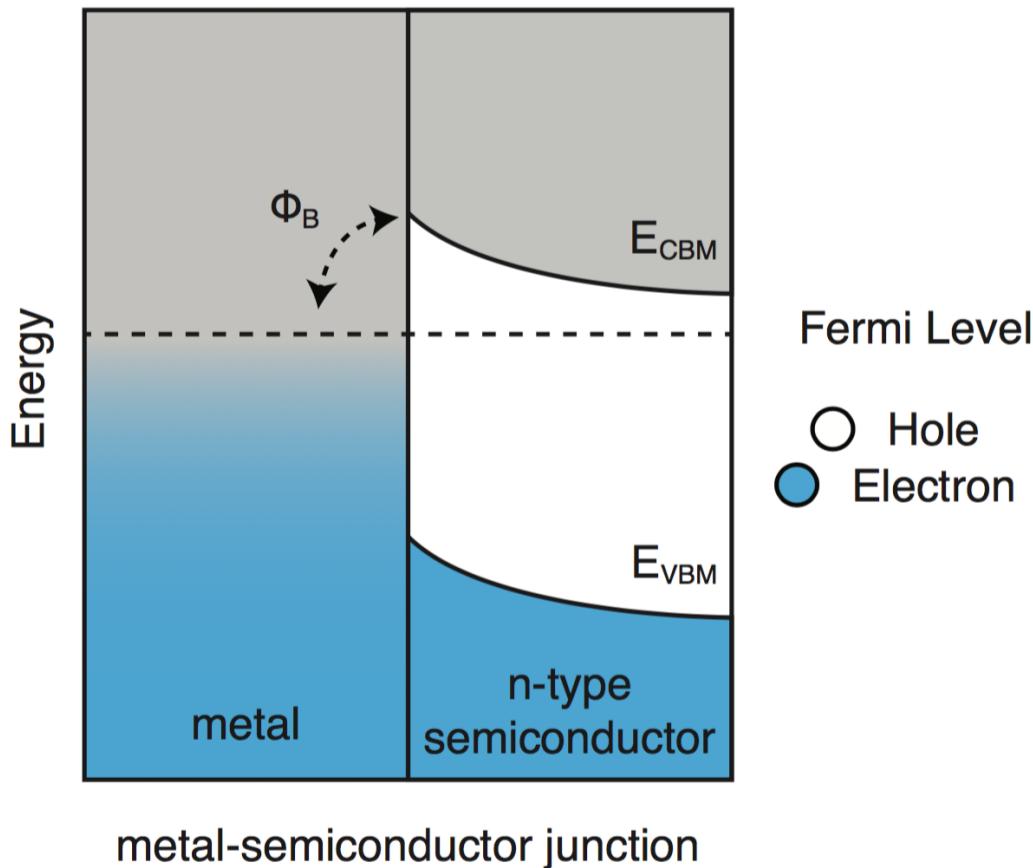


Electronic Structure of Solids (Refresh)



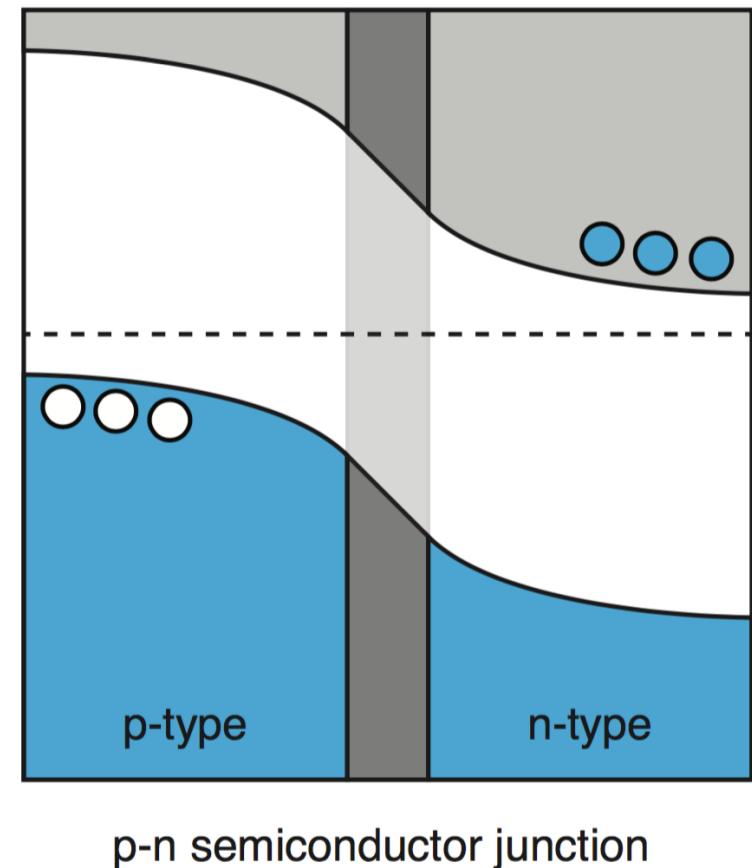
Electronic Interfaces (Refresh)

Real Space



metal-semiconductor junction

Cu/ZnO

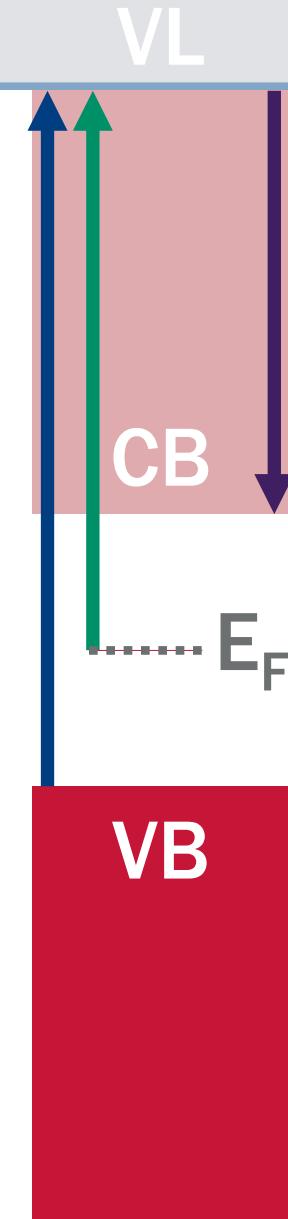


p-n semiconductor junction

$\text{Cu}_2\text{O/ZnO}$

Semiconductor Terminology

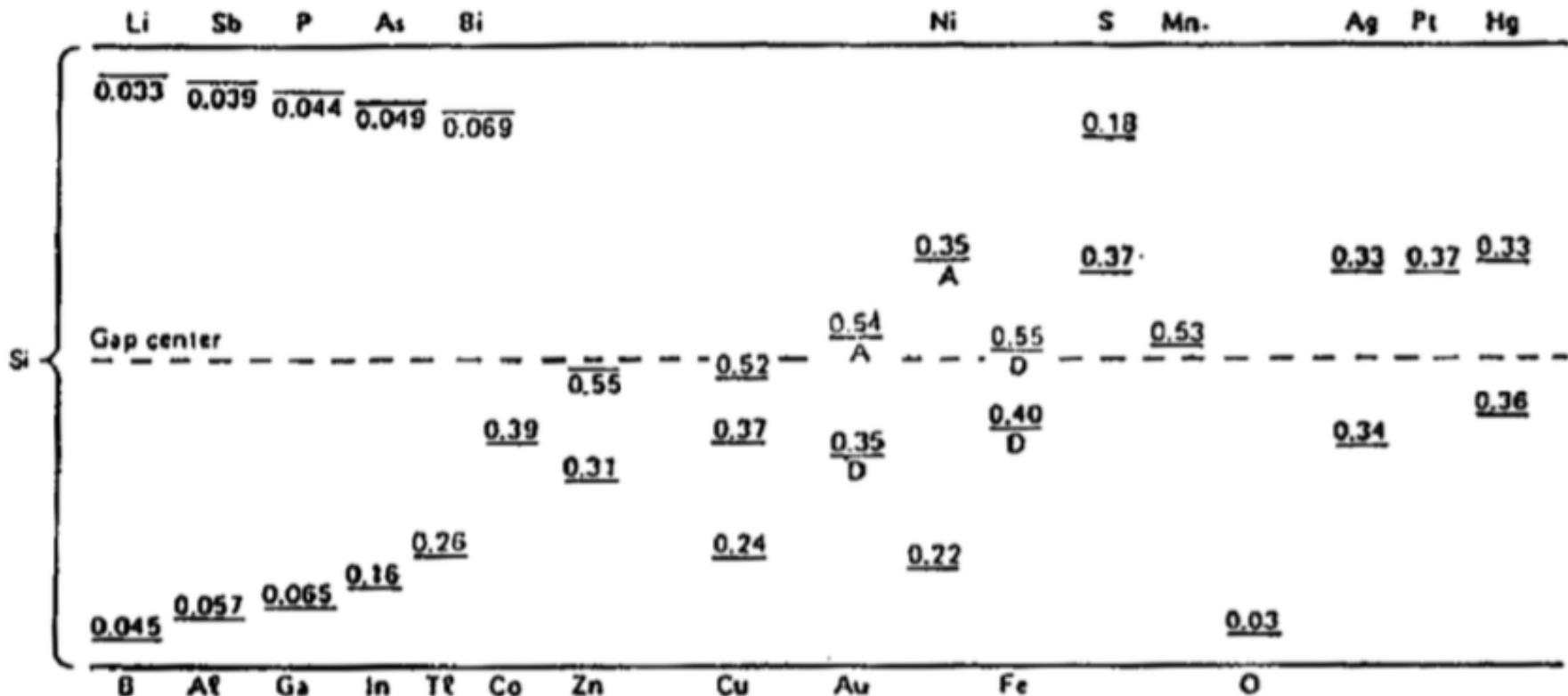
- 1. Ionisation Potential** – Energy to remove electron from valence band (VB) to the vacuum level (VL)
- 2. Workfunction** – Energy to remove electron from the Fermi level (E_F) to the vacuum level
- 3. Electron Affinity** – Energy to add an electron to the conduction band (CB) from the vacuum level



Semiconductor Terminology

Donors ($N+1$ electrons)

Deep levels – avoid!



Acceptors ($N-1$ electrons)

Source: Photovoltaic Solar Energy Conversion (Springer, 2005)

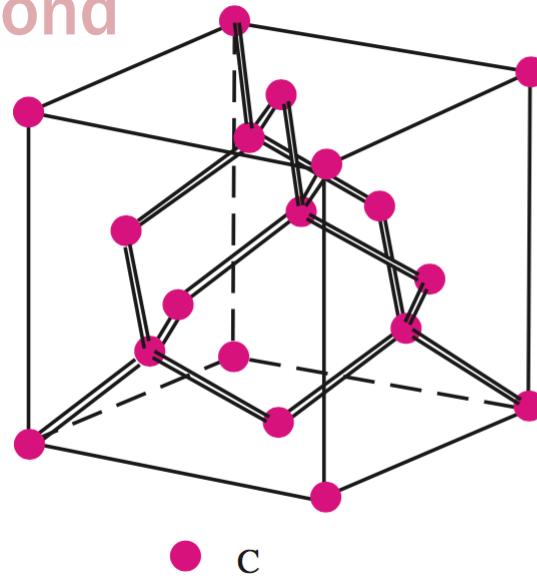
Talk Outline: Semiconductors

- 1. Crystal Structure**
- 2. Electronic Structure**
- 3. Band Engineering**

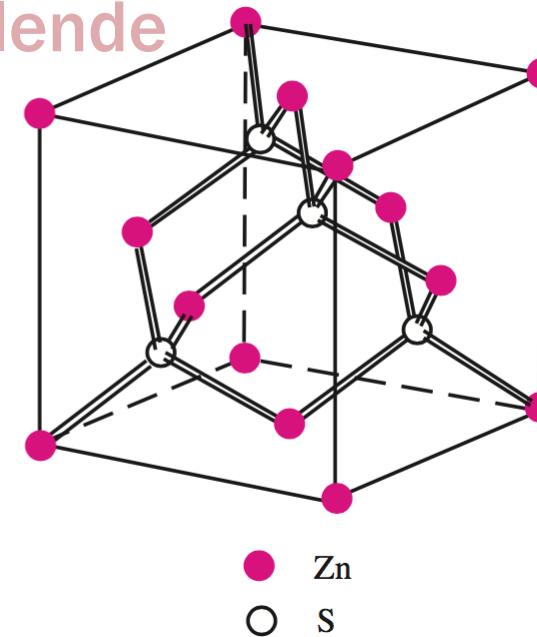
Tetrahedral Semiconductors

“Tetrahedrally bonded semiconductors form the mainstay of the electronics industry and the cornerstone of modern technology”

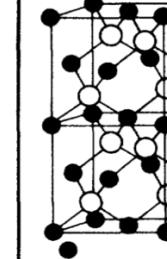
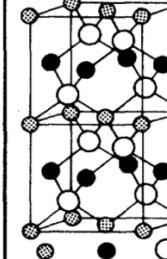
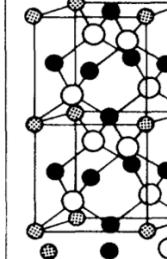
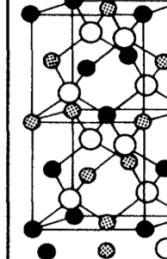
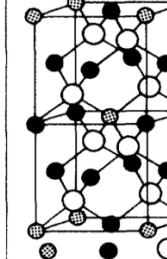
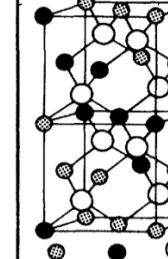
Diamond



Zinc-blende



Tetrahedral Semiconductor Alloys

Ordering Vectors	(0,0,0)	(0,0,1)		(2,0,1)		(1,1,1)
Name (ternary)	Zincblende (Sphalerite)	Layered Tetragonal	"Luzonite"	Chalcopyrite	Famatinitite	Layered Trigonal
Formula	$n = 0,4; AC$	$n = 2; ABC_2$	$n = 1,3; A_3BC_4$	$n = 2; ABC_2$	$n = 1,3; A_3BC_4$	$n = 2; ABC_2$
						
Zn S type	InGaAs ₂ type	Cu ₃ AsS ₄ type	CuFeS ₂ type	Cu ₃ SbS ₄ type	CrCuS ₂ type (Na V S ₂)	
Bravais Lattice	Face centered cubic	Simple tetragonal	Simple cubic	Body centered tetragonal	Body centered tetragonal	Rhombohedral
Space Group	F $\bar{4}3m$ T_d^2 216	P $\bar{4}m2$ D_{2d}^5 115	P $\bar{4}3m$ T_d^1 215	I $\bar{4}2d$ D_{2d}^{12} 122	I $\bar{4}2m$ D_{2d}^{11} 121	R3m C_{3v}^5 160
Int. Tables						
Schoenflies						
Number						
Strukturbericht	B3		H ₂ 4	E1 ₁	H2 _a	
Pearson symbol	CF8		CP8	II16	II16	hR4
Atomic positions (ternary)	Zn: 4 a $\bar{4}3m$ S: 4 c $\bar{4}3m$	1A: 1 a $\bar{4}2m$ 1B: 1 c $\bar{4}2m$ 2C: 2 g mm	3 Cu: 3 c $\bar{4}2m$ 1 As: 1 a $\bar{4}3m$ 4 S: 4 e 3m	2 Cu: 4 a $\bar{4}$ 2 Fe: 4 b $\bar{4}$ 4 S: 8 d 2	1 Cu: 2 b $\bar{4}2m$ 2 Cu: 4 d $\bar{4}$ 1 Sb: 2 a $\bar{4}2m$ 4 S: 8 i m	1 A: 1 a 3m 1 B: 1 a 3m 1 C: 1 a 3m 1 C: 1 a 3m
Equivalent superlattice	None	(1,1) in [0 0 1] direction	None	(2,2) in [2 0 1] direction	(1,3) in [2 0 1] direction	(1,1) in [1 1 1] direction

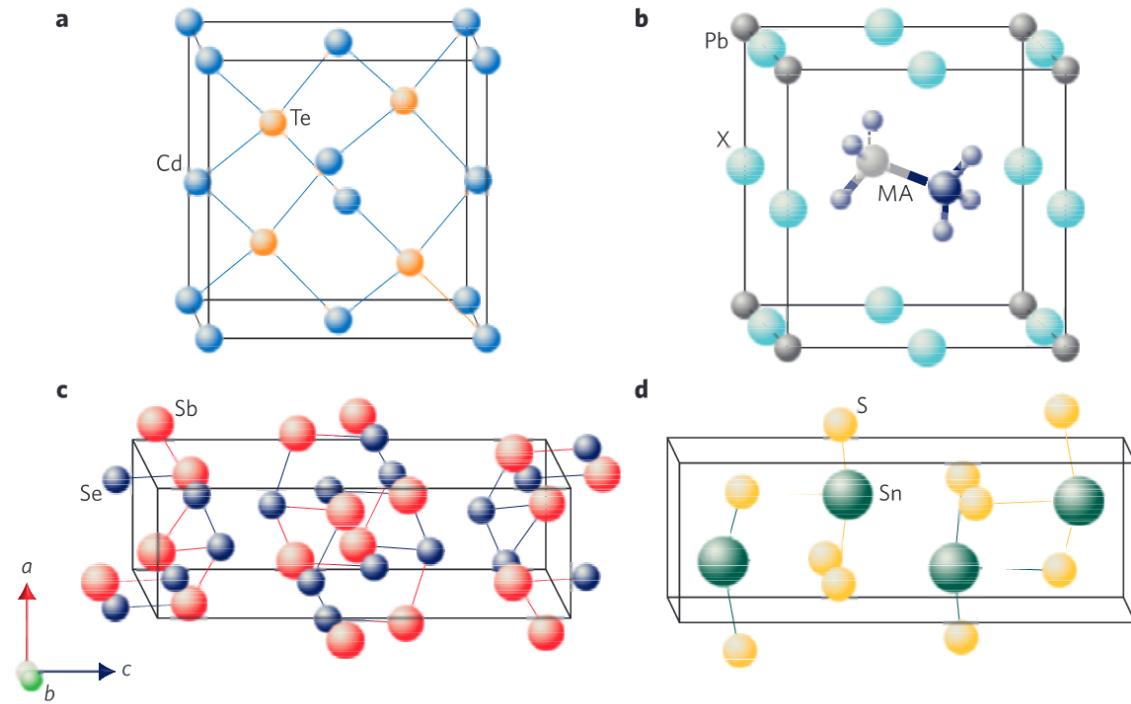
Recent Trend: Lower Symmetry

Non-cubic solar cell materials

Controlled growth of non-cubic, anisotropic solar cell materials, such as antimony selenide, is bringing new opportunities for efficient thin-film photovoltaics.

Vera Steinmann, Riley E. Brandt and Tonio Buonassisi

Photovoltaics (PVs) have the potential to be an inexpensive, ubiquitous, renewable energy technology by efficiently converting sunlight into electricity. Today, crystalline silicon-based PVs account for over 90% of worldwide module production. However, the fabrication of silicon photovoltaics is capital intensive, potentially limiting its ability to rapidly scale up with today's commoditized margins^{1,2}. High processing temperatures are needed because of silicon's high melting point of 1,414 °C, and high purity is needed because of its low tolerance to defects, which can adversely affect cell performance. In light of this, an important basic research challenge is to identify a PV material with high efficiency, low manufacturing cost (capital intensity), low materials use (thin-film with high absorptance), impeccable reliability (enabling low-interest-rate loans



Pauling's Rules For Structure

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 192]

THE PRINCIPLES DETERMINING THE STRUCTURE OF COMPLEX IONIC CRYSTALS

BY LINUS PAULING

RECEIVED SEPTEMBER 5, 1928

PUBLISHED APRIL 5, 1929

Factors determining stability of crystal structures:

1. Radius ratio (size matters)
2. Electrostatic valence (charge matters)
3. Polyhedral connectivity (corner > edge > face)
4. Different cations disfavour direct connectivity
5. Parsimony (simpler is better)

Talk Outline: Semiconductors

- 1. Crystal Structure**
- 2. Electronic Structure**
- 3. Band Engineering**

Electrons in Solids

The distribution of electrons in materials determines the crystal structure, chemical stability, and physical properties.

A rigorous treatment requires solving many-body quantum mechanics for $> 10^{23}$ electrons.

Electrons in Solids

Quantum Mechanics of Many-Electron Systems.

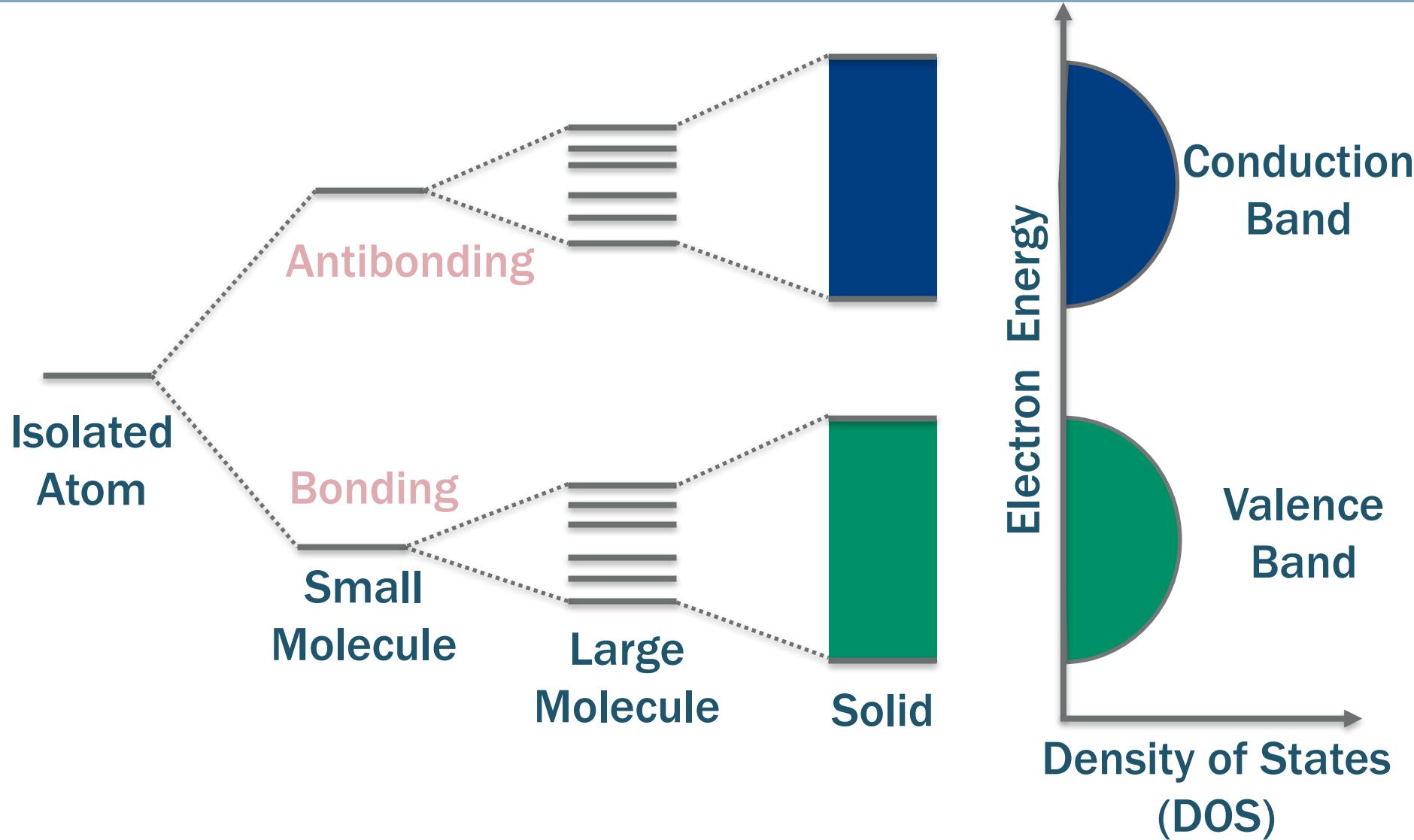
By P. A. M. DIRAC, St. John's College, Cambridge.

(Communicated by R. H. Fowler, F.R.S.—Received March 12, 1929.)

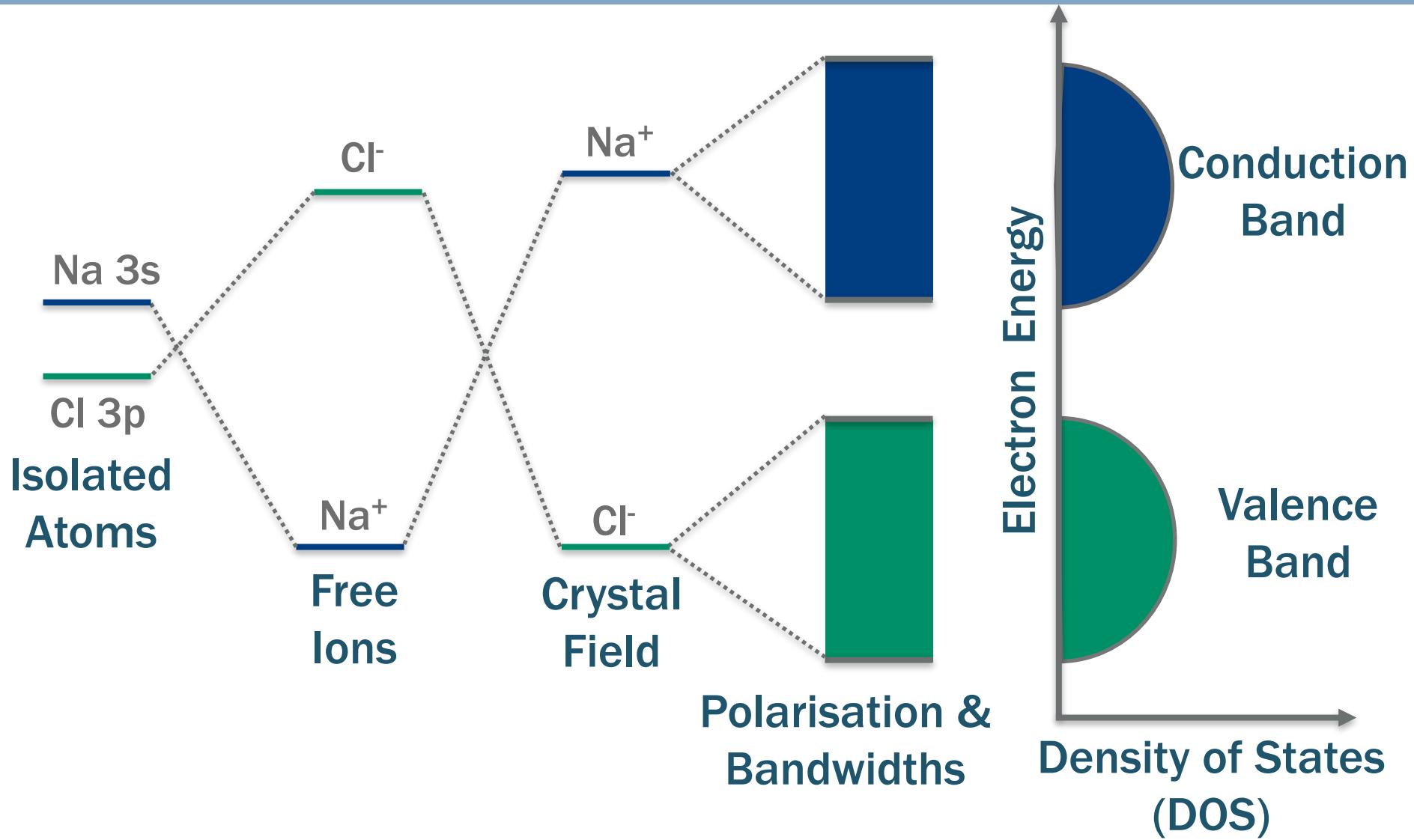
§ 1. *Introduction.*

The general theory of quantum mechanics is now almost complete, the imperfections that still remain being in connection with the exact fitting in of the theory with relativity ideas. These give rise to difficulties only when high-speed particles are involved, and are therefore of no importance in the consideration of atomic and molecular structure and ordinary chemical reactions, in which it is, indeed, usually sufficiently accurate if one neglects relativity variation of mass with velocity and assumes only Coulomb forces between the various electrons and atomic nuclei. The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.

From Atoms to Crystals: Covalent Model



From Atoms to Crystals: Ionic Model



Ionic vs Covalent Bonds

Ionic bonding: LiF

Electrostatics - close packing of ions

Covalent bonding: Si

Directional bonding - maximise orbital overlap

Many definitions, discussions, and debates in the literature. For two or more different elements, the bonding is best described as heteropolar.

Ionicity in Solids, Catlow and Stoneham, J. Phys. C 16, 432 (1983)

Misunderstanding of Chemical Concepts, Jansen and Wedig,
Angewandte Chemie 47, 10026 (2008)

Optical and Electronic Band Gaps

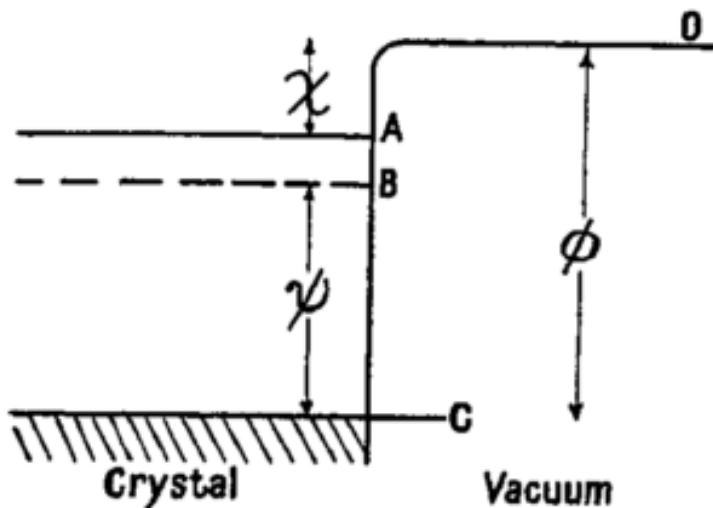


Figure 1. Energy levels in insulator.

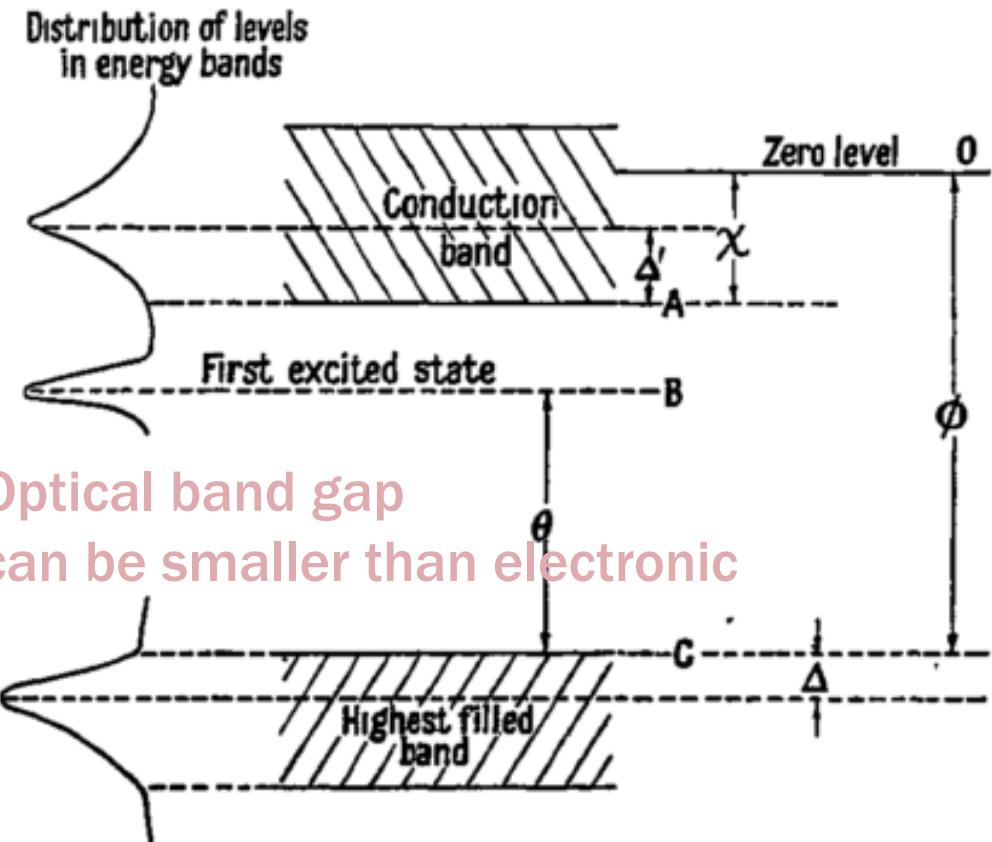


Figure 2. Energy levels in insulator including band width.

Talk Outline: Semiconductors

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Structure–Property Relationships

**Connection between macroscopic properties and
microscopic structure**

Structure–Property Relationships

Connection between macroscopic properties and microscopic structure

Structure includes:

- Crystal structure (lattice type)
- Chemical structure (composition)
- Electronic structure (electron distribution)
- Microstructure (extended defects)
- Morphology (surfaces and terminations)

Structure–Property Relationships

Connection between macroscopic properties and microscopic structure

Property includes:

- Mechanical (e.g. bulk modulus)
- Electrical (e.g. conductivity)
- Magnetic (e.g. Curie temperature)
- Optical (e.g. band gap)
- Thermal (e.g. thermal expansion)

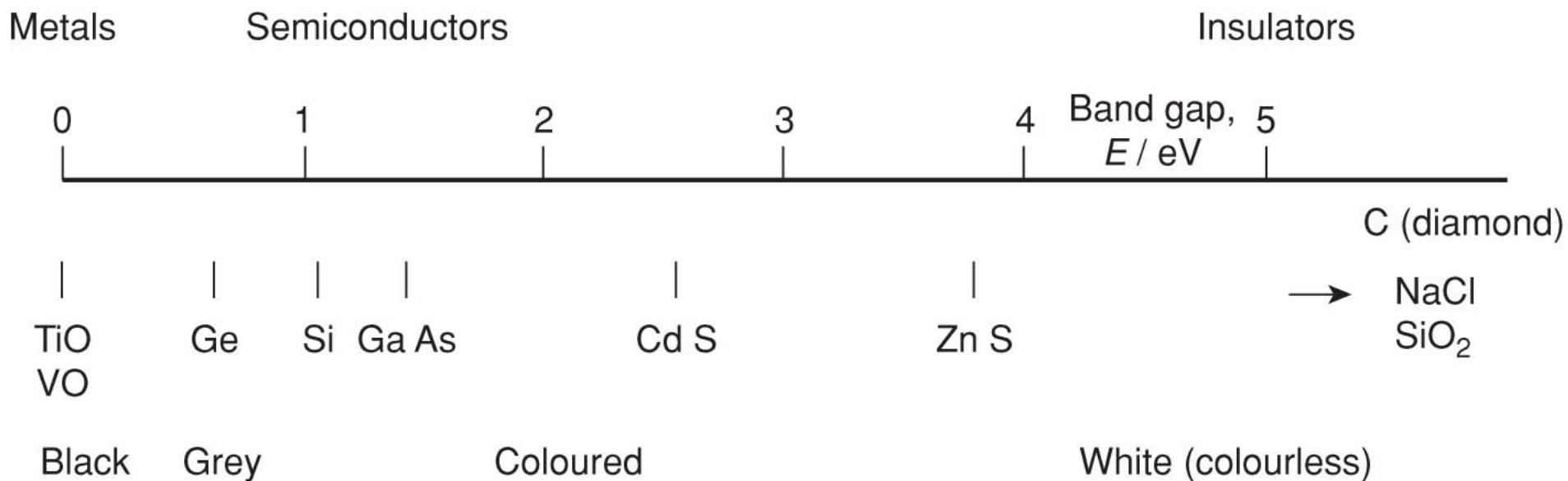
Structure–Property Relationships

Connection between macroscopic properties and microscopic structure

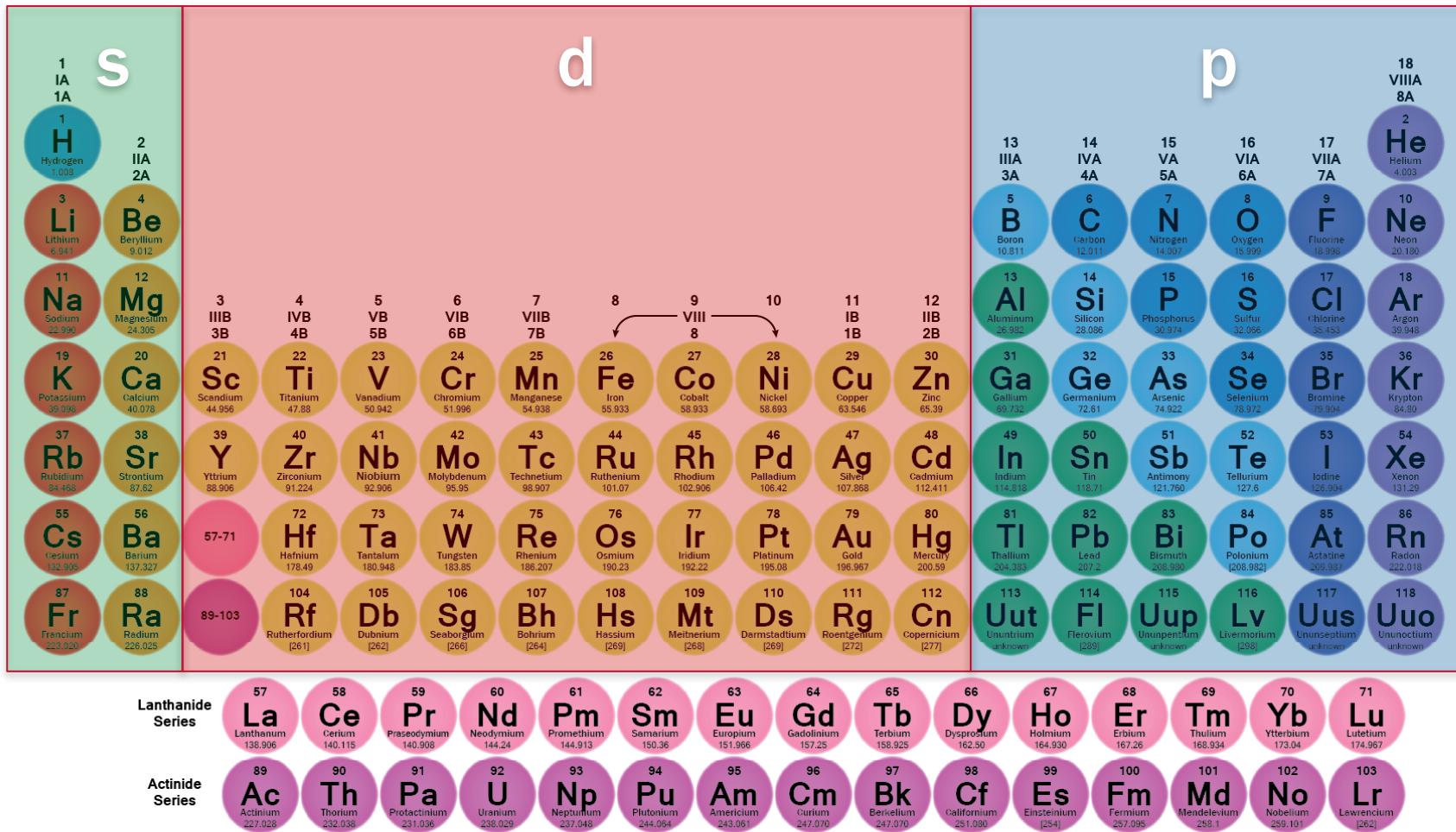
Categories of **property** include:

- Equilibrium (e.g. in thermal equilibrium)
- Steady-state (e.g. under constant illumination)
- Hysteretic (difference in stimulus ↑ and ↓)
- Irreversible (a permanent change)

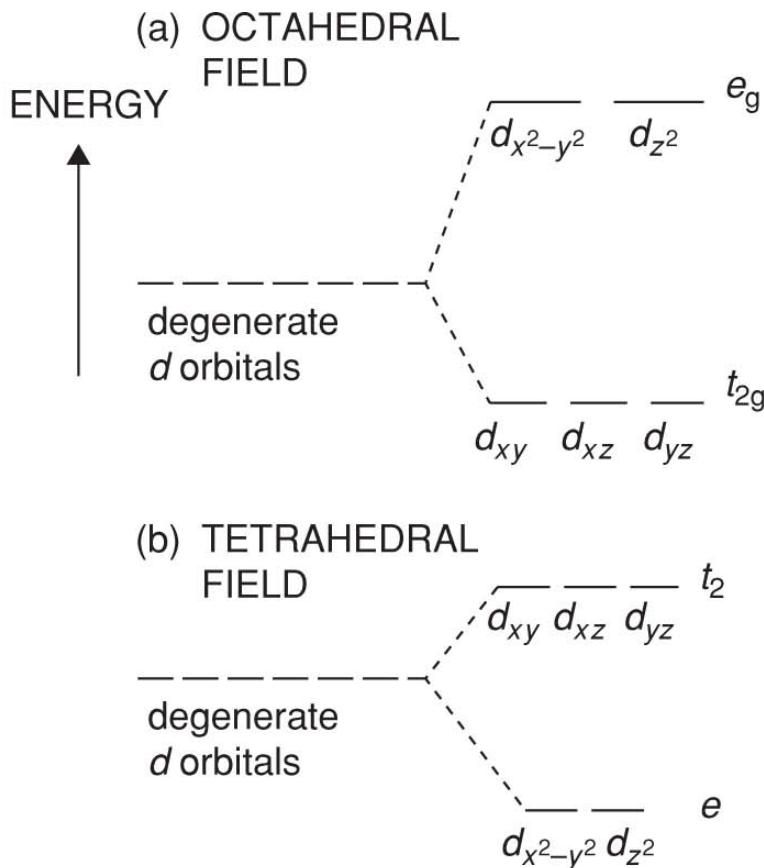
Band Gap Engineering



Valence Electronic Configuration



Transition Metal Compounds



4 Step Electronic Structure

1. Determine oxidation state
2. Count d electrons
3. Environment for d splitting
4. Fill in the electrons

Quick insights into structural
distortions, magnetic and
optical properties

Transition Metal Compounds

Low energy d-d optical transitions below the electronic band gap

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INSULATING OXIDES

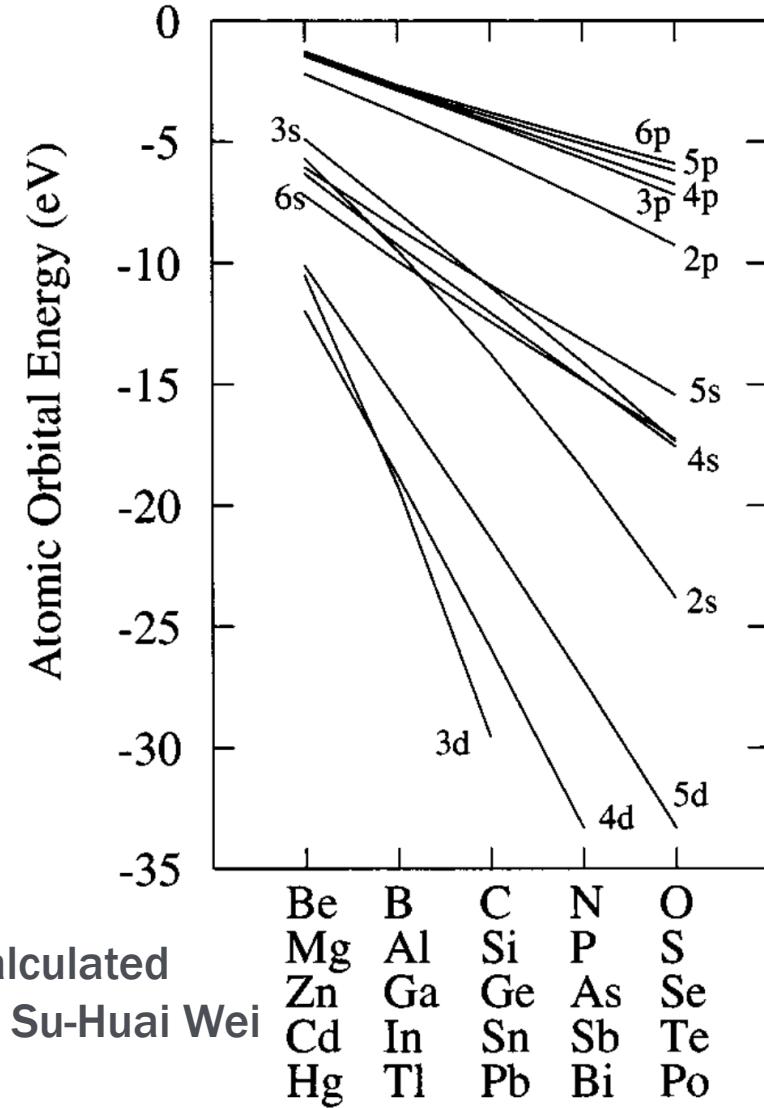
Table 3.6 *Properties of some magnetic insulators^a*

Compound	Band gap (eV)	<i>d</i> – <i>d</i> transitions (eV)	Magnetic properties ^b		
			S	Θ (K)	T_N (K)
Binaries					
Cr ₂ O ₃	3.3	2.1, 2.6	$\frac{3}{2}$	–550	308
MnO	3.6	2.2, 2.9, 3.5	$\frac{5}{2}$	–417	118
MnO ₂	–	–	$\frac{3}{2}$	–1000	92
FeO	2.4	1.2	2	–500	198
α -Fe ₂ O ₃	1.9	1.4, 2.1, 2.6, 2.9	$\frac{5}{2}$	–3000	950 ^c
CoO	2.6	1.1, (2.0), 2.3	$\frac{3}{2}$	–300	292
NiO	3.8	1.1, 1.8, 3.2	1	–2000	523
CuO	1.4	None (?)	$\frac{1}{2}$	–	226

Detrimental for
solar energy
conversion

Why?

Trends in Atomic Energy Levels



“Band energies are not so far away from neutral atom energies”

P. A. Cox (pg 50)

Useful for understanding trends in band gaps, band offsets, and impurity levels

Frontier Crystalline Orbitals

Cation: metal that donates charge, e.g. Mg, Ca, Sr

Anion: higher electronegativity element that accepts charge, e.g. O, Se, Se, Te

Common Electronic Structure

Upper valence band: anion (e.g. O 2p in ZnO)

Lower conduction band: cation (e.g. Zn 4s in ZnO)

Compositional Engineering

Conduction Band

Sensitive to binding energy of cation s orbitals, e.g.



Increase binding energy + decrease band gap

Valence Band

Sensitive to binding energy of anion p orbitals, e.g.



Decrease binding energy + decrease band gap

Compositional Engineering

Al_2O_3 ($E_g = 8.8 \text{ eV}$), Al_2Se_3 ($E_g = 3.1 \text{ eV}$)

In_2O_3 ($E_g = 2.9 \text{ eV}$), In_2Te_3 ($E_g = 1.0 \text{ eV}$)

Group 13 Chalcogenides

Lattice changes can alter expected trends

	Chalcogenide				
	O	S	Se	Te	
Metal	Al	Al_2O_3 corundum 5.9 eV	Al_2S_3 d-wurtzite 2.8 eV	Al_2Se_3 d-wurtzite 1.8 eV	Al_2Te_3 layered 1.0 eV
	Ga	Ga_2O_3 monoclinic 2.0 eV	Ga_2S_3 d-wurtzite 1.7 eV	Ga_2Se_3 d-zincblende 1.0 eV	Ga_2Te_3 d-zincblende 0.6 eV
	In	In_2O_3 bixbyite 0.9 eV	In_2S_3 monoclinic 1.1 eV	In_2Se_3 hexagonal 1.0 eV	In_2Te_3 cubic 0 eV

Cation Electronic Configuration

Pre-transition metals

Hard ions – s^0 , e.g. Mg(II), Ca(II)

Transition metals

Sensitive to electron count – d^n

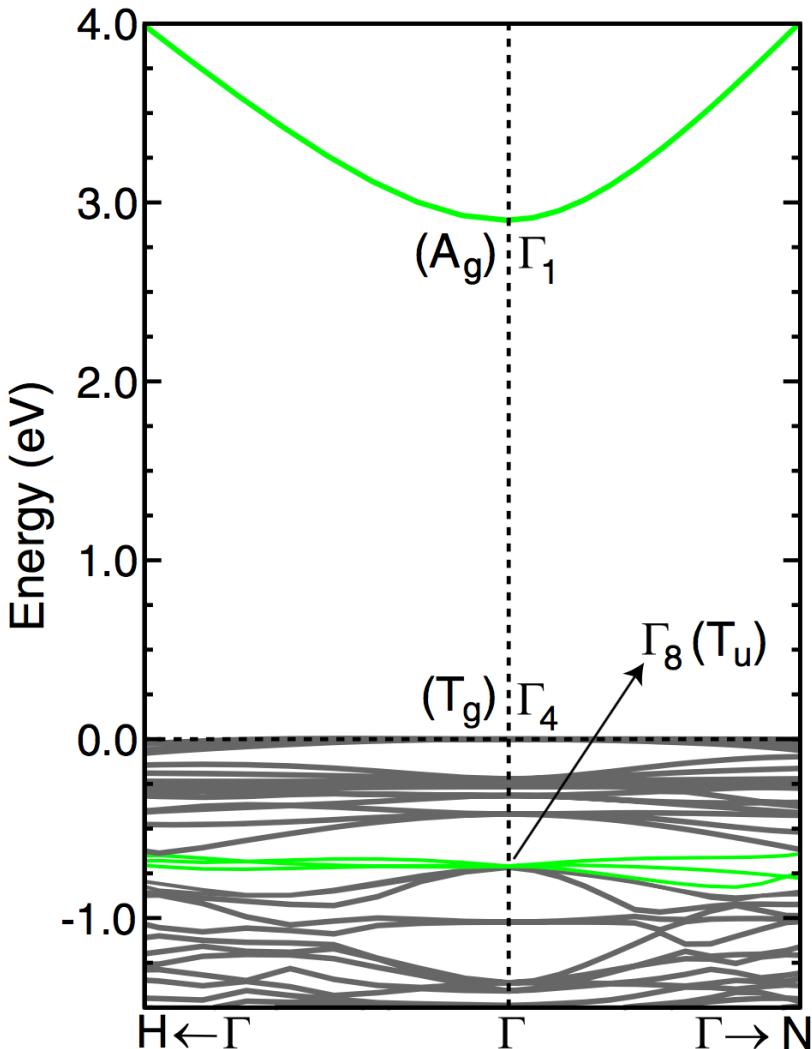
e.g. d^5 Fe(III) very different to d^6 Fe(II)

Post-transition metals

Soft ions with mixed behaviour – s^0 and p^0

e.g. s^0 for In(III) and p^0 for Pb(II)

Cation Electronic Configuration



Delocalised conduction band (In s)

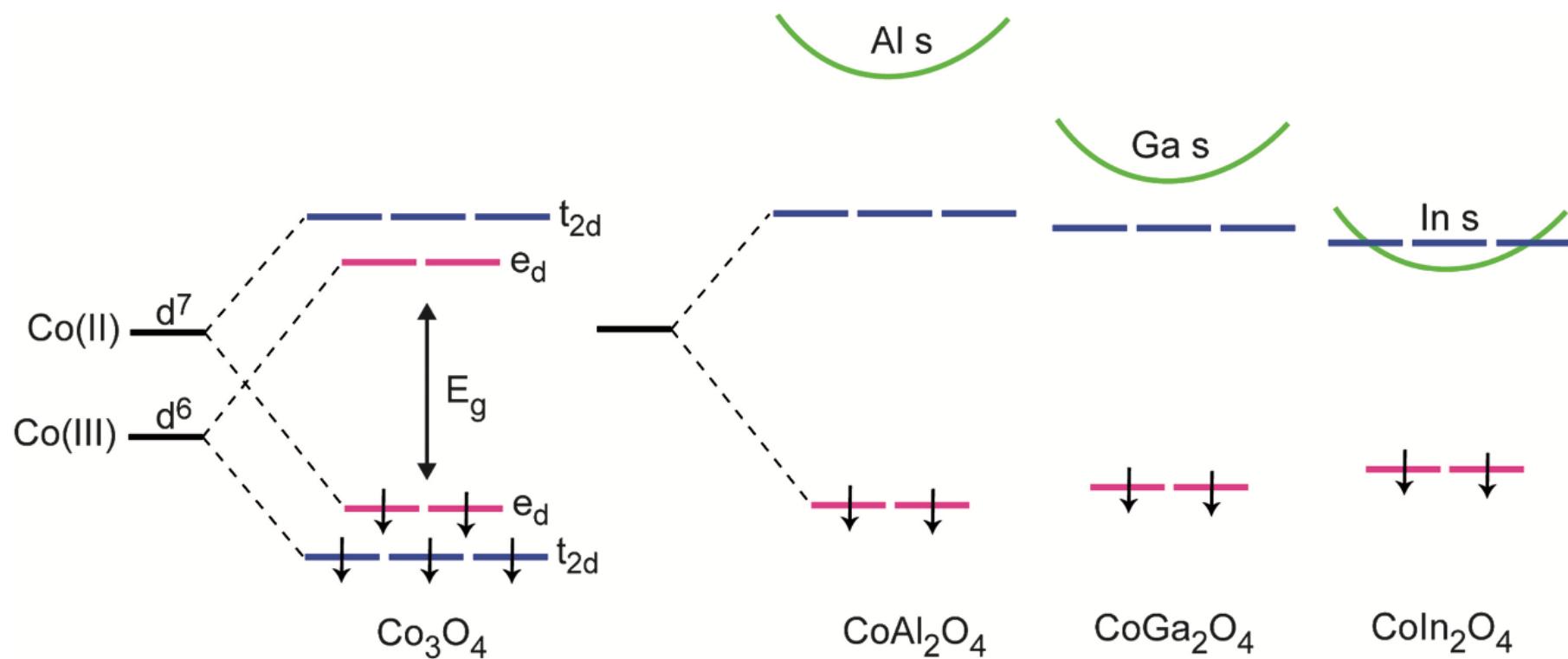
Band structure of In_2O_3

Physical Review Letters 100, 167402 (2008)

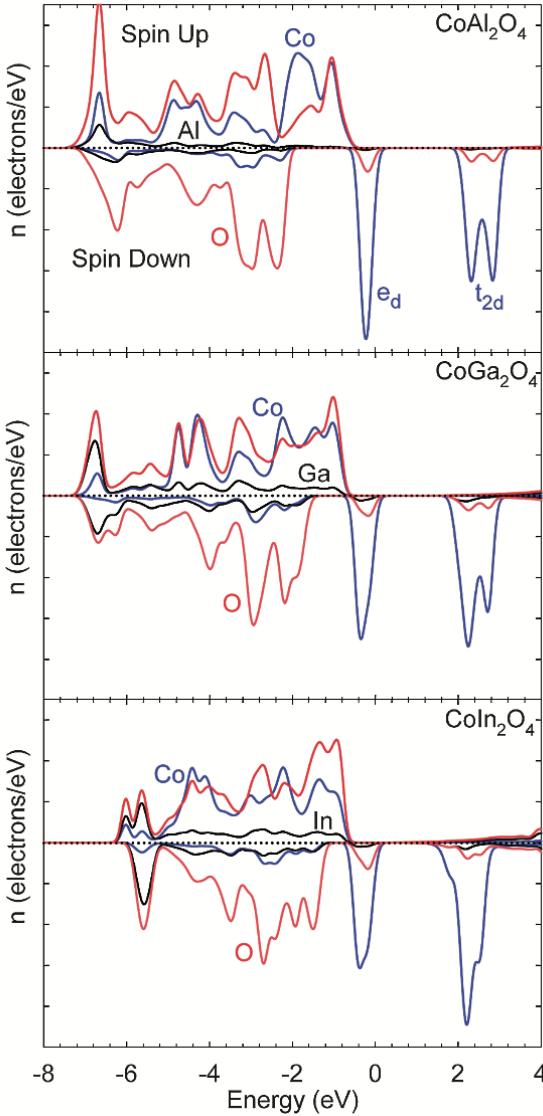
Localised valence band (O p)

Cation Electronic Configuration

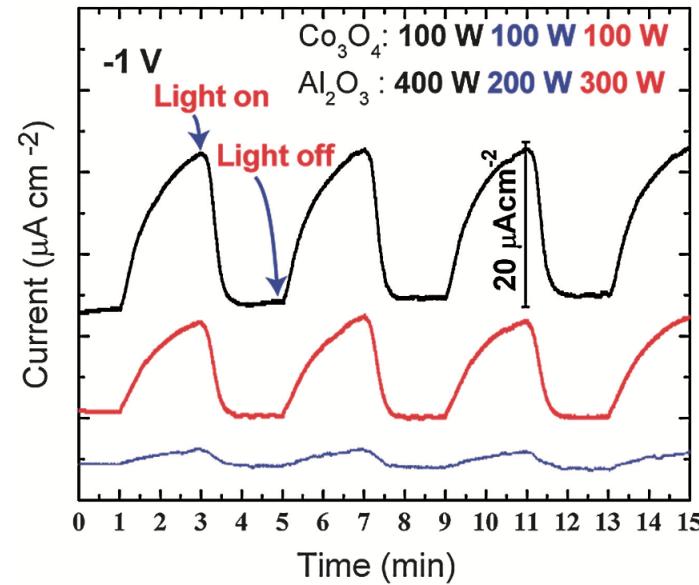
Band structure trends in CoX_2O_4 spinel oxides



Cation Electronic Configuration



Calculated electronic
density of states



Measured photoresponse
(co-sputtered thin films)

Valence Band *Active* Cations

In some cases, the cation influences the valence band, helping to tune conductivity / band gap

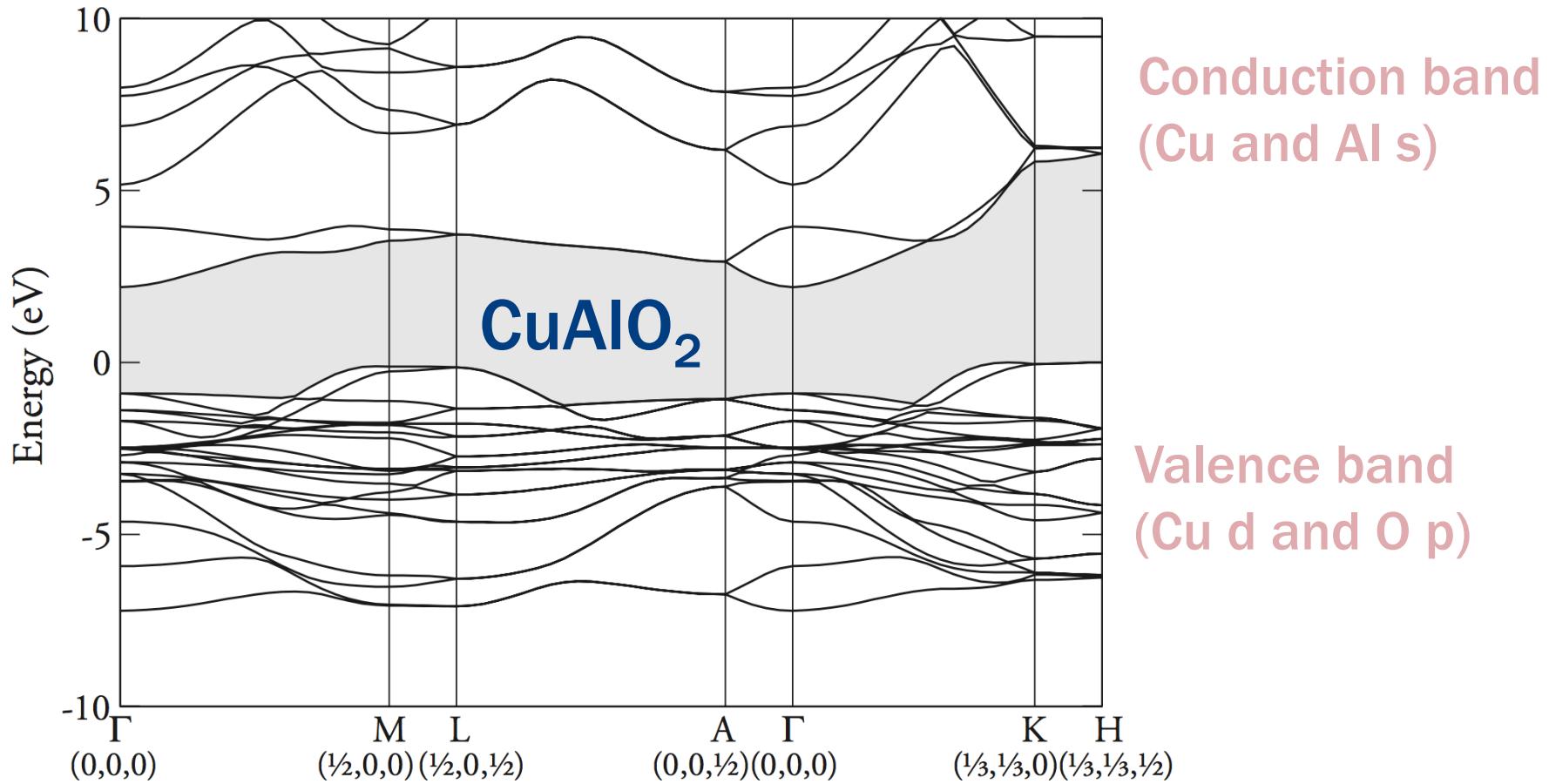
d¹⁰ configuration

Low binding energy d band couples with anion p
e.g. Ag(I) and Cu(I)

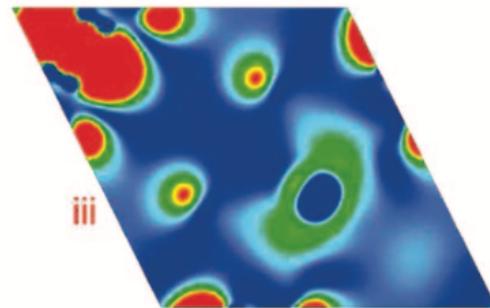
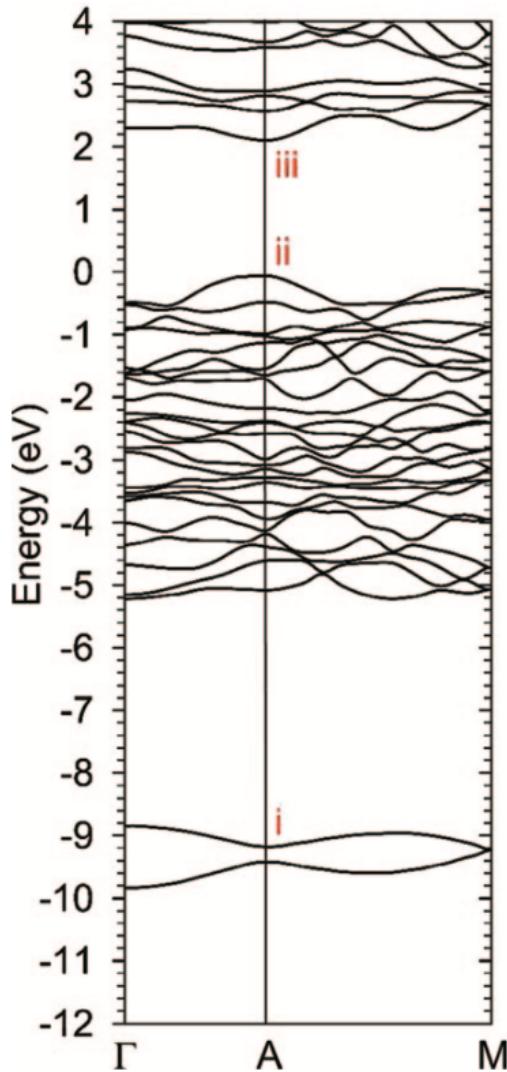
s² configuration

Low binding energy s band couples with anion p
e.g. Sn(II), Pb(II), Sb(III), Bi(III)

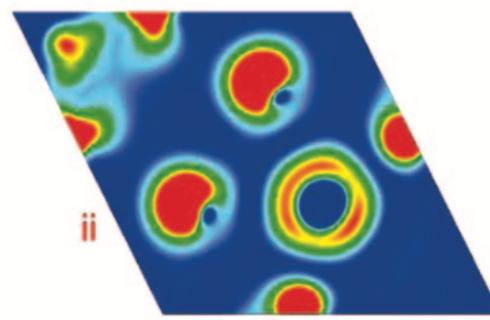
Valence Band *Active* Cations



Valence Band *Active* Cations



Conduction band
(V d and Bi p)

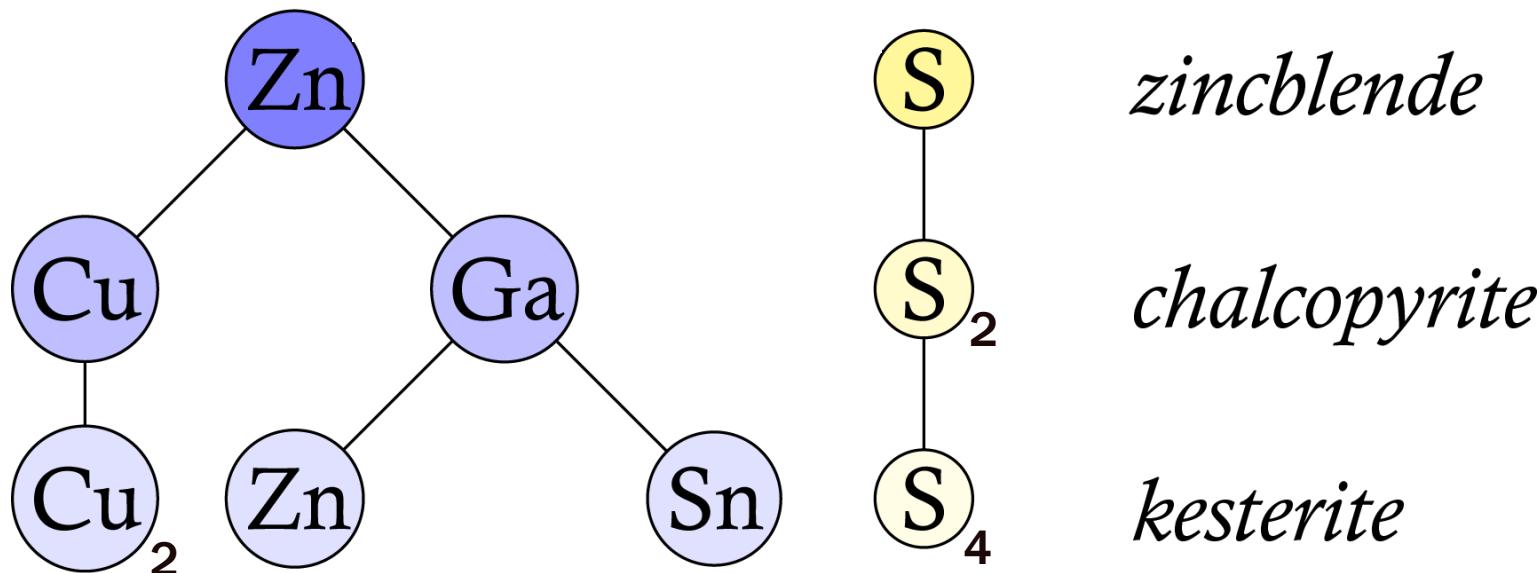


Valence band
(O p and Bi s)

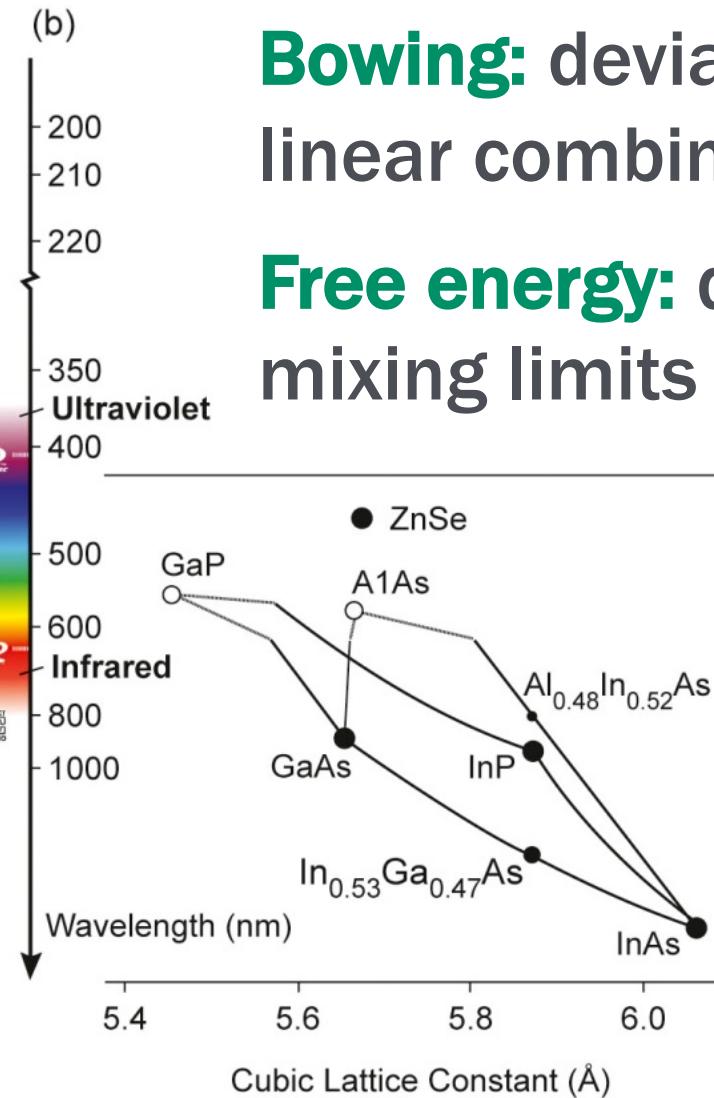
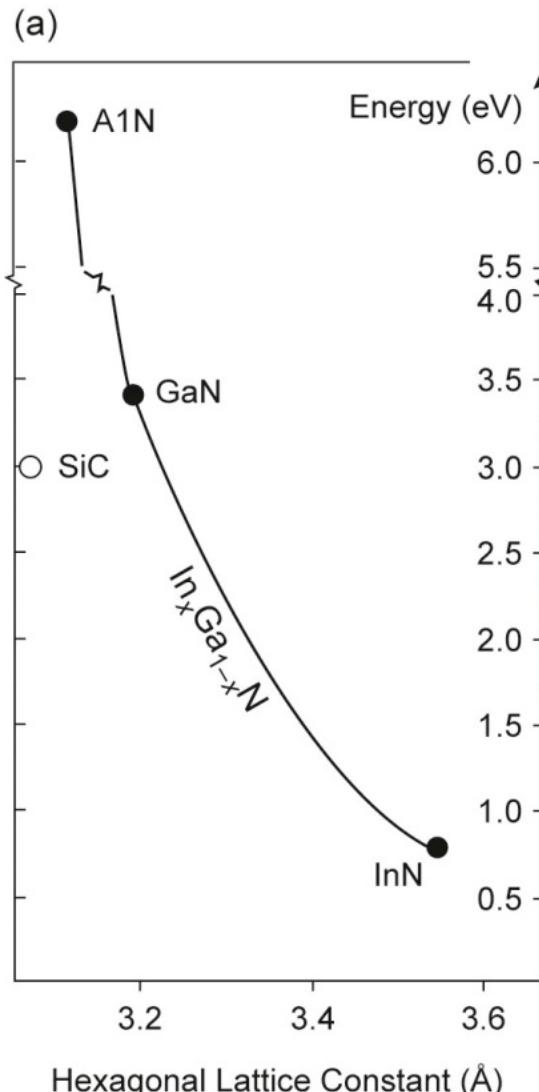
BiVO_4

Class Question

Expected band gap trend?



Alloys: Mix Two or More Elements



Bowing: deviation from linear combination of A+B

Free energy: determines mixing limits

Summary – Key Points

- Band structure and band gaps are determined by chemical bonding
- Chemical bonding can be understood from the electronic configuration of the atoms used to form the solid
- Band gaps can be engineered by chemical substitutions