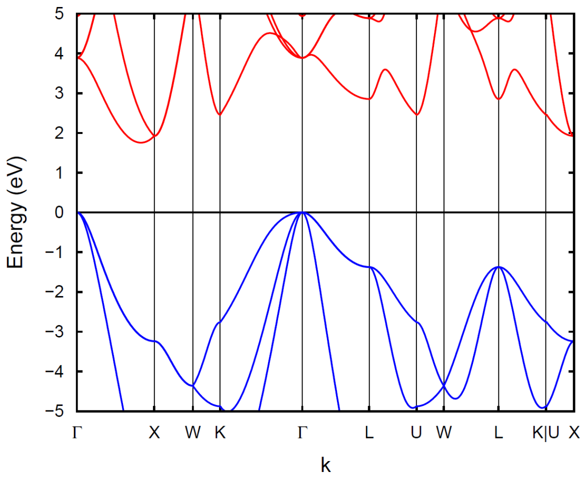
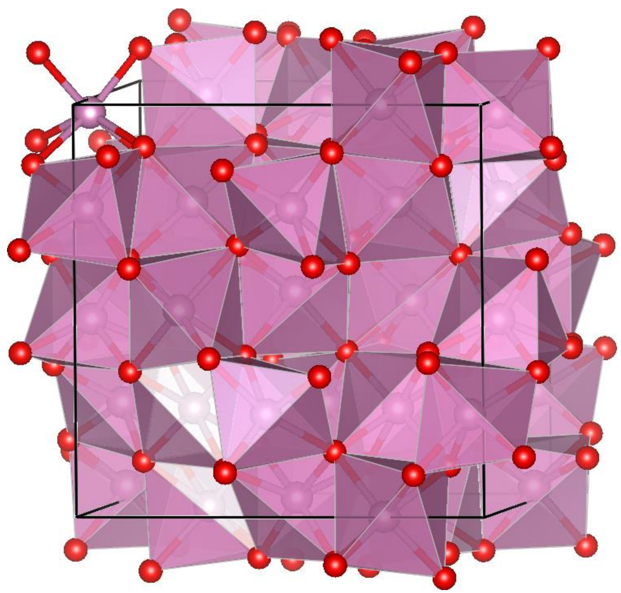
# Lecture 14: Semiconductors

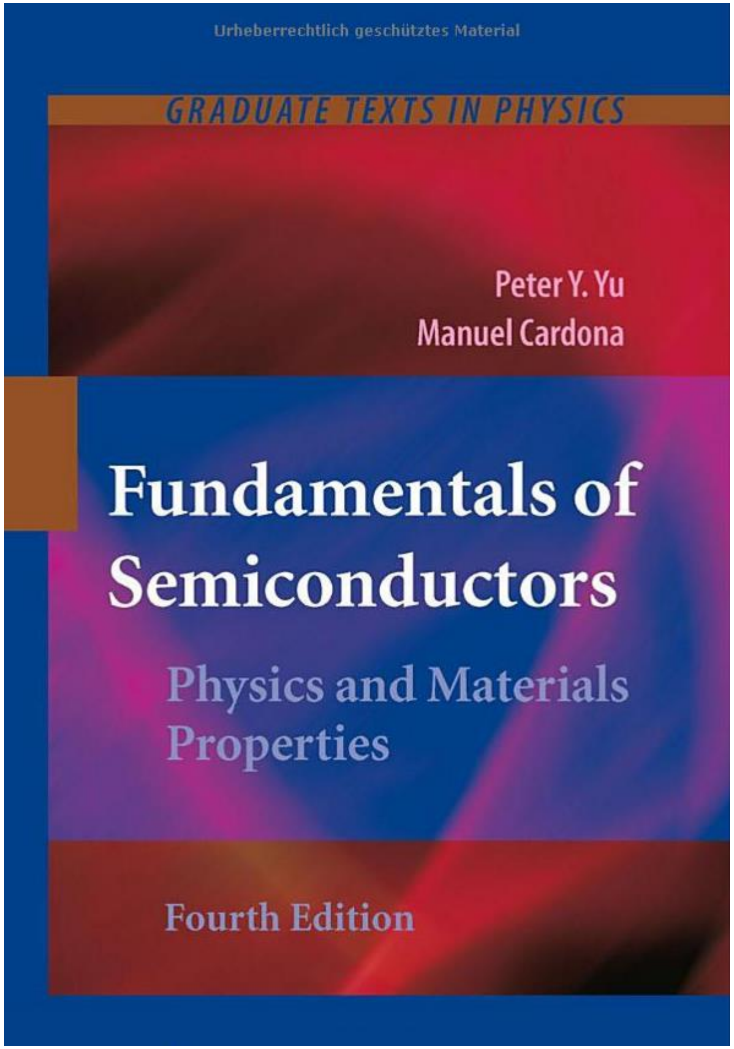
- Definitions
  - Band structure, band gap
- Basic principles
  - Doping
  - Electrical properties
- Important semiconductor materials
  - Main group semiconductors
  - Metal oxide semiconductors
- Applications of semiconductors
- Organic semiconductors are **not** discussed here

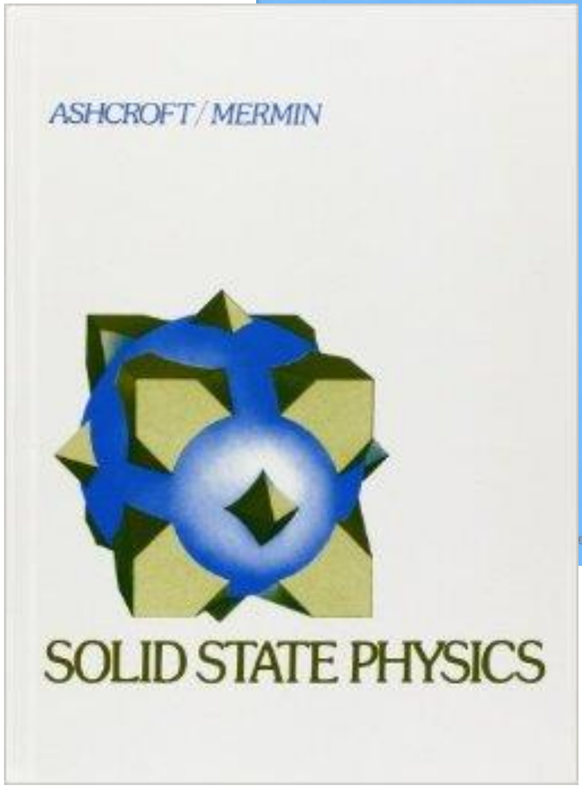


Figures: AJK

# Literature


Urheberrechtlich geschütztes Material
GRADUATE TEXTS IN PHYSICS
Peter Y. Yu
Manuel Cardona
Fundamentals of Semiconductors
Physics and Materials Properties
Fourth Edition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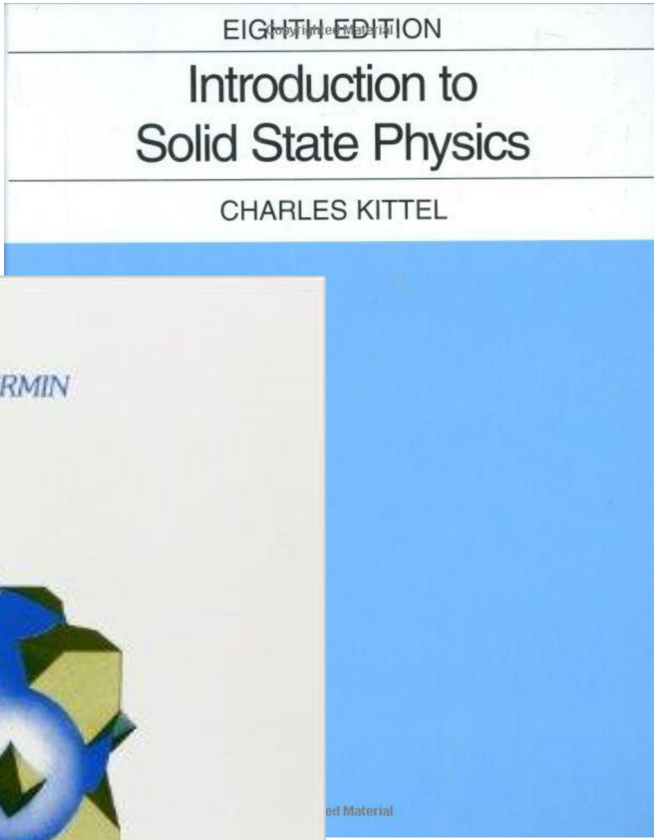

EIGHTH EDITION
Introduction to Solid State Physics
CHARLES KITTEL

# Definitions

- A semiconductor is usually defined rather loosely as a material with electrical resistivity $\rho$ lying in the range of $\rho = 10^{-2} - 10^{9}\ \Omega$ cm.
  - Examples of materials that are **not** semiconductors:
    Cu metal: $\rho = 1.7 \times 10^{-6}\ \Omega$ cm
    Fused quartz: $\rho = 7.5 \times 10^{19}$
- Alternatively, semiconductors can be defined as materials whose band gap (energy gap) lies between zero and about 4 eV (electron volts)
  - Materials with zero gap are called metals
  - Materials with gap > 4 eV are called insulators

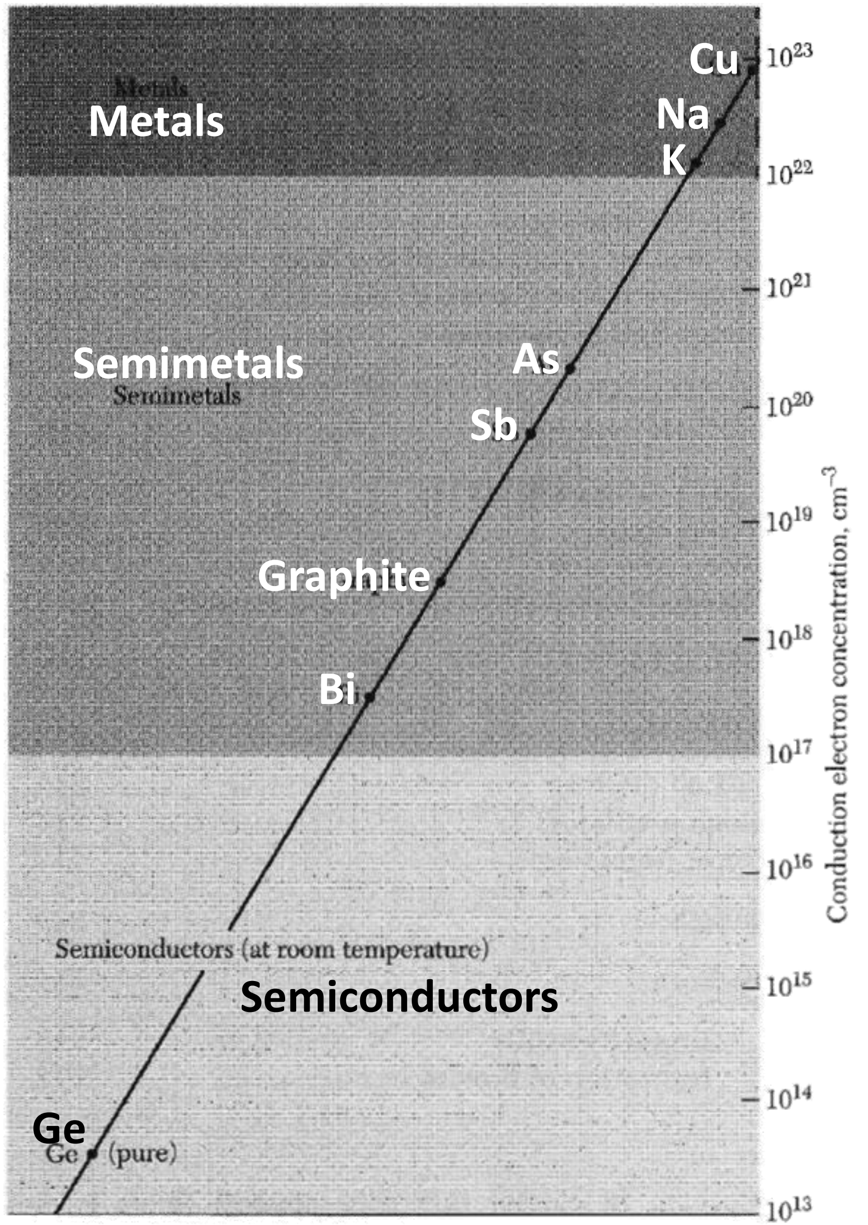
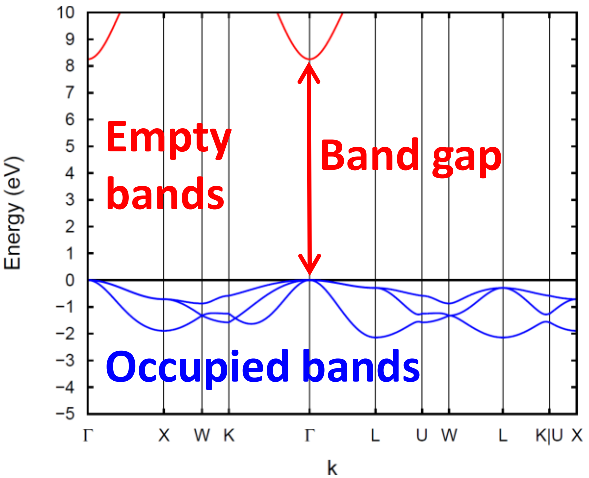



**Figure 1** Carrier concentrations for metals, semimetals, and semiconductors. The semiconductor range may be extended upward by increasing the impurity concentration, and the range can be extended downward to merge eventually with the insulator range.

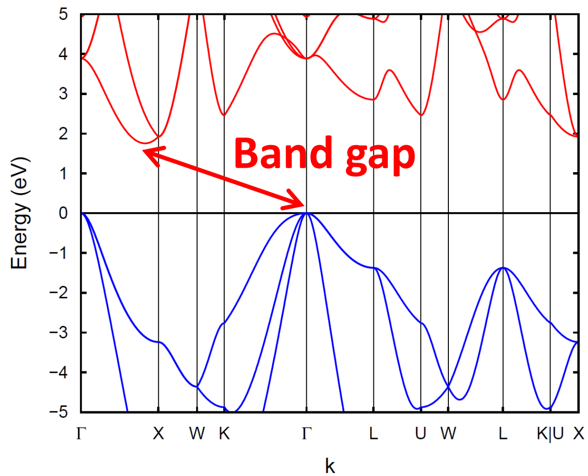
Ref: Cardona p . 1

Figure: Kittel p. 186

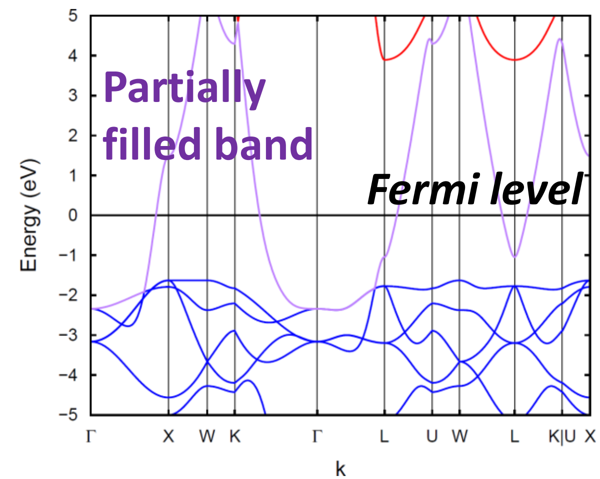
# Band structure and band gap




NaCl: **insulator**, large energy gap between occupied and non-occupied bands
Band gap: 8.75 eV (DFT)




Silicon: **semiconductor**, energy gap between occupied and non-occupied bands. **Indirect** band gap (~2 eV in the plot, experimentally ~1.1 eV at room temperature)



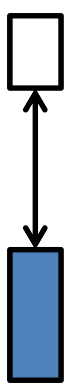

Copper: **metal**, partially filled bands

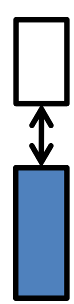
No band gap

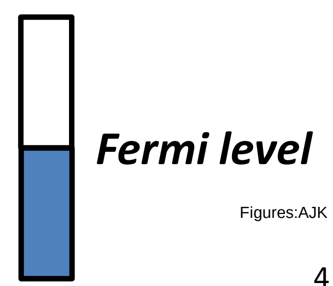
**Schematic view:**

Empty bands:

Occupied bands:








Figures:AJK

# Band gaps for various materials

Table 28.1
**ENERGY GAPS OF SELECTED SEMICONDUCTORS**

| MATERIAL | $E_g$ ($T = 300$ K) | $E_g$ ($T = 0$ K) | $E_0$ (LINEAR EXTRAPOLATION TO $T = 0$) | LINEAR DOWN TO |
|---|---|---|---|---|
| Si | 1.12 eV | 1.17 | 1.2 | 200 K |
| Ge | 0.67 | 0.75 | 0.78 | 150 |
| PbS | 0.37 | 0.29 | 0.25 | |
| PbSe | 0.26 | 0.17 | 0.14 | 20 |
| PbTe | 0.29 | 0.19 | 0.17 | |
| InSb | 0.16 | 0.23 | 0.25 | 100 |
| GaSb | 0.69 | 0.79 | 0.80 | 75 |
| AlSb | 1.5 | 1.6 | 1.7 | 80 |
| InAs | 0.35 | 0.43 | 0.44 | 80 |
| InP | 1.3 | | 1.4 | 80 |
| GaAs | 1.4 | | 1.5 | |
| GaP | 2.2 | | 2.4 | |
| Grey Sn | 0.1 | | | |
| Grey Se | 1.8 | | | |
| Te | 0.35 | | | |
| B | 1.5 | | | |
| C (diamond) | 5.5 | | | |

Sources: C. A. Hogarth, ed., *Materials Used in Semiconductor Devices*, Interscience, New York, 1965; O. Madelung, *Physics of III–V Compounds*, Wiley, New York, 1964; R. A. Smith, *Semiconductors*, Cambridge University Press, 1964.

Ref: Ashcroft & Mermin p. 566

# Doping (1)

- Very pure semiconductors are called **intrinsic** semiconductors
  - Conduction band electron can only come from a valence band level, leaving holes behind (equal number of excited electrons and holes)
  - **Carrier concentration** is determined mainly by thermal excitations (at room temperature, thermal energy available is $k_B T \approx 0.0257$ eV)
  - For example, in intrinsic silicon with approximately $5 \times 10^{22}$ atoms per cm$^3$, the carrier concentration at RT is $\approx 10^{10}$ cm$^{-3}$ ($\approx e^{-\Delta E/(2kBT)}$).
  - Resistivity of intrinsic Si: 3.2 x $10^5$ $\Omega$ cm

***Conduction band minimum***
Electron excited to the conduction band during the thermal excitation

***Valence band maximum***
Hole created in the valence band during the thermal excitation

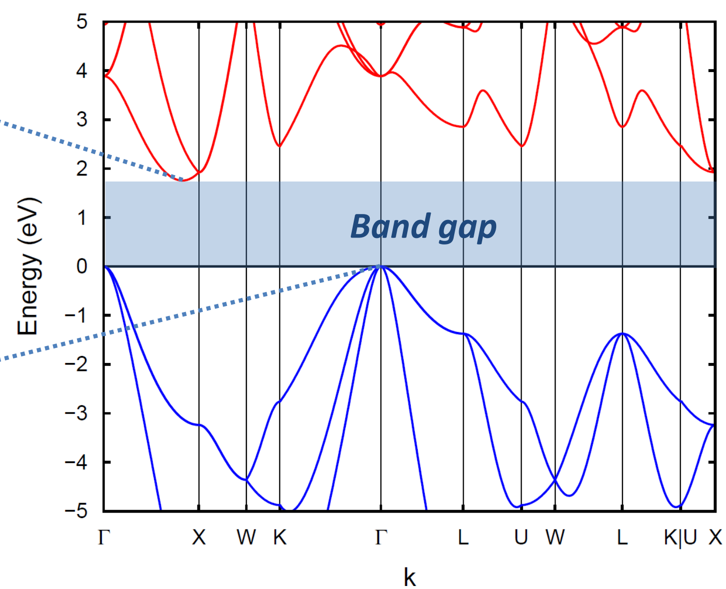
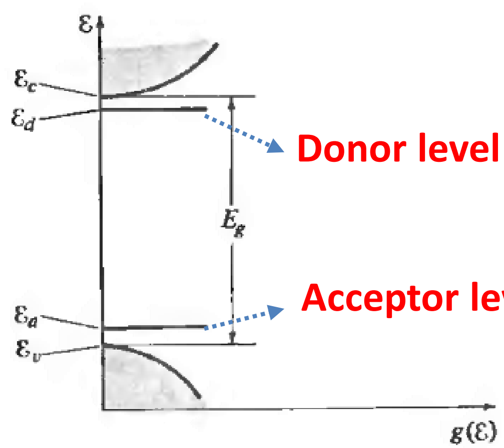



Figure: AJK

# Doping (2)

- In an **extrinsic** semiconductor, impurities have been introduced either on purpose or by accident.
  - An extrinsic semiconductor can be ***n*-type** (electrons as majority carriers) or ***p*-type** (holes as majority carriers)
  - Doping silicon with P (donor) -> *n*-type
  - Doping silicon with B (acceptor) -> *p*-type
  - $10^{15}$ cm$^{-3}$ would already be rather high doping level, $10^{17}$ cm$^{-3}$ very high
  - Resistivity of B-doped Si ($10^{15}$ cm$^{-3}$): 13.5 Ω cm
- For semiconductors, resistivity **decreases** as $T$ increases (more carriers)
- For metals, resistivity **increases** as $T$ increases (more electron-phonon scattering)

**Figure 28.12**
Level density for a semiconductor containing both donor and acceptor impurities. The donor levels $\mathcal{E}_d$ are generally close to the bottom of the conduction band, $\mathcal{E}_c$ compared with $E_g$, and the acceptor levels, $\mathcal{E}_a$, are generally close to the top of the valence band, $\mathcal{E}_v$.




Ref: Ashcroft & Mermin p. 579

# Doping (3)

- It is much easier to thermally excite an electron into conduction band from a donor level, or a hole into valence band from an acceptor level!
- In practical applications, the conductivity is controlled by external electric fields (see for example ***field effect transistor***, FET)

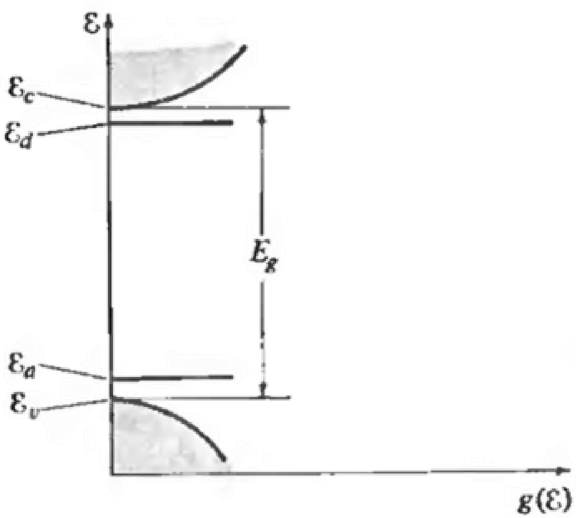



Table 28.2 **15** **13**

**LEVELS OF GROUP V (DONORS) AND GROUP III (ACCEPTORS) IMPURITIES IN SILICON AND GERMANIUM**

GROUP III ACCEPTORS (TABLE ENTRY IS $\mathcal{E}_a - \mathcal{E}_v$)

| | B | Al | Ga | In | Tl |
|---|---|---|---|---|---|
| Si | 0.046 eV | 0.057 | 0.065 | 0.16 | 0.26 |
| Ge | 0.0104 | 0.0102 | 0.0108 | 0.0112 | 0.01 |

GROUP V DONORS (TABLE ENTRY IS $\mathcal{E}_c - \mathcal{E}_d$)

| | P | As | Sb | Bi |
|---|---|---|---|---|
| Si | 0.044 eV | 0.049 | 0.039 | 0.069 |
| Ge | 0.0120 | 0.0127 | 0.0096 | — |

ROOM TEMPERATURE ENERGY GAPS ($E_g = \mathcal{E}_c - \mathcal{E}_v$)

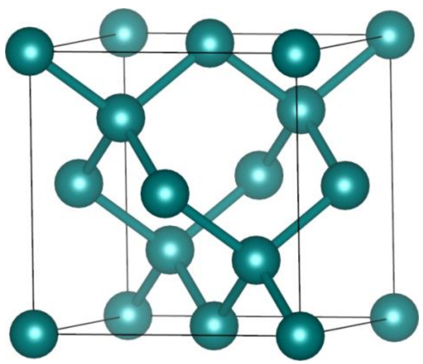
| | |
|---|---|
| Si | 1.12 eV |
| Ge | 0.67 eV |

Source: P. Aigrain and M. Balkanski, *Selected Constants Relative to Semiconductors*, Pergamon, New York, 1961.

Ref: Ashcroft & Mermin p. 580

# Group 14 elemental semiconductors

- Silicon and germanium are both prototypical semiconductor materials
- Silicon is by far the most important semiconductor material
- Germanium has in principle better semiconducting properties
  - Higher electron and hole mobility -> higher operating frequencies
- However, Si dominates due to its **abundance** and **processability**
  - From lecture 9: Si:Ge ratio in the Earth's crust is almost $10^6$:1!



α-Si / α-Ge / α-Sn
(*Fd-3m*)

Figure: AJK

| | | **RT band gaps** |
|---|---|---|
| C | 2.55 | 5.4 eV (insulator) |
| Si | 1.90 | 1.1 eV (semiconductor) |
| Ge | 2.01 | 0.66 eV (semiconductor) |
| Sn | 1.96 | 0 eV (α-tin; β is metal) |
| Pb | 1.87 | Metal |

# Details of silicon band structure

Band structure from quantum chemical calculation (DFT-PBE0/TZVP)

**Experimental values at 300 K:**

**Indirect band gap**
**Photon absorption must be coupled with a lattice vibration (*phonon*)**
$E_{gap\text{-}i}$ = 1.1 eV

**Direct band gap**
**Direct absorption of a photon**
$E_{gap\text{-}d}$ = 3.4 eV

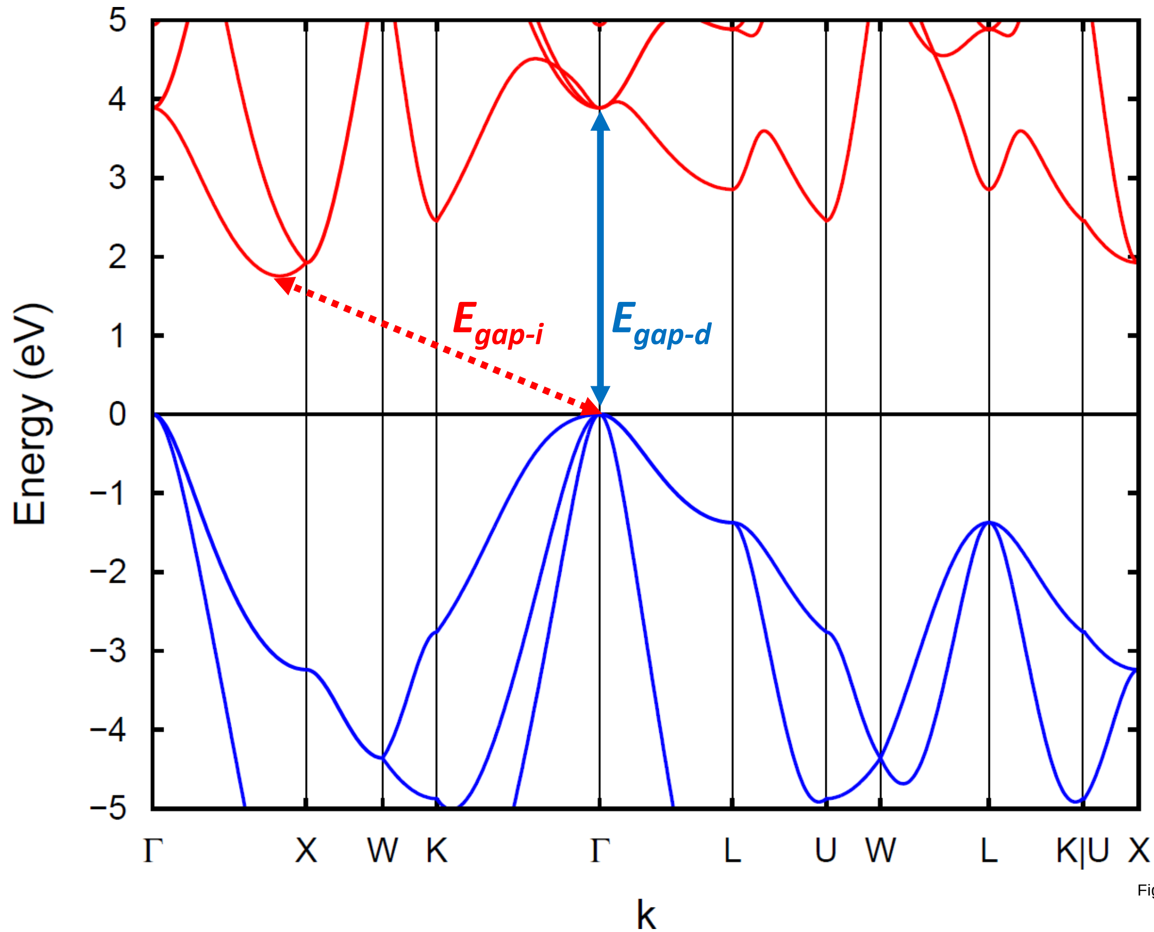



Figure: AJK

**Discovery of an easily accessible silicon modification with a direct band gap could have huge technological impact for silicon optoelectronics (solar cells, LEDs)**

# Group 14 compound semiconductors

- $Si_{1-x}Ge_x$
  - Diamond structure
  - Adjustable band gap (by tuning *x*)
  - Highly reliable thermoelectric devices (running for > 40 years on Voyager missions)
- SiC
  - High temperatures and high voltages
  - Mechanically very hard
  - Uses in early LEDs, power electronics
  - Very rich polymorphism, over 250 polymorphs are known
  - 3C, 2H, 4H, 6H (the best studied)

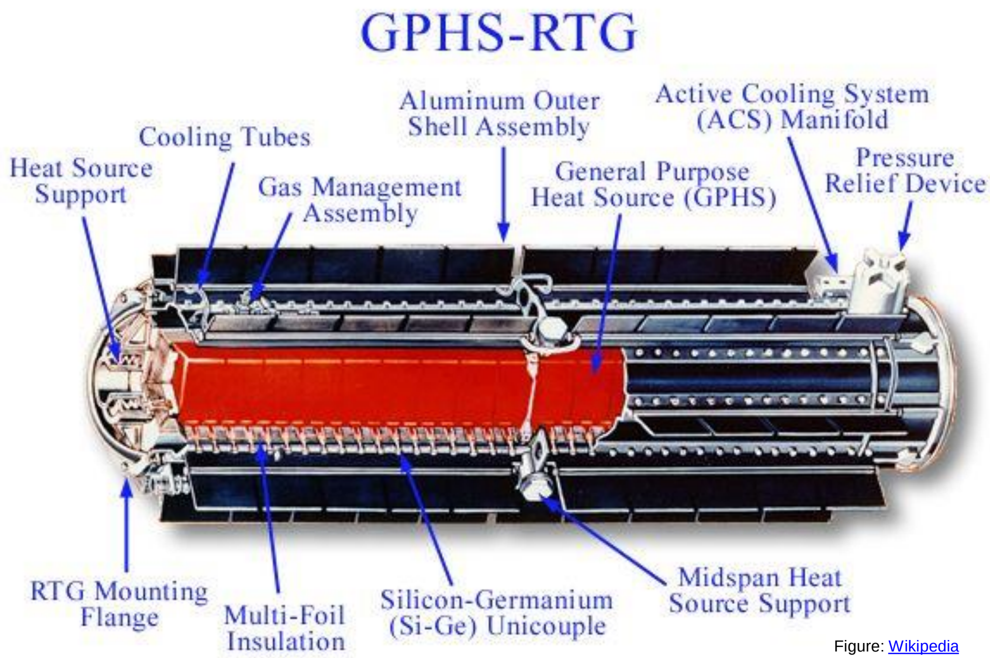



Figure: Wikipedia

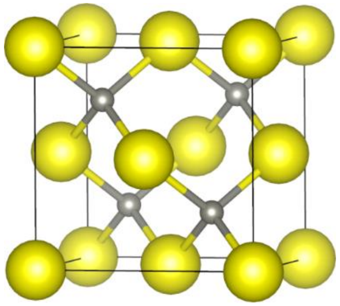
- **SiGe** radioisotope thermoelectric generator (RTG)
- The thermopile composed of the SiGe unicouples on both sides of the $^{238}PuO_2$ heat source converts the heat into electrical energy
- 157 W of electrical power (6.5% efficiency)
- Voyager 1 and 2 probes launched in 1977 are powered by three RTGs
- Each RTG had a total weight of 37.7 kg including about 4.5 kg of Pu-238 (half-life 87.7 years)

# Group 13-15 semiconductors

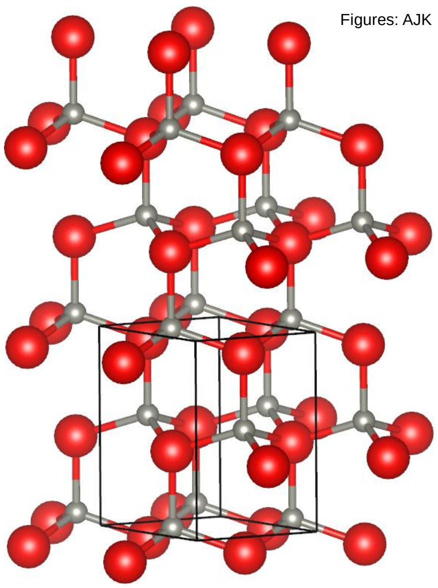
- Adopt either the **zincblende** (ZB) or **wurtzite** (W) structure
- **ZB**: BP, BAs, AlP, AlAs, AlSb, GaP, GaAs, GaSb, InP, InAs, InSb
- **W**: AlN, GaN, InN
- Various ternary, quaternary, and even pentanary alloys also used (InGaN, InGaAsP, GaInAsSbP, …)
- Numerous applications in electronics and optoelectronics, for example:
- GaAs: second most used after Si. Some superior properties, but less abundant, more difficult to fabricate with high purity
  - In theory, CPU clock frequencies that are 100 times larger than for Si
- GaN: Blue LEDs

| | | |
|---|---|---|
| B 2.04 | C 2.55 | N 3.04 |
| Al 1.61 | Si 1.90 | P 2.19 |
| Ga 1.81 | Ge 2.01 | As 2.18 |
| In 1.78 | Sn 1.96 | Sb 2.05 |
| Tl 1.62 | Pb 1.87 | Bi 2.02 |

Figures: AJK



Zincblende ($F\text{-}43m$)



Wurtzite ($P6_3mc$)

Ref: Wikipedia

# Group 12-16 semiconductors

- ZnO (W)
  - Discussed later (oxide semiconductors)
- ZnS (ZB, W)
  - Phosphor material (ZnS:Mn), electroluminescent displays (ALD)
- ZnSe (ZB)
  - Blue lasers and LEDs
- ZnTe (ZB)
  - Versatile semiconductor: blue LEDs, solar cells, microwave generators, …
- CdS (ZB, W)
  - Used in first solar cells, CdS/$Cu_2S$
- CdSe (ZB, W)
  - Quantum dots (luminescence)
- CdTe (ZB)
  - Thin-film solar cells, quantum dots

| | | | | |
|---|---|---|---|---|
| | B 2.04 | C 2.55 | N 3.04 | O 3.44 |
| | Al 1.61 | Si 1.90 | P 2.19 | S 2.58 |
| Zn 1.65 | Ga 1.81 | Ge 2.01 | As 2.18 | Se 2.55 |
| Cd 1.69 | In 1.78 | Sn 1.96 | Sb 2.05 | Te 2.1 |
| Hg 2.00 | Tl 1.62 | Pb 1.87 | Bi 2.02 | Po 2.0 |


Figure: http://nanocluster.mit.edu/

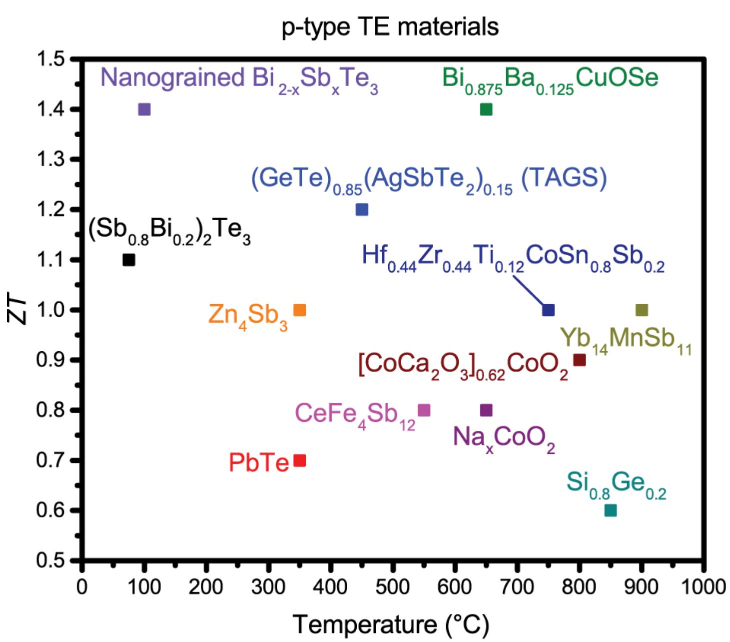
Ref: Wikipedia

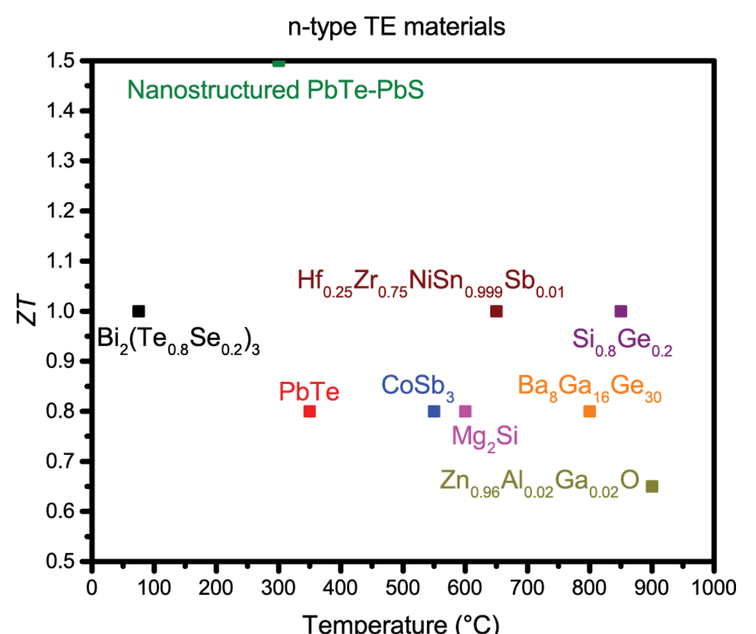
# Group 14-16 semiconductors

- PbS (mineral Galena, rocksalt structure)
  - One the first semiconductor materials in practical use (already in the late 19th century, before semiconductors were really understood, see [Cat's-whisker detector](#))
  - The oldest material used in infrared detectors
- PbSe, PbTe (rocksalt structure)
  - Mid-temperature thermoelectric materials

| | | |
|---|---|---|
| C 2.55 | N 3.04 | O 3.44 |
| Si 1.90 | P 2.19 | S 2.58 |
| Ge 2.01 | As 2.18 | Se 2.55 |
| Sn 1.96 | Sb 2.05 | Te 2.1 |
| Pb 1.87 | Bi 2.02 | Po 2.0 |

Ref: [Wikipedia](#)



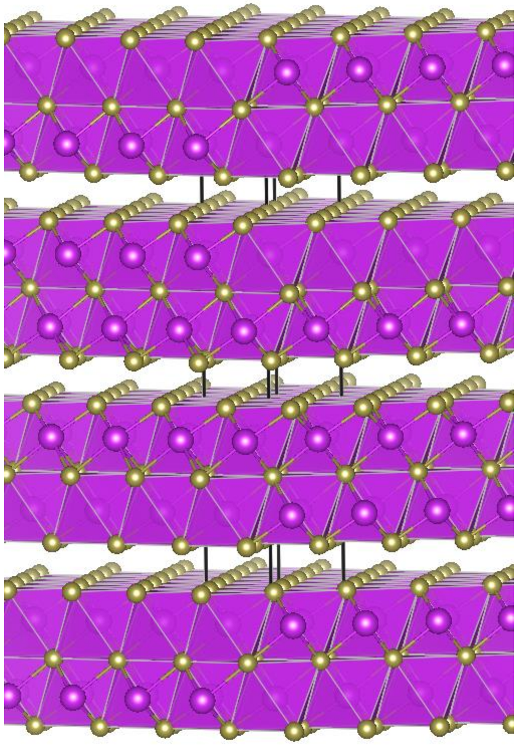

Figures: AJK ([DOI](#))

***ZT* = thermoelectric figure of merit -> The higher the better**

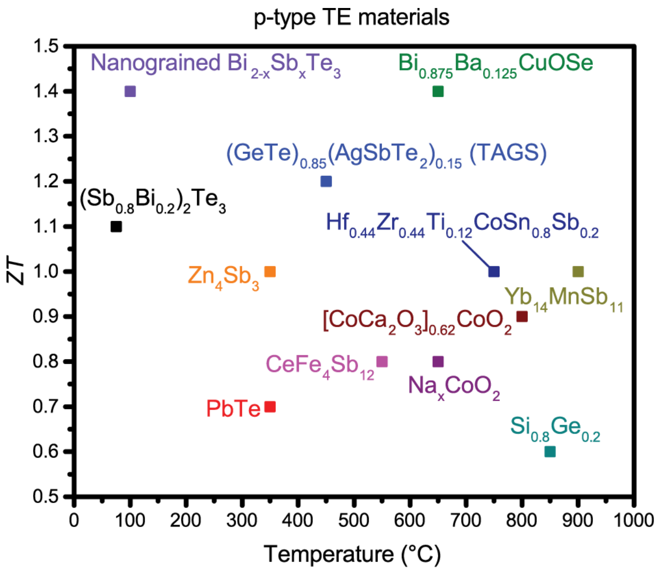
# Group 15-16 semiconductors

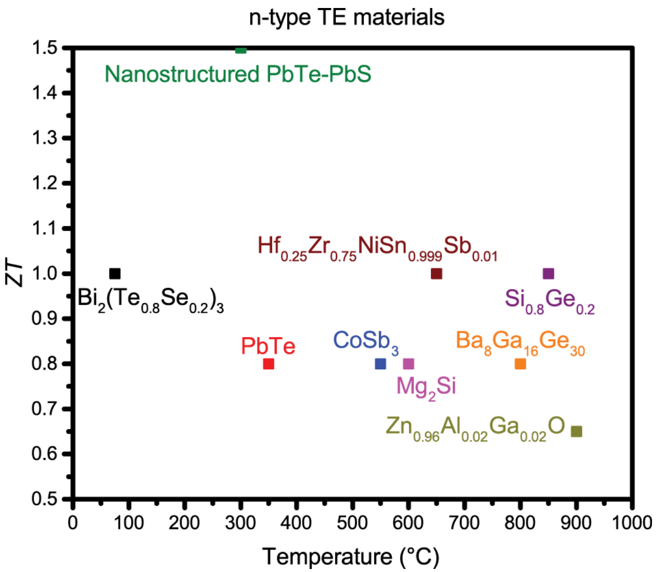
- $Bi_2Te_3$
  - Layered material
  - Room-temperature thermoelectric material
  - Alloyed with Sb / Te
  - Also $Sb_2Te_3$, $Sb_2Se_3$, $Bi_2Se_3$

| | |
|---|---|
| N<br>3.04 | O<br>3.44 |
| P<br>2.19 | S<br>2.58 |
| As<br>2.18 | Se<br>2.55 |
| Sb<br>2.05 | Te<br>2.1 |
| Bi<br>2.02 | Po<br>2.0 |



$Bi_2Te_3$ ($R$-3$m$)

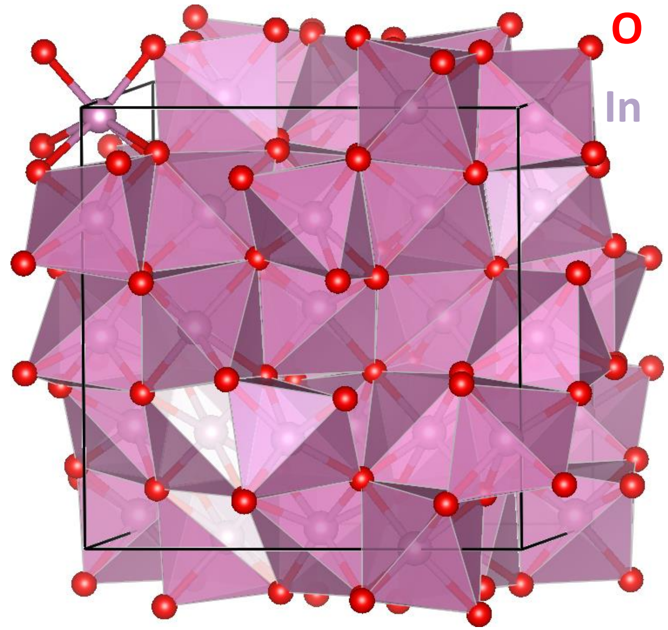



Figures:AJK

# Oxide semiconductors (1)

- Indium-Tin-Oxide (ITO) – *n*-type large bandgap semiconductor (close to 4 eV)
  - Parent oxide $In_2O_3$
  - Typical composition 74% In, 18% $O_2$, and 8% Sn by weight
  - Most common transparent conducting oxide (touch screens etc.)
- ZnO (wurtzite structure)
  - Doped with Al (*n*-type) and possibly Ga
  - *p*-type doping not successful despite decades of various efforts
  - Possible replacement of ITO (ZnO:Al)
  - High-*T* thermoelectric material
- $TiO_2$ (rutile and anatase structures)
  - Solar cell material (dye-sensitized solar cells)

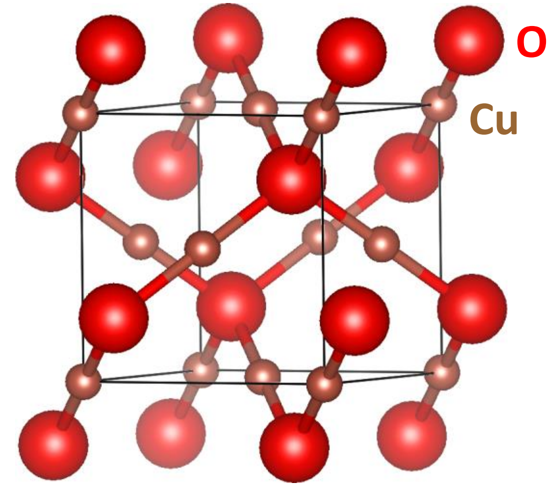



$In_2O_3$ (*Ia*-3)
*Bixbyite* structure, $(Mn,Fe)_2O_3$

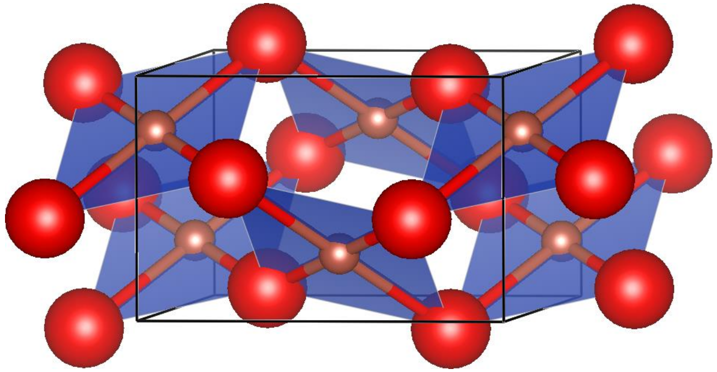
Figure: AJK

# Oxide semiconductors (2)

- $Cu_2O$
  - p-type semiconductor
  - Historically very important, many basic semiconducting properties discovered for $Cu_2O$ (e.g. diodes)
  - Band gap of 2.1 eV, potential thermoelectric p-type oxide
- CuO
  - p-type semiconductor
  - Narrow band gap of 1.2 eV, potential thermoelectric p-type oxide
- Many perovskites and spinels
  - E.g. $SrTiO_3$ as n-type thermoelectric material
  - Copper aluminate $CuAl_2O_4$ as TCO or p-type thermoelectric material
- Many layered oxides (lecture 15)




$Cu_2O$ (*Pn-3m*)
Copper(I) oxide, cuprous oxide
Diamagnetic



CuO (*C2/c,* monoclinic)
Copper(II) oxide, cupric oxide
Antiferromagnetic

Figures: AJK

# Other main group semiconductors

- Zintl compounds (lecture 10)
- In particular semiconducting clathrates
  - Tunable band gap (~0.5 eV in $Ba_8[Ga_{16}Ge_{30}]$) *via* controlled atomic substitution
  - Low thermal conductivity (good for thermoelectrics

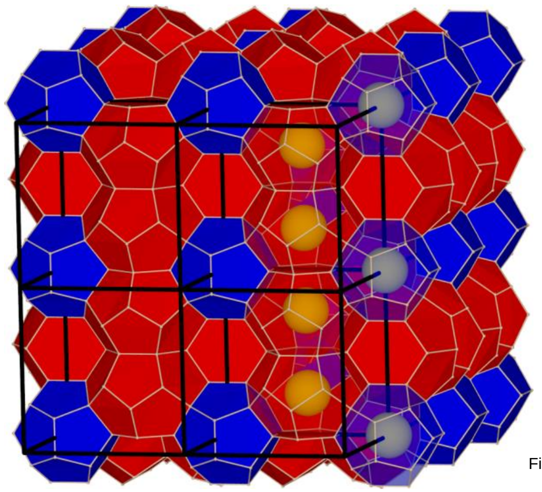


Figure: AJK


13 gram single crystal of $Ba_8[Ga_{16}Ge_{30}]$

- **Clathrate-I** (*Pm*-3*n*, 46 framework atoms in the unit cell)
- $Ba_8[Ga_{16}Ge_{30}]$ (**anionic** framework)
- Each Ba atom donates $2e^-$
- Ga atoms have $1e^-$ less than Ge, so the 4-coordinated framework needs $16e^-$

**Thermoelectric clathrates of type I**

**Mogens Christensen, Simon Johnsen and Bo Brummerstedt Iversen***

*Dalton Trans.*, 2010, **39**, 978–992

# Brief history of semiconductors

- Transistor invented at Bell Labs in 1947
  - Required improved understanding of the quantum theory of solids and semiconductors
  - Nobel prize in physics in 1956 (Shockley, Bardeen, Brattain)
- The first transistors were made out of Ge, but by mid-50s Si became preferred
- First version of an integrated circuit (IC) invented at Texas Instruments 1958
  - Nobel prize in physics in 2000 (Kilby)
- Moore’s law 1965/1975: exponential increase of transistors within an IC (doubling every two years)
  - The ”law” does not really hold any more – the transistors are becoming too small (currently: 10 nm)


Figure: Wikipedia

Replica of the first transistor

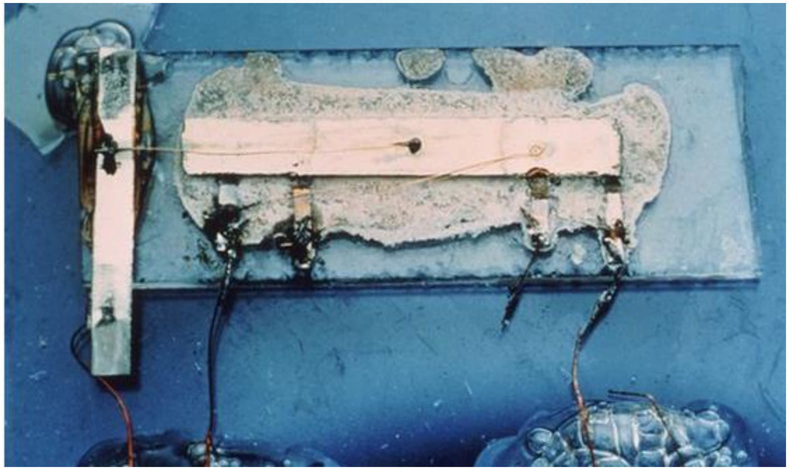


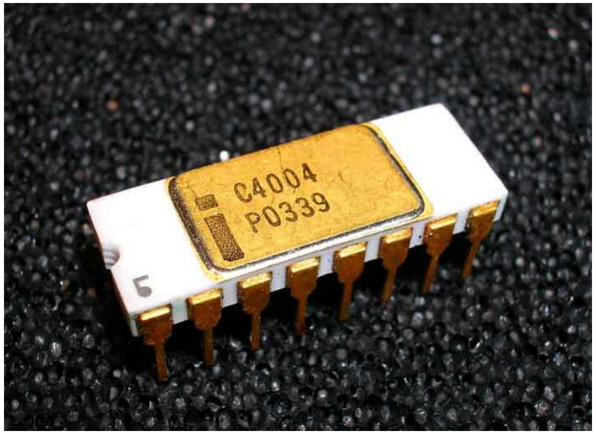
Figure: Wikipedia

First integrated circuit

# Applications of semiconductors

- Transistors
- Integrated circuits
  - Set of electronic circuits on one chip of semiconductor material
  - Can include billions of transistors
  - Commercial production: feature widths of 10 nm in 2019
- Practically all microelectronics
  - Computers, mobile devices, everything
- Energy conversion
  - Solar cells
  - Thermoelectrics
- Light-emitting diodes
- Lasers
- Power-control applications

Figure: Wikipedia




Intel 4004, the first commercial microprocessor (1971)

Figure: Wikipedia

# Fabrication of semiconductor devices

- The value of the semiconductor market is > 350 x $10^9$ EUR (yearly sales in 2017)
- A single semiconductor device fabrication plant (”fab”) can cost 1-10 x $10^9$ EUR
- Numerous state-of-the-art technologies are involved in the fabrication of semiconductor devices (possibly the most advanced technological process there is)
- For example, Intel with revenue of > 60 x $10^9$ EUR, spends ~ 12 x $10^9$ EUR on R&D
- Lots of solid state chemistry! See the appendix material: **Intel 2011 - Sand-to-Silicon**