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Electronic Structure of Materials

Lecture 7

Ionic vs. Covalent Bonding

Ionic Radii

Lattice Enthalpy

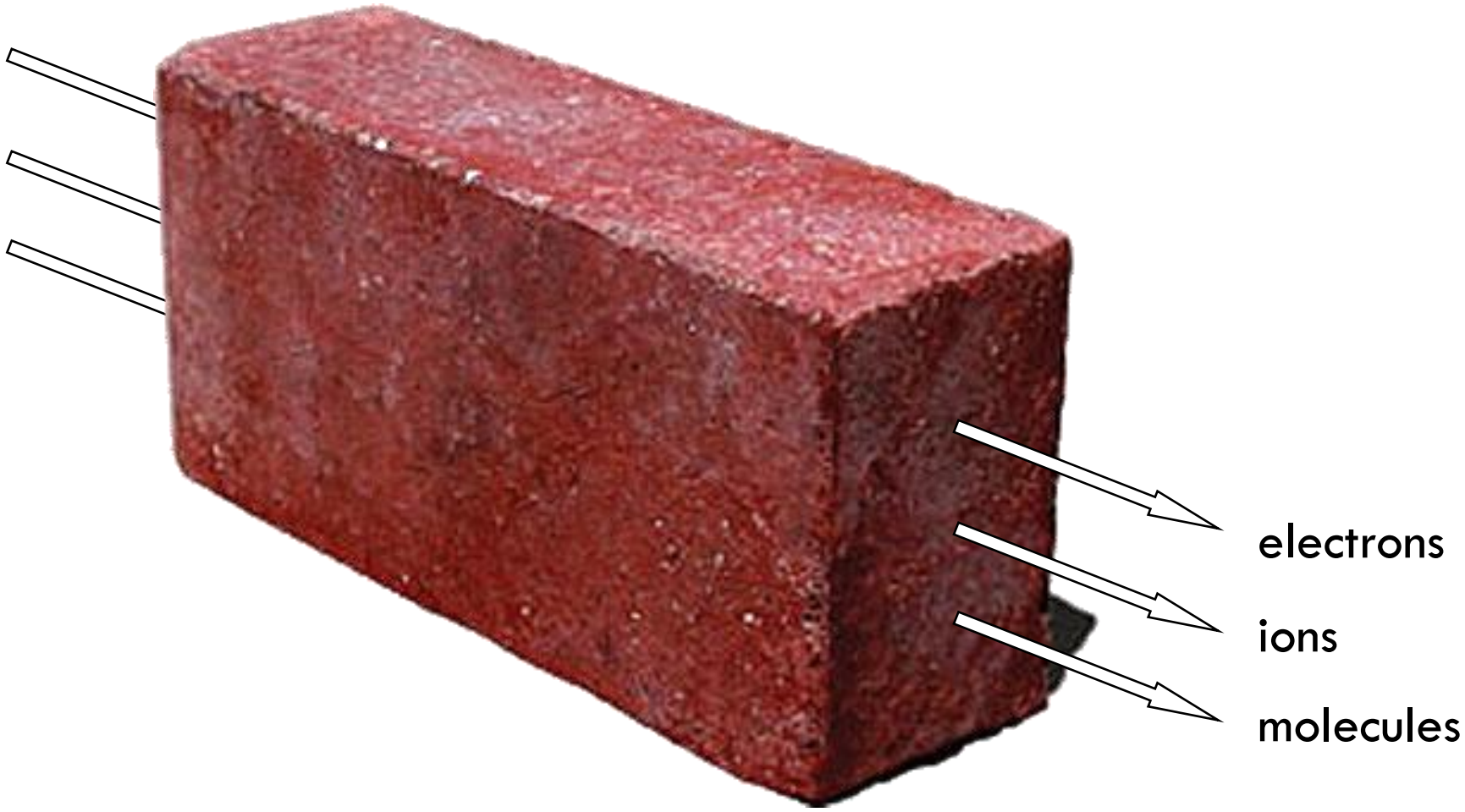
Lecture 8

Electronic Structure of Materials

Lecture 9

Electronic Properties of Materials

Transport in Materials



Classification of Charge-Conducting Materials

Conduction of Charge Through a Material

Electronic

Ionic

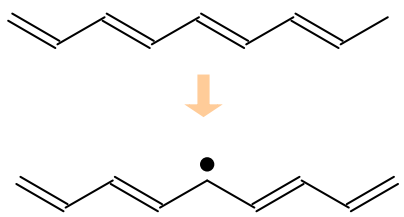
- Ion-exchange in porous materials & intercalates
- Ionic conduction
  - E.g., solid battery electrolytes like Na β-alumina
  - E.g., battery electrodes

Delocalised

- Metals: Cu, Na, Fe, …
- Semiconductors: Si, Ge, …
- Graphite, C_8K, …
- TiS_2, …
- A_3C_{60}, …

Localised

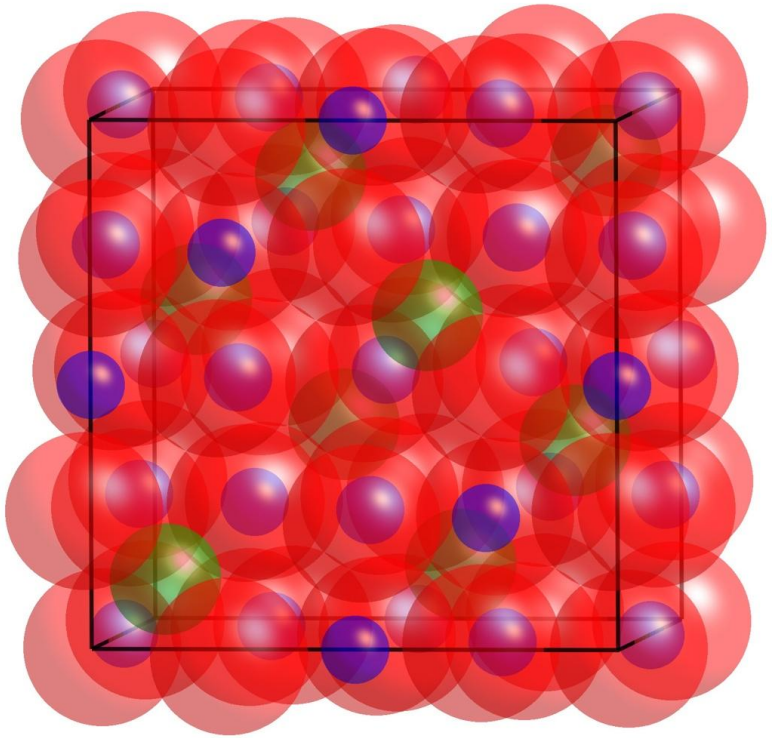
- Doped polymers



Outline

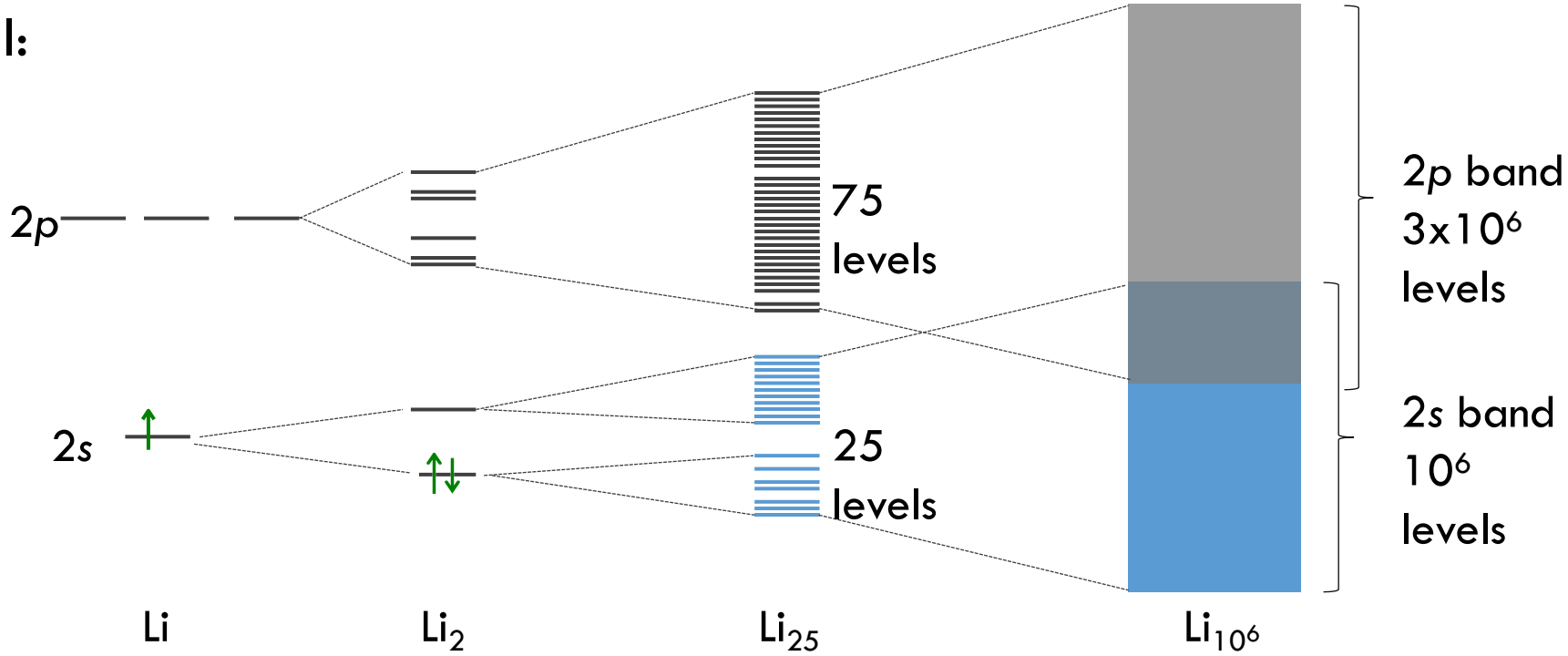
Electronic Structure of Solids

- Band structures
- 1-D , 2-D and 3-D conductors
- Electron localisation (Mott-Hubbard insulators)



The Tight-Binding Approximation

As we increase the number of atoms, the number of molecular orbitals increases.
In a crystal, with a very large number of atoms, these form a continuum of orbitals, called a **band**.
The band of occupied orbitals is called the **valence band**.
The band of unoccupied orbitals is called the **conduction band**.
E.g., for Li metal:

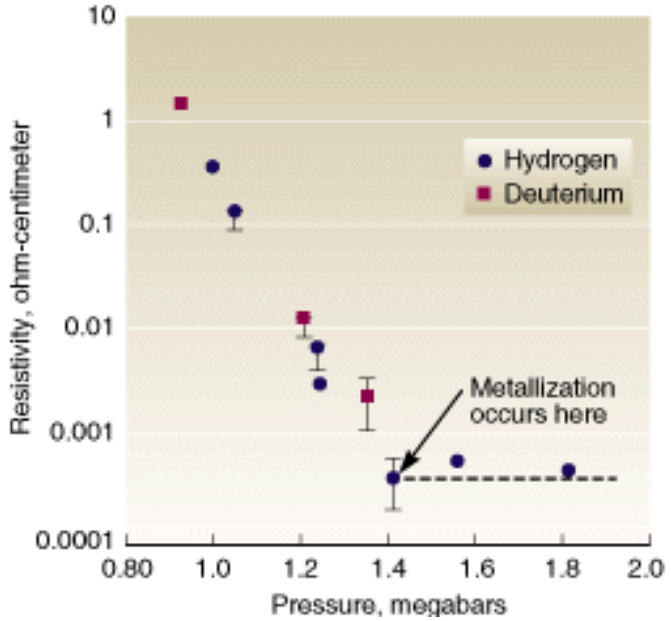


From Orbitals to Bands: Effect on Properties

Application of enormous pressures converts hydrogen from

gas → semiconducting liquid → metal

which influences its properties (e.g., resistivity) and has helped to understand many phenomena (e.g., Jupiter's magnetic properties)



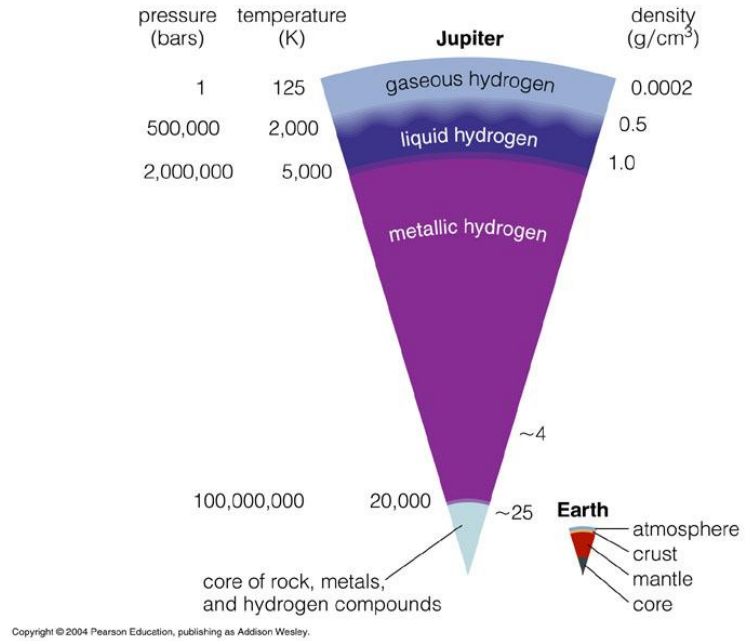
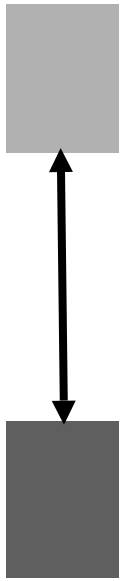


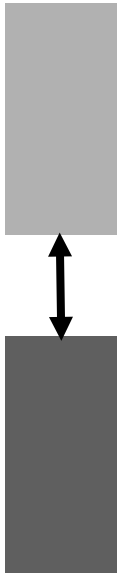
Figure from Silberberg "Chemistry: The Molecular Nature of Matter and Change"

Conductivity of Solids



Insulator

Large band gap – electrons cannot be promoted to conduction band



Intrinsic semiconductor

Electrons can be promoted from valence to conduction band upon heating



Metal

No band gap

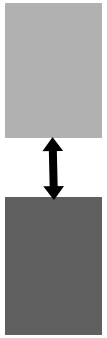
Band Structures

Metals: When a band is not completely full the electrons close to the Fermi level can easily be promoted to near by empty levels. The electrons can move freely through the solid, and the material is an **electrical conductor**.



Metal

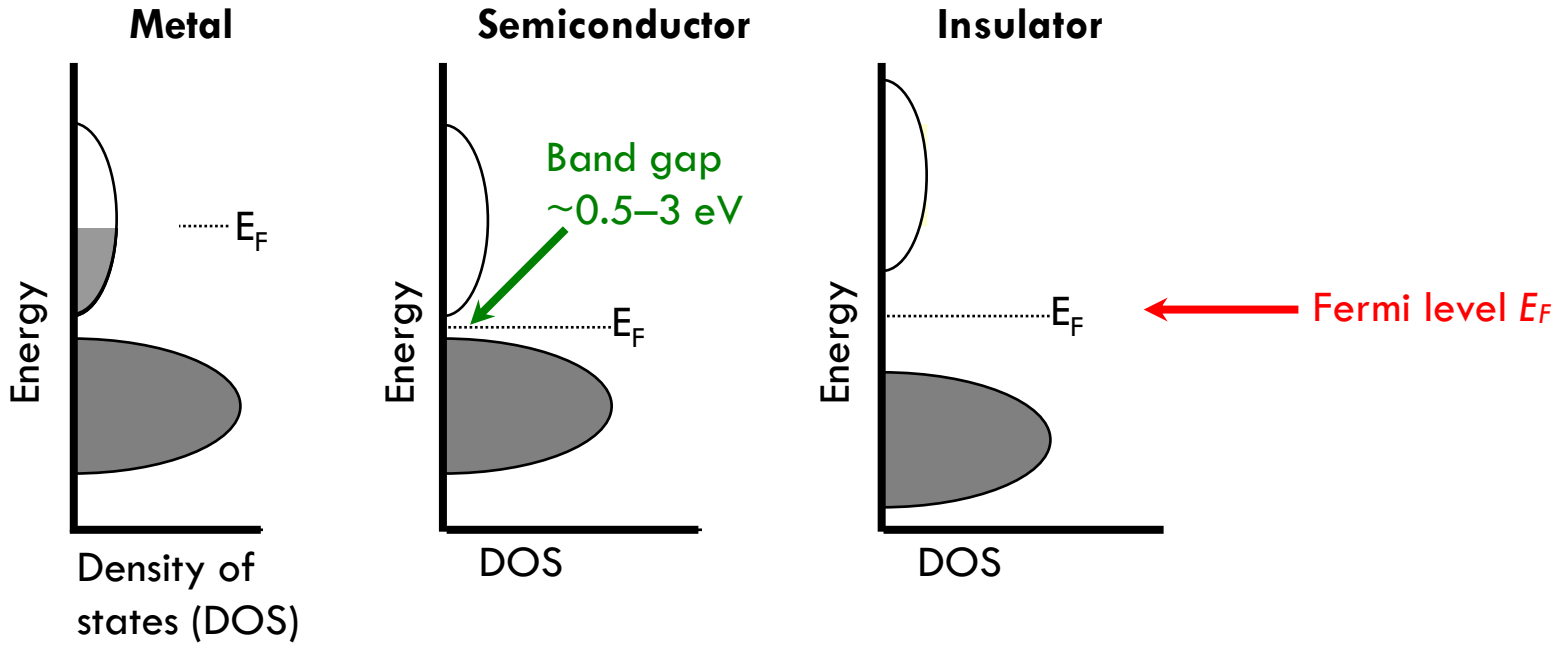
Semiconductors: When a band is filled but the band gap is sufficiently small (i.e., in the order of kT, where k is Boltzmann's constant) that thermal energy provides electrons with enough energy to populate the next band, the material is a semiconductor.



Intrinsic semiconductor

Band Structures

We can classify the electronic properties of materials according to their **band structures** and Fermi levels.



We can **manipulate the electronic properties** of materials by changing their band structures and Fermi levels.

Band Structures – Definitions

We can classify the electronic properties of materials according to their **band structures** and Fermi levels.

Density of states (DOS) is the number of permitted electronic states in an interval of energy (related to the number of orbitals at a specific energy)

Band gap is the energy difference between the highest occupied state in the valence band and the lowest unoccupied state in the conduction band.

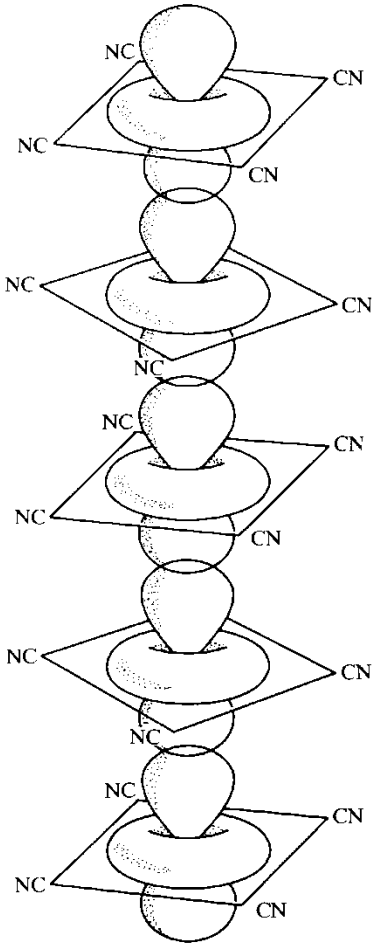
Fermi level (E_F) is the hypothetical electron energy at which the probability of occupation is 50 %

1-D Conductors

The Krogmann Salts, $K_2[Pt(CN)_4]X_x \cdot nH_2O$

Discovery:

In 1842, oxidation of $K_2[Pt(CN)_4]$ with chlorine or bromine vapour was found to give the crystals a metallic sheen. "The First Molecular Metal".



1-D Conductivity:

$\sigma_z \sim 300$ S cm^{-1} $\sigma_{x,y} \sim 10^{-3}$ S cm^{-1}

1-D Conductors

The Krogmann Salts, $K_2[Pt(CN)_4]X_x \cdot nH_2O$

Structure (1968):

$K_2[Pt(CN)_4]$ contains 1-D chains of face-to-face $[Pt(CN)_4]^{2-}$ units (eclipsed)

Oxidation of $K_2[Pt(CN)_4]$ with Cl_2 or Br_2:

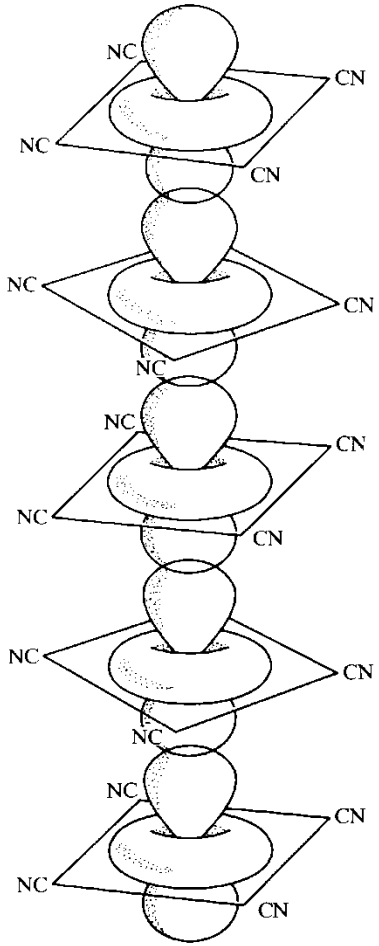
oxidation states

2(+1) +2 4(-1) 0 2(+1) +2.3 4(-1) 0.3(-1)

$$K_2[Pt(CN)_4].3H_2O + 0.15X_2 \longrightarrow K_2[Pt(CN)_4]X_{0.3}.3H_2O$$

The product, $K_2[Pt(CN)_4]X_{0.3}.3H_2O$ (X = Cl or Br), contains 1-D chains of face-to-face $[Pt(CN)_4]^{1.7-}$ units (staggered)

The change in Pt oxidation state alters the band structure, going from a filled valence band to a partially-filled band characteristic of a metal.

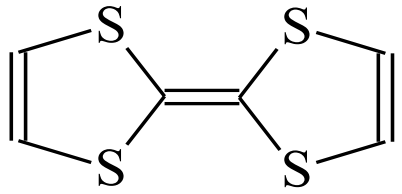


See Q7 in Tutorial 2 (week 4)

1-D Conductors

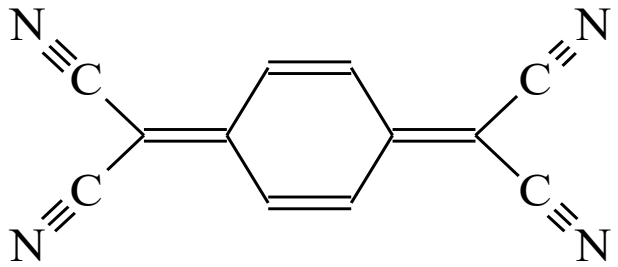
TTF-TCNQ: "The first organic metal" (1973)

Two insulating molecules can be combined to form a crystal structure (1-D chains running into the screen) that exhibits conductivity in 1-D.



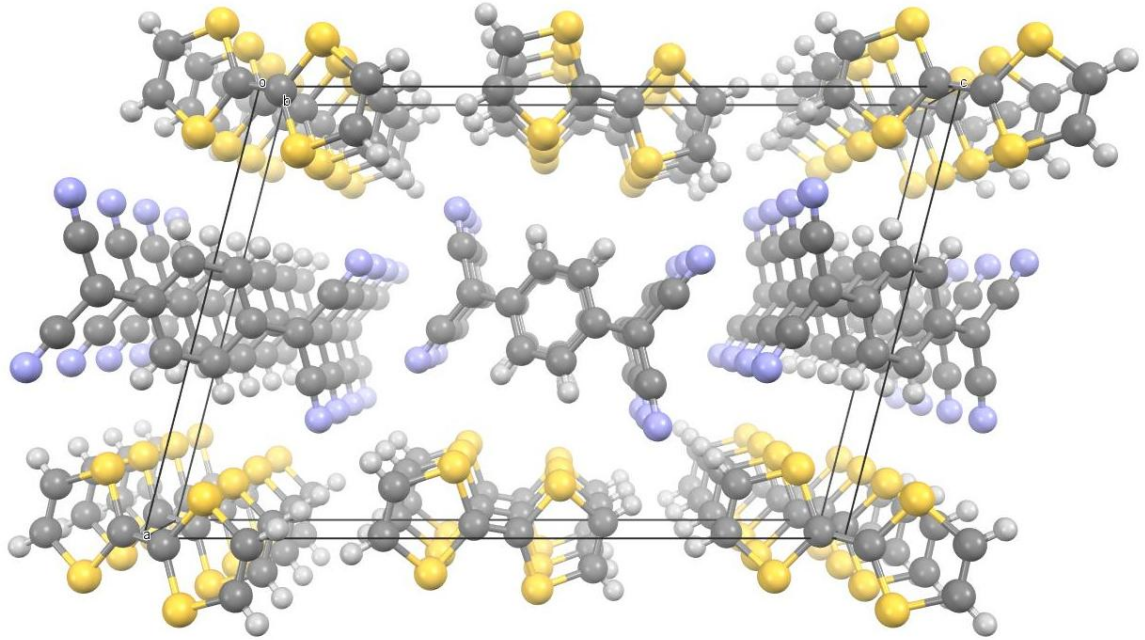
tetrathiafulvalene (TTF)

(a good electron donor)



7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ)

(a good electron acceptor)



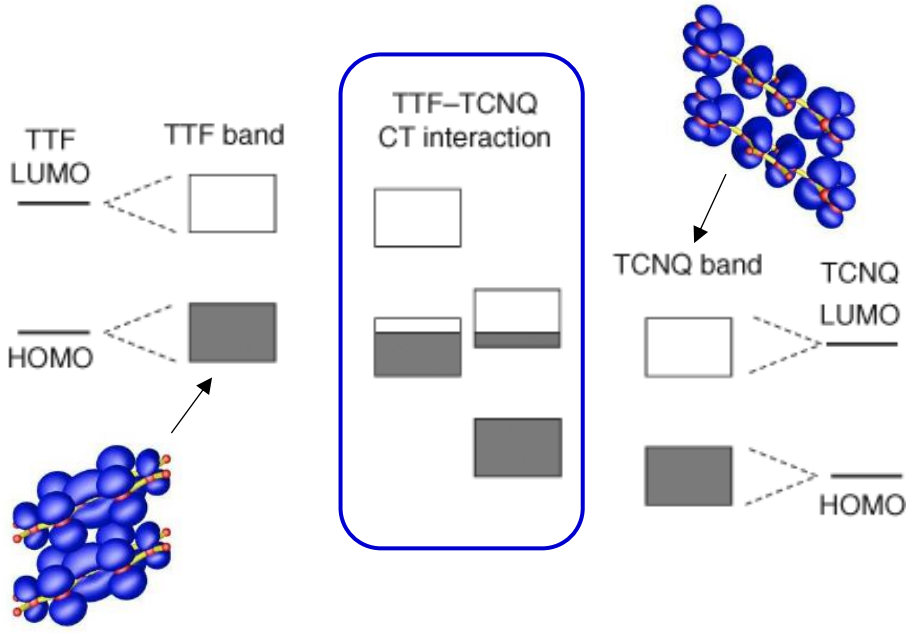
$(TTF)^{\delta+}(TCNQ)^{\delta-}$

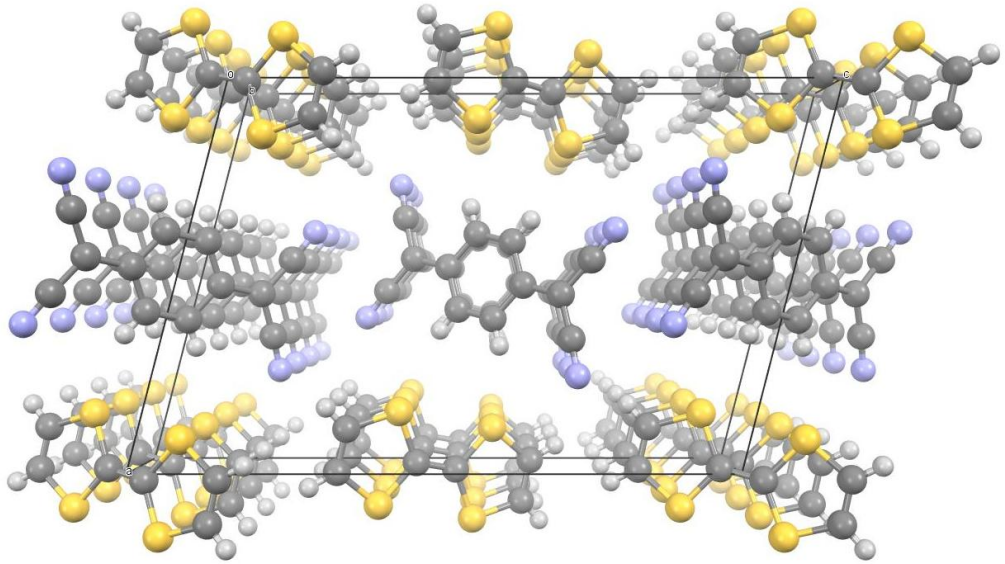
1-D Conductors

TTF-TCNQ: "The first organic metal" (1973)

Two insulating molecules can be combined to form a crystal structure (1-D chains running into the screen) that exhibits conductivity in 1-D.

Orbital overlap and charge transfer, from electron donator to electron acceptor, creates a partially-filled band and a band structure characteristic of a metal.





$(TTF)^{\delta+}(TCNQ)^{\delta-}$

2-D Conductors

Graphite

Ethene



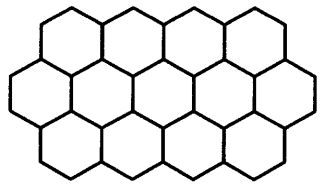
- Hybridised sp^2 orbitals make σ bonds
- Overlap of p_z orbitals makes a π bond that lies above and below the plane of the molecule

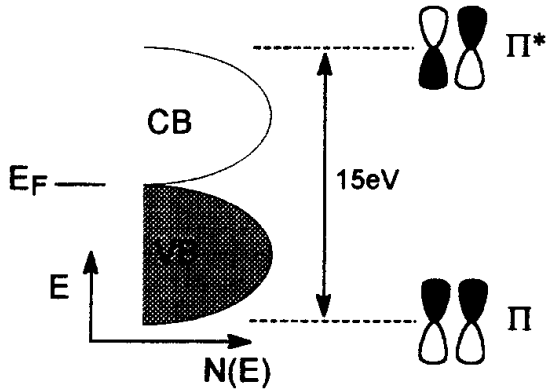
Benzene



- The π bonds create a continuous ring of electron density shared around the molecule

Graphite





- The overlap of orbitals creates a valence band and a conduction band
- Conductivity in 2-D in the carbon planes
- Graphite is a semi-metal: a small number of electrons are promoted into the conduction band by thermal energy

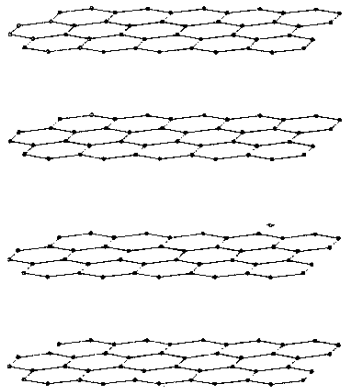
Figures from Weller "Inorganic Materials Chemistry"

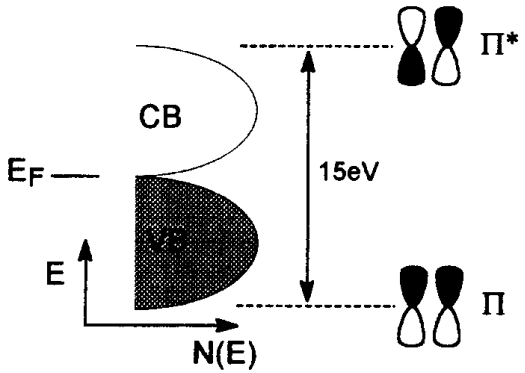
2-D Conductors

Graphite and Intercalation

Graphite

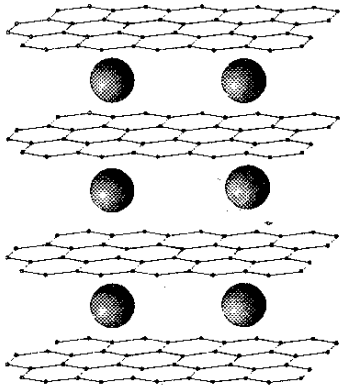
- Semi-metal
- $\sigma_{x,y}$ ~ 20,000 S cm^{-1}
- σ_z ~ 200 S cm^{-1}

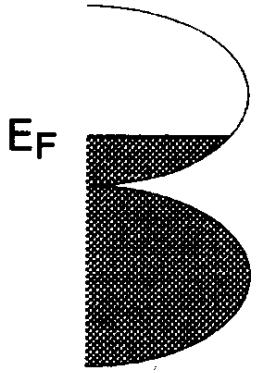




Intercalation of K into graphite, KC_8

- Metal
- $\sigma_{x,y}$ ~ 1,000,000 S cm^{-1}
- Charge transfer, from K to the carbon sheet, creates a partially-filled band and a band structure characteristic of a metal

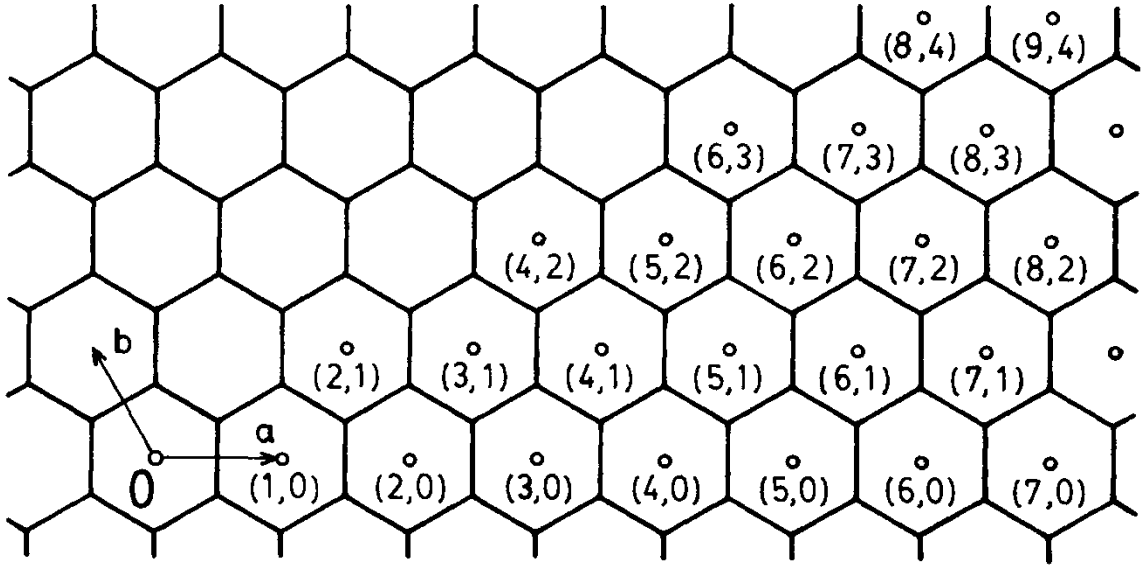




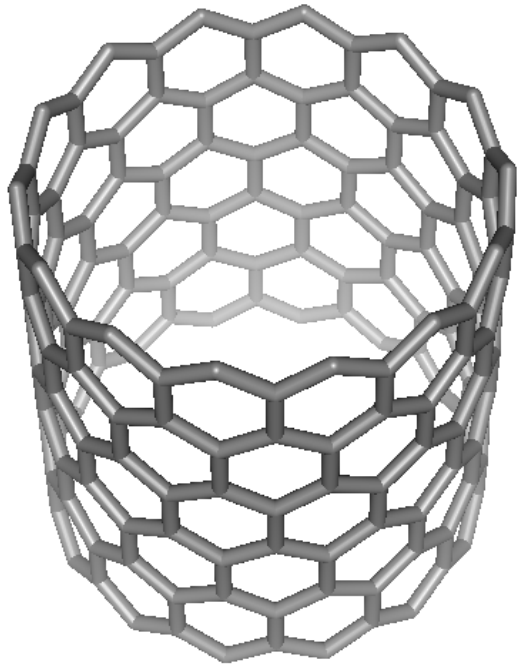
Figures from Weller "Inorganic Materials Chemistry"

Carbon Nanotubes

Isomer classification of carbon nanotubes (CNTs)



The (a,b) naming scheme



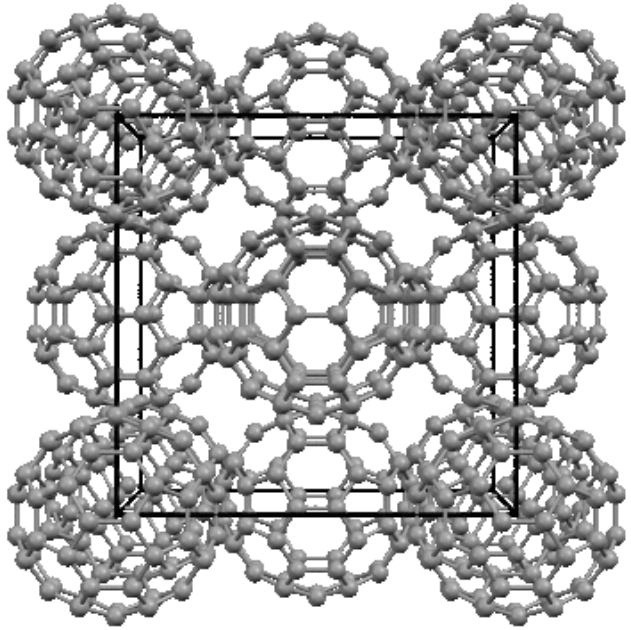
The (13,0) nanotube

The structure is linked to the electrical properties

The (a, b) nanotube behaves as a *metal* if a = b and a *quasi-metal* if (a – b) is a multiple of 3 and n ≠ m, with conductivity along the tubular axis. Otherwise, it behaves as a *semiconductor*.

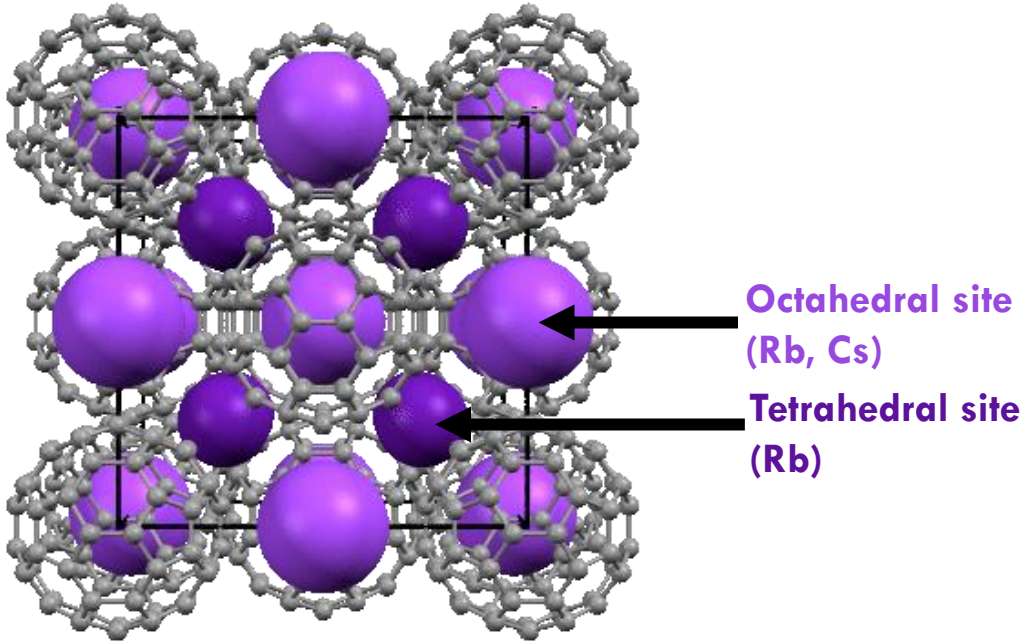
3-D Conductors

Fullerene Intercalation Compounds



350 °C

Rb, Cs



Buckminsterfullerene, C_{60}

a = 14.17 Å

Cubic space group $Fm\bar{3}$

Semiconductor

Band gap = 1.6 eV

Rb_2CsC_{60}

a = 14.43 Å

Cubic space group $Fm\bar{3}$

Metal with ½-filled t_{1u} band

Superconductor T_c = 31 K

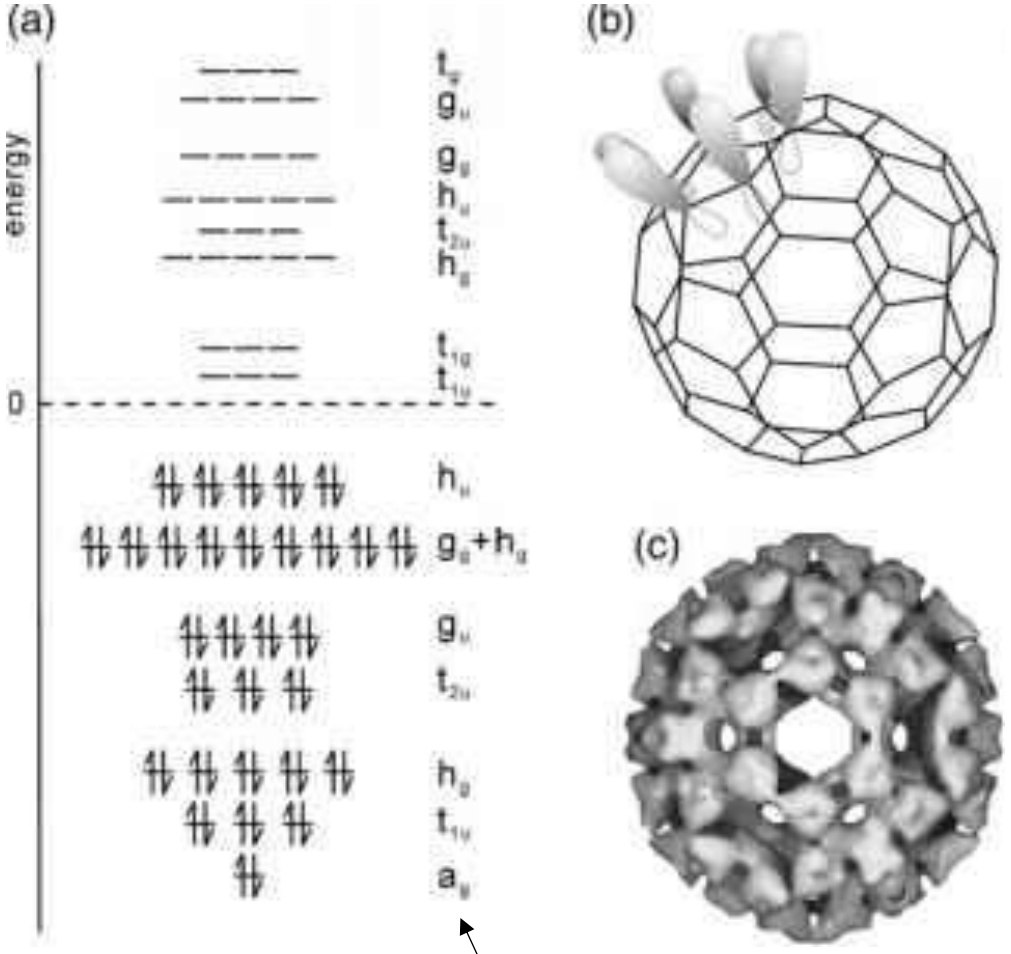
Molecular Orbitals of C_{60}

Consider an isolated C_{60} molecule:

C_{60} has 240 valence electrons (4 valence electrons × 60 carbon atoms) and 90 carbon-carbon bonds:

- 180 valence electrons fill 90 σ-bonding molecular orbitals (not shown)
- The remaining 60 electrons fill 30 π-bonding molecular orbitals (see (a))
- The HOMO (h_u) and LUMO (t_{1u}) are π-type molecular orbitals that project outwards (and inwards) (see (b), (c))

π-Type Molecular Orbitals of C_{60}

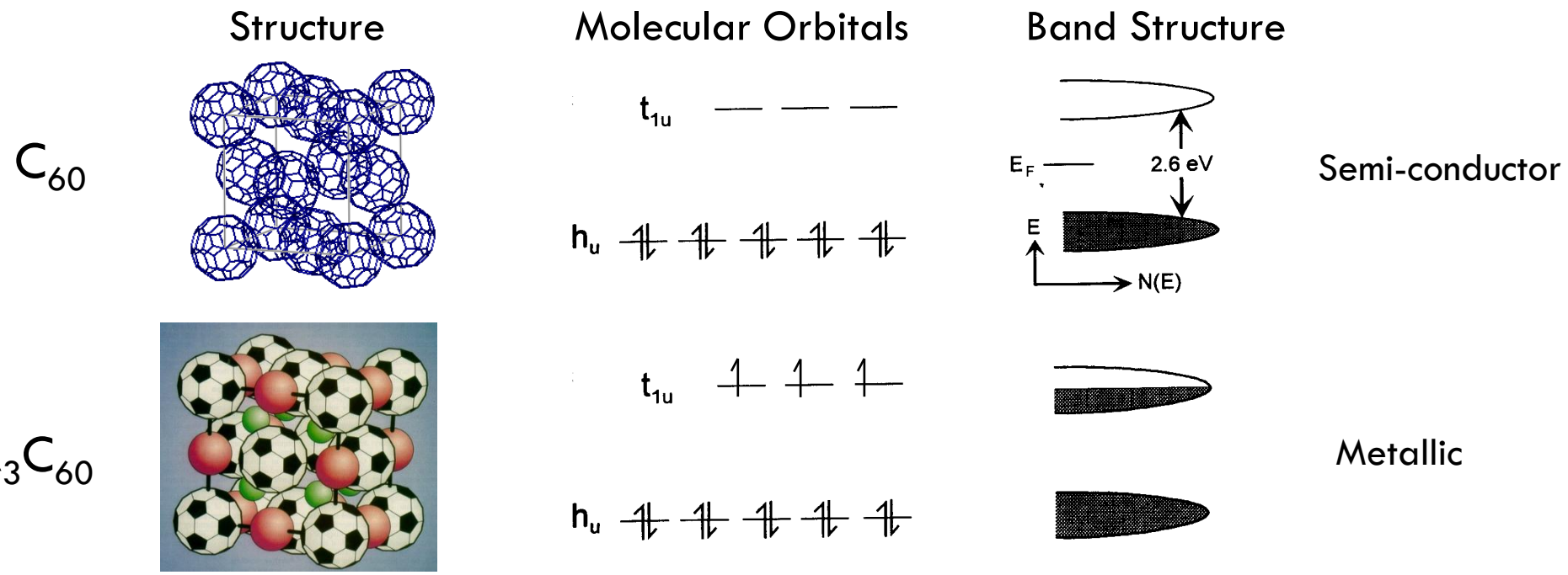


Symbols relate to symmetry (beyond our scope)

3-D Conductors

Fullerene Intercalation Compounds

In a crystal, the molecular orbitals that project outwards from a C_{60} molecule overlap with those of neighbouring C_{60} molecules, forming bands.



Charge transfer, from the host, A, to the C_{60} molecules, creates a partially-filled band and a band structure characteristic of a metal.

Superconductivity

Discovery

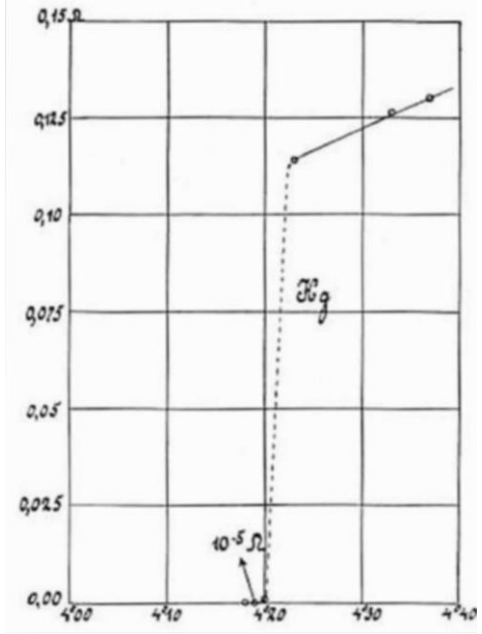
1908 July: At Leiden University, Netherlands, Heike Kamerlingh Onnes liquefies He (boiling point -269 °C, 4.2 K) by cooling to 1.5 K.

1911 April: Kamerlingh Onnes found that at 4.2 K the resistance of a solid Hg wire immersed in liquid He was reduced to zero. This was termed “superconductivity”.

1913: Lead and tin also found to be superconductors at 6 K and 4 K.

1913: Awarded Nobel Prize in Physics

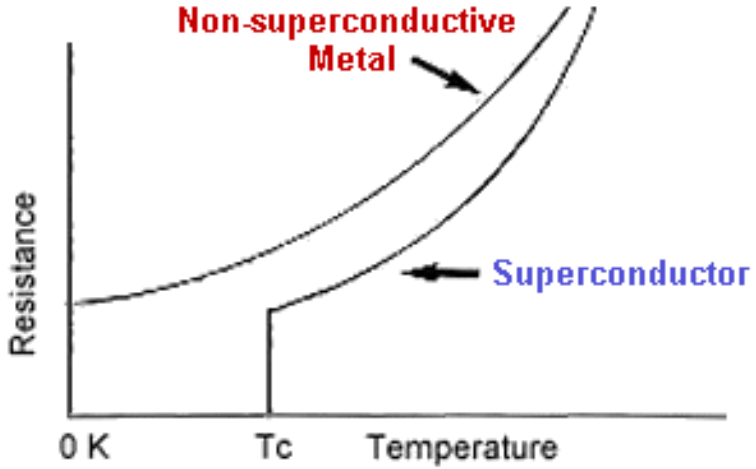
1914 January: Meissner Effect observed.



Superconductivity

Zero Resistance

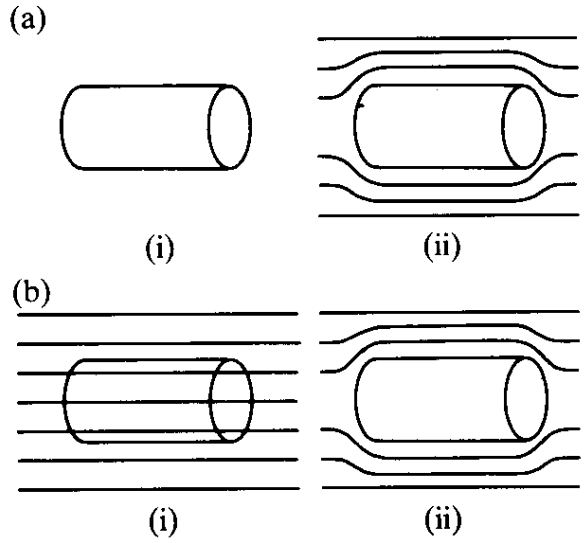
Below the critical temperature, T_c, the resistivity of superconductors is equal to zero.



Perfect Diamagnetism

Below the critical temperature, T_c, superconductors completely expel magnetic fields (see Figure a).

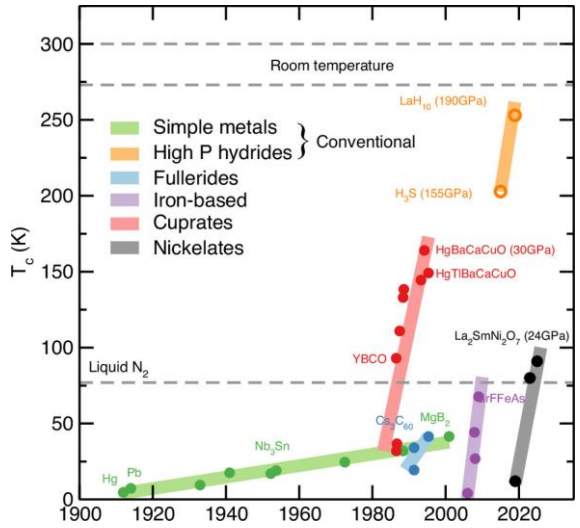
Meissner Effect: on cooling through T_c, magnetic fields are expelled (see Figure b).



The Quest for a Room Temperature Superconductor

The first (1911) reported superconducting material had a T_c of 4.2 K.
Current record (9 March 2026) for "high-temperature" superconductivity is 151 K (-122 °C), beating a record that stood for more than 30 years.

https://www.sciencedaily.com/releases/2026/05/260527023220.htm





https://www.pnas.org/doi/10.1073/pnas.2520324123

Claims of room temperature superconductivity have not stood up to testing.



https://www.science.org/content/article/short-spectacular-life-viral-room-temperature-superconductivity-claim
https://physicsworld.com/a/room-temperature-superconductor-lk-99-fails-replication-tests

BCS (Bardeen-Cooper-Schrieffer) Theory

Quantum mechanics is used to explain superconductivity as the formation of electron pairs (Cooper pairing) at low temperature, which flow through the lattice without scattering and zero resistance.

The critical temperature, T_c, can be determined by:

$$k_B T_c = \hbar\omega \exp\left(\frac{-1}{VN(E_f)}\right)$$

where

$N(E_f)$ is the density of states at the Fermi Energy

V is the attractive interaction strength of electrons

$\hbar\omega/k_B$ is the Debye temperature and represents collective or acoustic vibration shifts to an independent thermal vibration

BCS was proposed in 1957 and awarded the Nobel Prize in Physics in 1972.

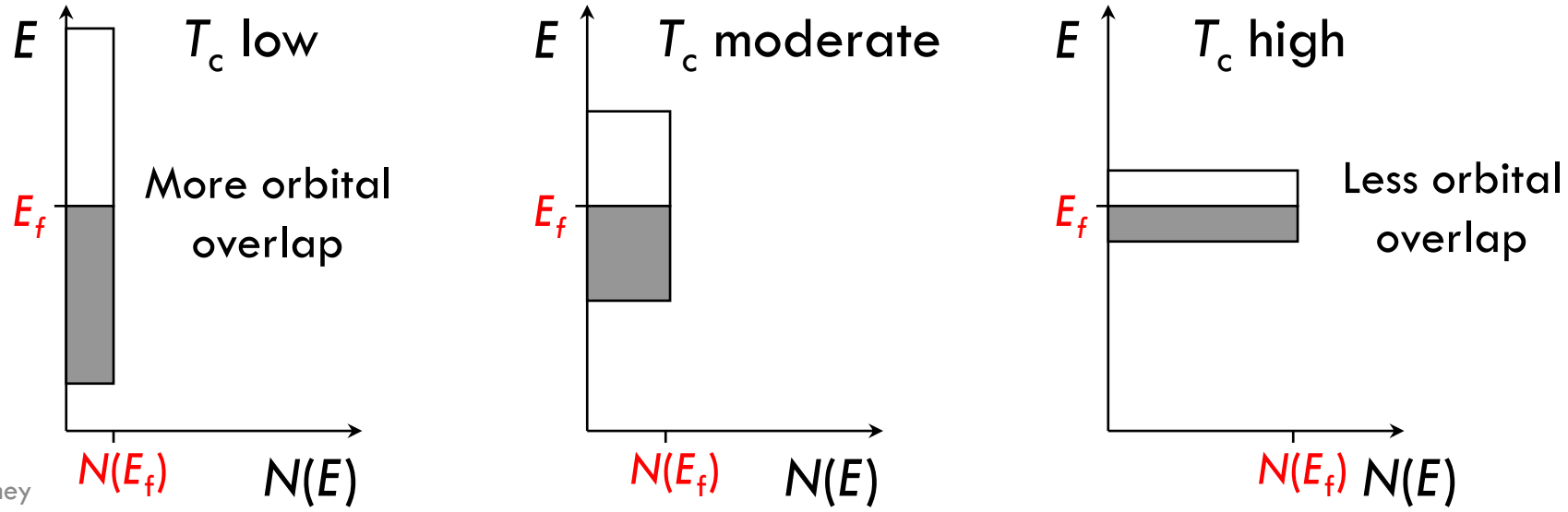
BCS (Bardeen-Cooper-Schrieffer) Theory

Tuning $N(E_f)$ chemically allows us to design new materials with desirable properties.

$N(E_f)$ is related to the **width of the band** in terms of energy (y-axis).

The width of the band is determined by the **orbital overlap**. More orbital overlap results in more **orbital splitting** (larger energy difference) and a wider band.

$$k_B T_c = \hbar\omega \exp\left(\frac{-1}{VN(E_f)}\right)$$



Superconductivity of Fullerene Intercalates

Large
~~Small~~ intercalating cations

⇓

far apart (large a)
C_{60} molecules ~~close together (small a)~~

⇓

Weak
~~Strong~~ overlap between C_{60} molecules

⇓

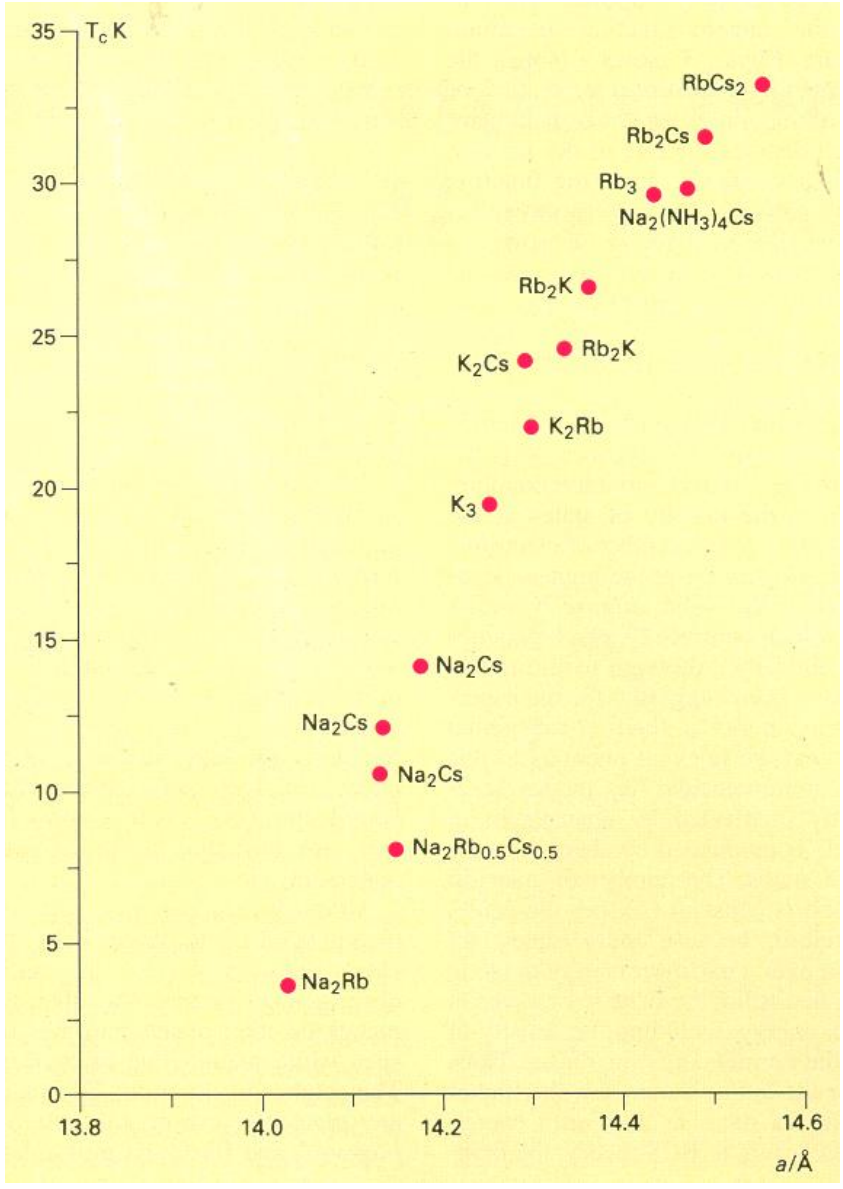
small
Band width ~~large~~

⇓

large
$N(E_f)$ ~~small~~

⇓

Higher
~~Lower~~ T_c



Mott-Hubbard Localisation

As atoms are moved further apart, the electronic band model breaks down, and electrons become localised on individual atoms/molecules.

Crystal Orbitals

(Band Conductor)

Mott-Hubbard ↕ transition

Atomic/Molecular Orbitals

(Mott-Hubbard Insulator)

The calculated band structure of sodium as a function of the Na–Na distance

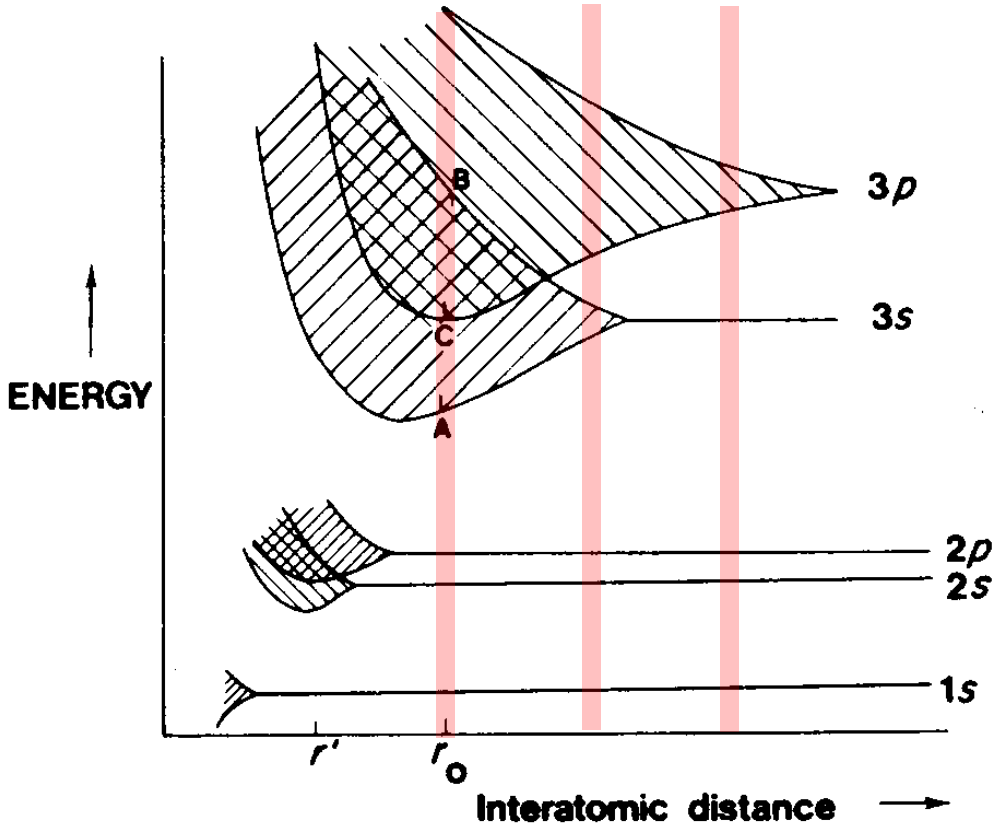


Figure from West "Basic Solid State Chemistry"

Superconductivity of Fullerene Intercalates

$(NH_3)_xA_3C_{60}$ Fullerene Intercalates

Intercalation of ammonia into the A_3C_{60} phases

⇩

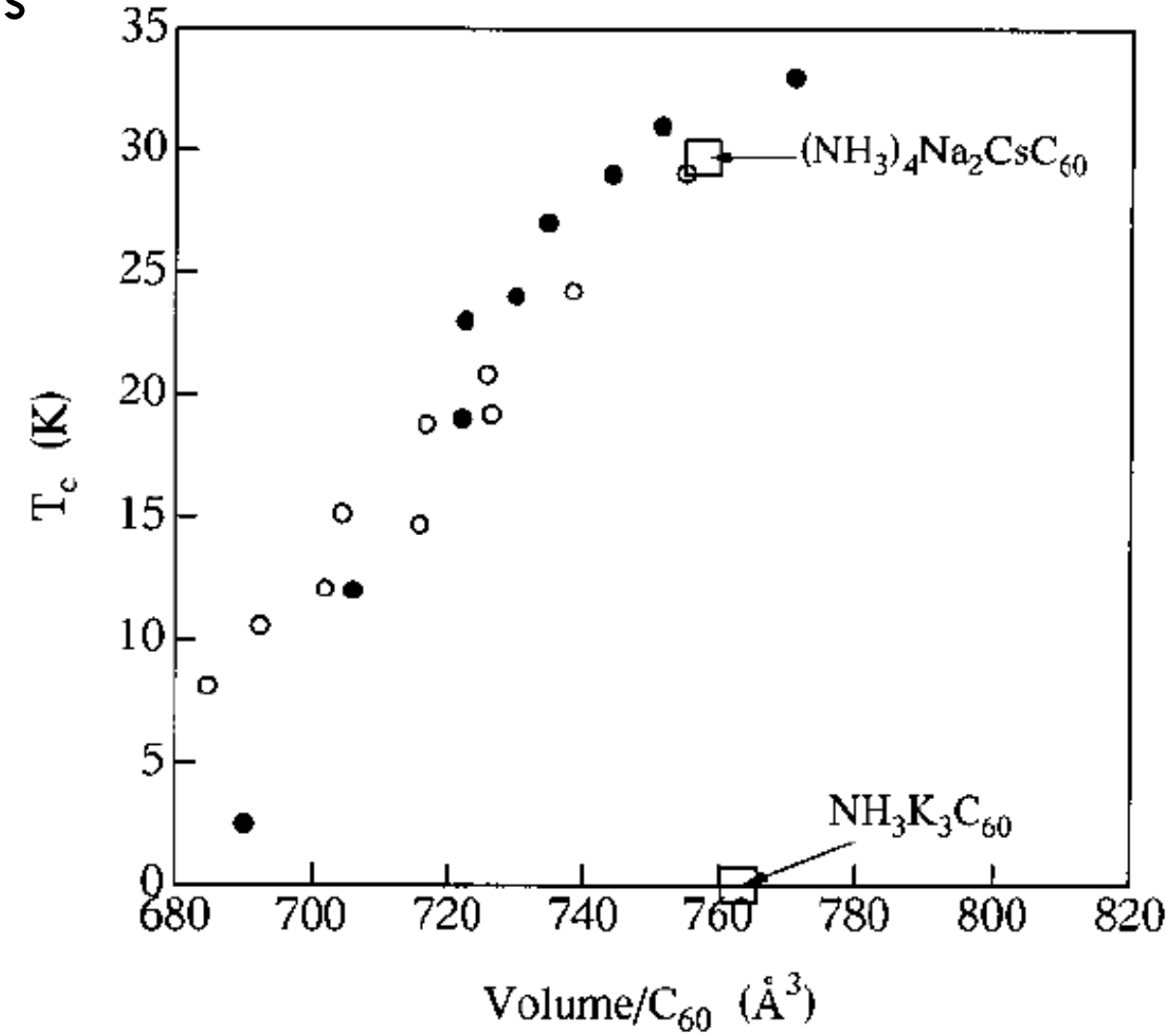
Increased separation of the C_{60} molecules

⇩

Increased T_c

OR

Mott-Hubbard localisation



Learning outcomes

After this lecture and pre-lecture video you should be able to

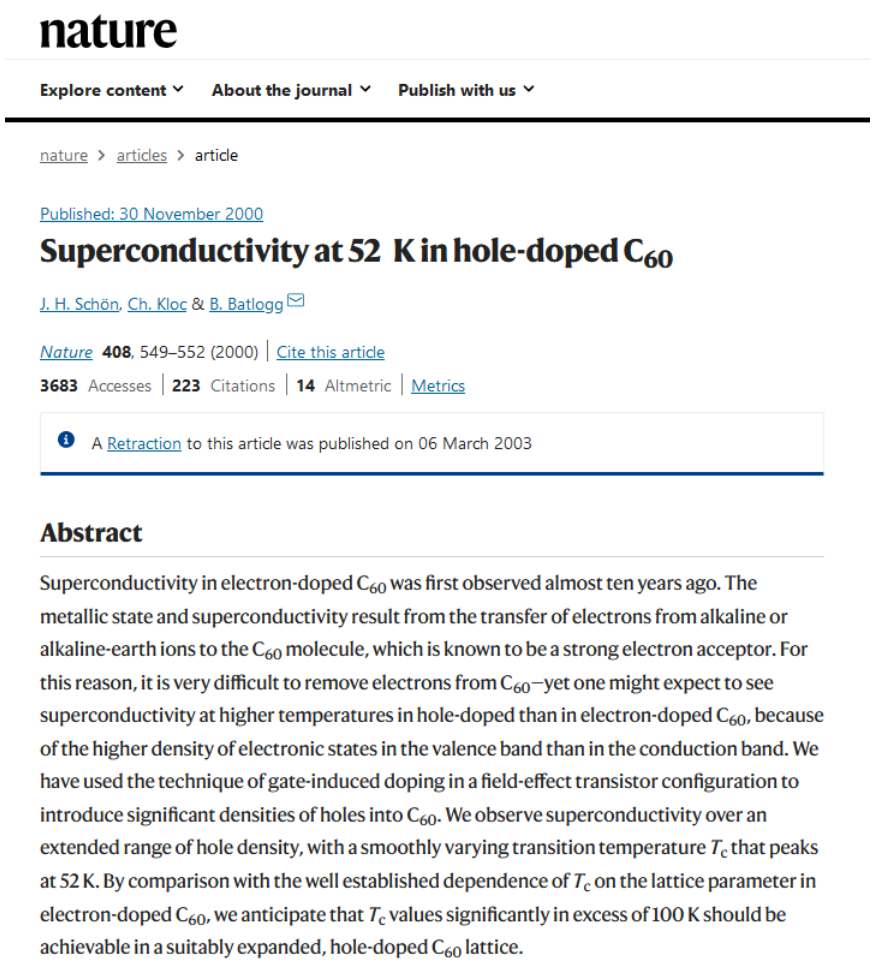
- Explain the origin of electronic band structures and understand the associated densities-of-states (qualitatively!)
- Predict and interpret electron localisation processes (Mott-Hubbard insulators)
- Apply the electronic bonding model to solids
- Complete the lecture worksheet, Q7 of Tutorial 2 (week 4), and answer all questions in this week's on-line quiz (covering the structure and bonding of materials, diffraction, and electronic structure).

Further reading: Weller, Overton, Rourke & Armstrong, Inorganic Chemistry 6th Ed. OUP, 2014, Chapter 3.1–3.5; Weller, Inorganic Materials Chemistry, OUP, 1994, Chapter 5; West, Basic Solid State Chemistry, Wiley, 1999, Chapter 2.

For interest

The Schön Scandal: "biggest fraud in physics in the last 50 years"

https://en.wikipedia.org/wiki/Schon_scandal



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Published: 30 November 2000

Superconductivity at 52 K in hole-doped C_{60}

J. H. Schön, Ch. Kloc & B. Batlogg

Nature **408**, 549–552 (2000) | Cite this article

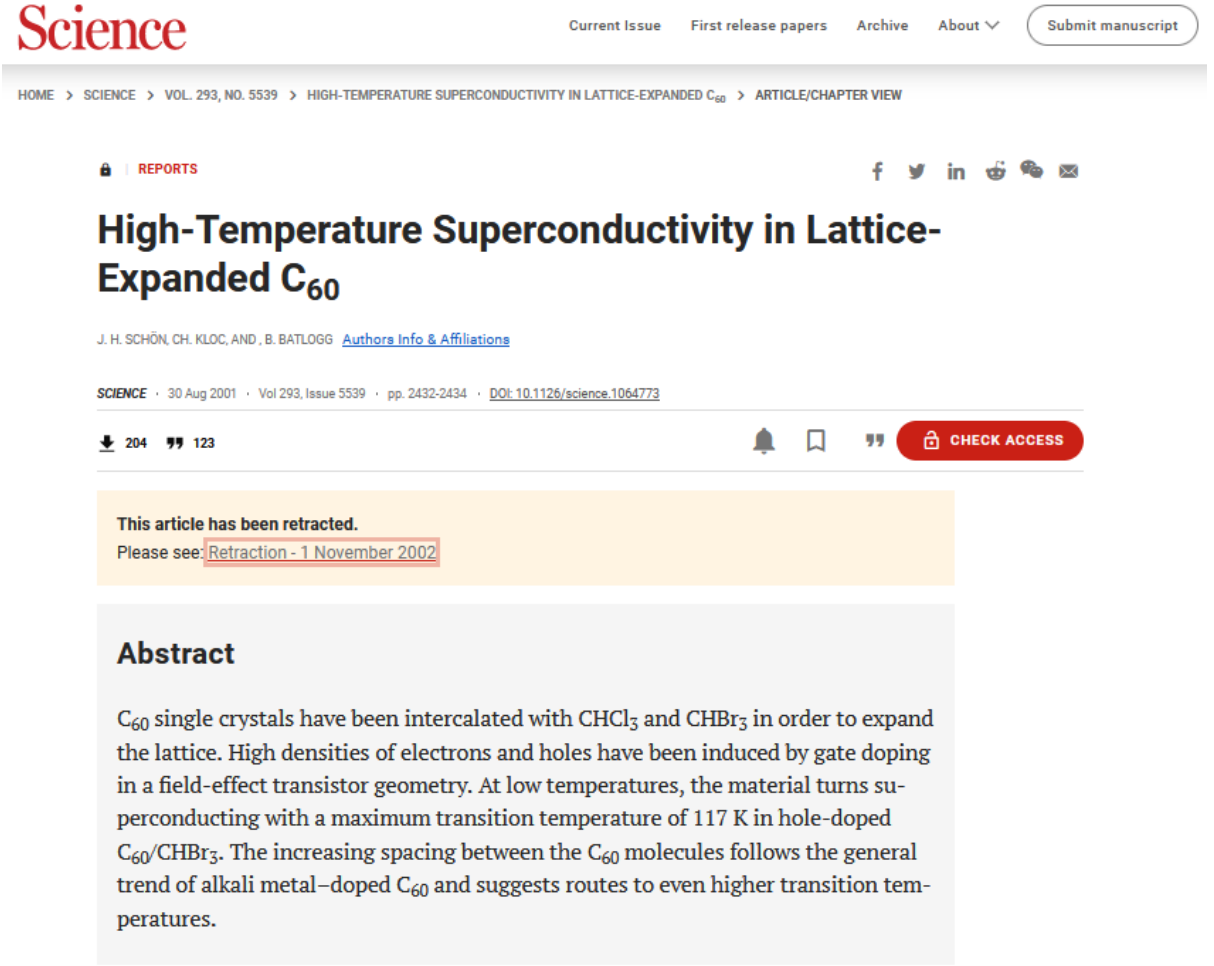
3683 Accesses | **223** Citations | **14** Altmetric | Metrics

A Retraction to this article was published on 06 March 2003

Abstract

Superconductivity in electron-doped C_{60} was first observed almost ten years ago. The metallic state and superconductivity result from the transfer of electrons from alkaline or alkaline-earth ions to the C_{60} molecule, which is known to be a strong electron acceptor. For this reason, it is very difficult to remove electrons from C_{60}—yet one might expect to see superconductivity at higher temperatures in hole-doped than in electron-doped C_{60}, because of the higher density of electronic states in the valence band than in the conduction band. We have used the technique of gate-induced doping in a field-effect transistor configuration to introduce significant densities of holes into C_{60}. We observe superconductivity over an extended range of hole density, with a smoothly varying transition temperature T_c that peaks at 52 K. By comparison with the well established dependence of T_c on the lattice parameter in electron-doped C_{60}, we anticipate that T_c values significantly in excess of 100 K should be achievable in a suitably expanded, hole-doped C_{60} lattice.

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REPORTS

High-Temperature Superconductivity in Lattice-Expanded C_{60}

J. H. SCHÖN, CH. KLOC, AND , B. BATLOGG Authors Info & Affiliations

SCIENCE · 30 Aug 2001 · Vol 293, Issue 5539 · pp. 2432-2434 · DOI: 10.1126/science.1064773

204 123 CHECK ACCESS

This article has been retracted.
Please see: Retraction - 1 November 2002

Abstract

C_{60} single crystals have been intercalated with $CHCl_3$ and $CHBr_3$ in order to expand the lattice. High densities of electrons and holes have been induced by gate doping in a field-effect transistor geometry. At low temperatures, the material turns superconducting with a maximum transition temperature of 117 K in hole-doped $C_{60}/CHBr_3$. The increasing spacing between the C_{60} molecules follows the general trend of alkali metal–doped C_{60} and suggests routes to even higher transition temperatures.

www.science.org/doi/pdf/10.1126/science.1064773