1.021, 3.021, 10.333, 22.00 : Introduction to Modeling and Simulation : Spring 2012

Part II – Quantum Mechanical Methods : Lecture 6

# From Atoms to Solids

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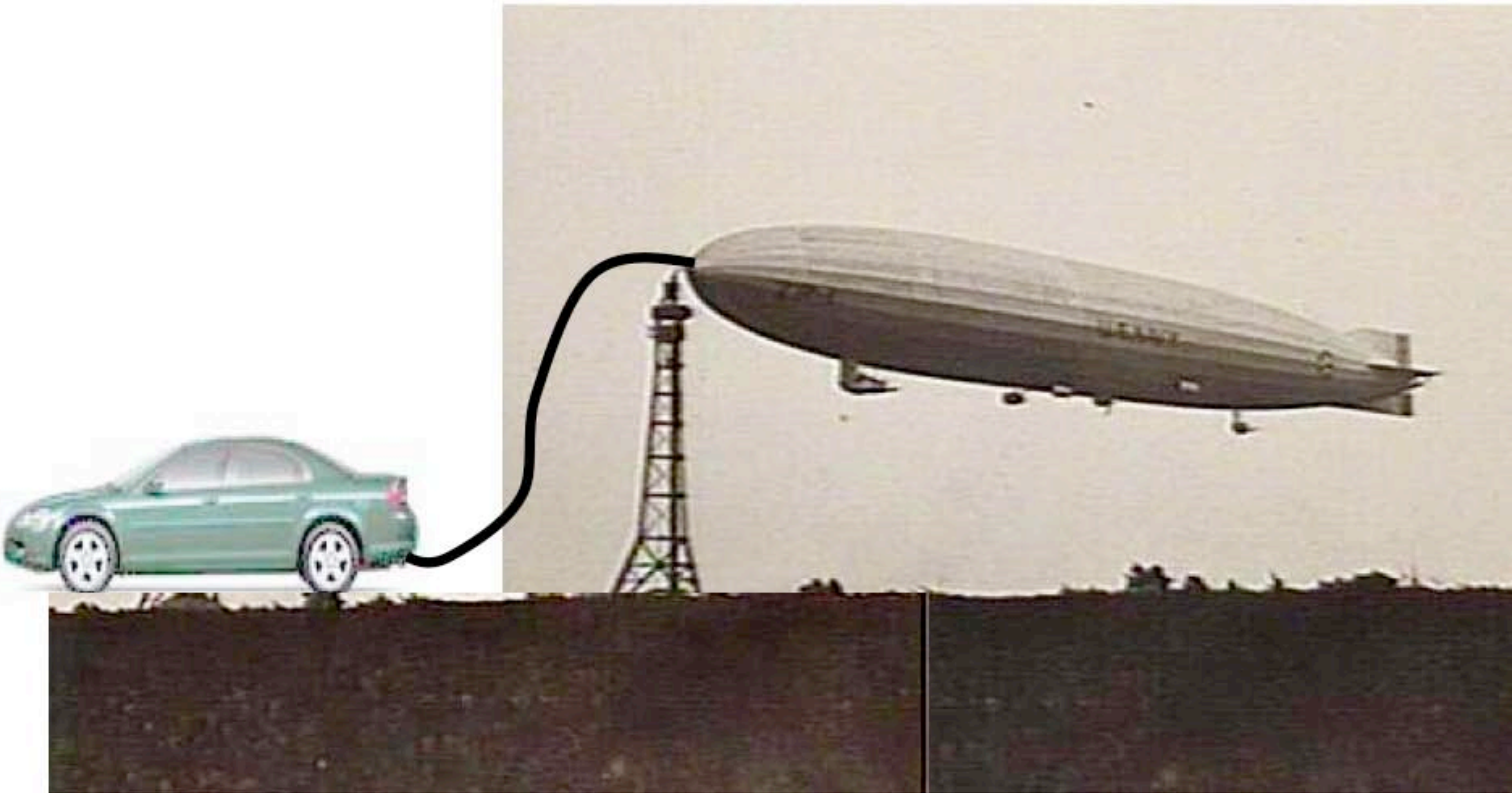
# Part II Topics

1. It's a Quantum World: The Theory of Quantum Mechanics
2. Quantum Mechanics: Practice Makes Perfect
3. From Many-Body to Single-Particle; Quantum Modeling of Molecules
4. Application of Quantum Modeling of Molecules: Solar Thermal Fuels
5. Application of Quantum Modeling of Molecules: Hydrogen Storage
6. From Atoms to Solids
7. Quantum Modeling of Solids: Basic Properties
8. Advanced Prop. of Materials: What else can we do?
9. Application of Quantum Modeling of Solids: Solar Cells Part I
10. Application of Quantum Modeling of Solids: Solar Cells Part II
11. Application of Quantum Modeling of Solids: Nanotechnology

# Lesson outline

- Briefly hydrogen storage
- Periodic potentials
- Bloch's theorem
- Energy bands

# Hydrogen Storage



# President Bush Launches the Hydrogen Fuel Initiative

"Tonight I am proposing $1.2 billion in research funding so that America can lead the world in developing clean, hydrogen-powered automobiles.

"A simple chemical reaction between hydrogen and oxygen generates energy, which can be used to power a car producing only water, not exhaust fumes.

"With a new national commitment, our scientists and engineers will overcome obstacles to taking these cars from laboratory to showroom so that the first car driven by a child born today could be powered by hydrogen, and pollution-free.

"Join me in this important innovation to make our air significantly cleaner, and our country much less dependent on foreign sources of energy."

**2003 State of the Union Address**
**January 28, 2003**

From Patrovic & Milliken (2003)

autobloggreen

WE OBSESSIVELY COVER THE GREEN SCENE



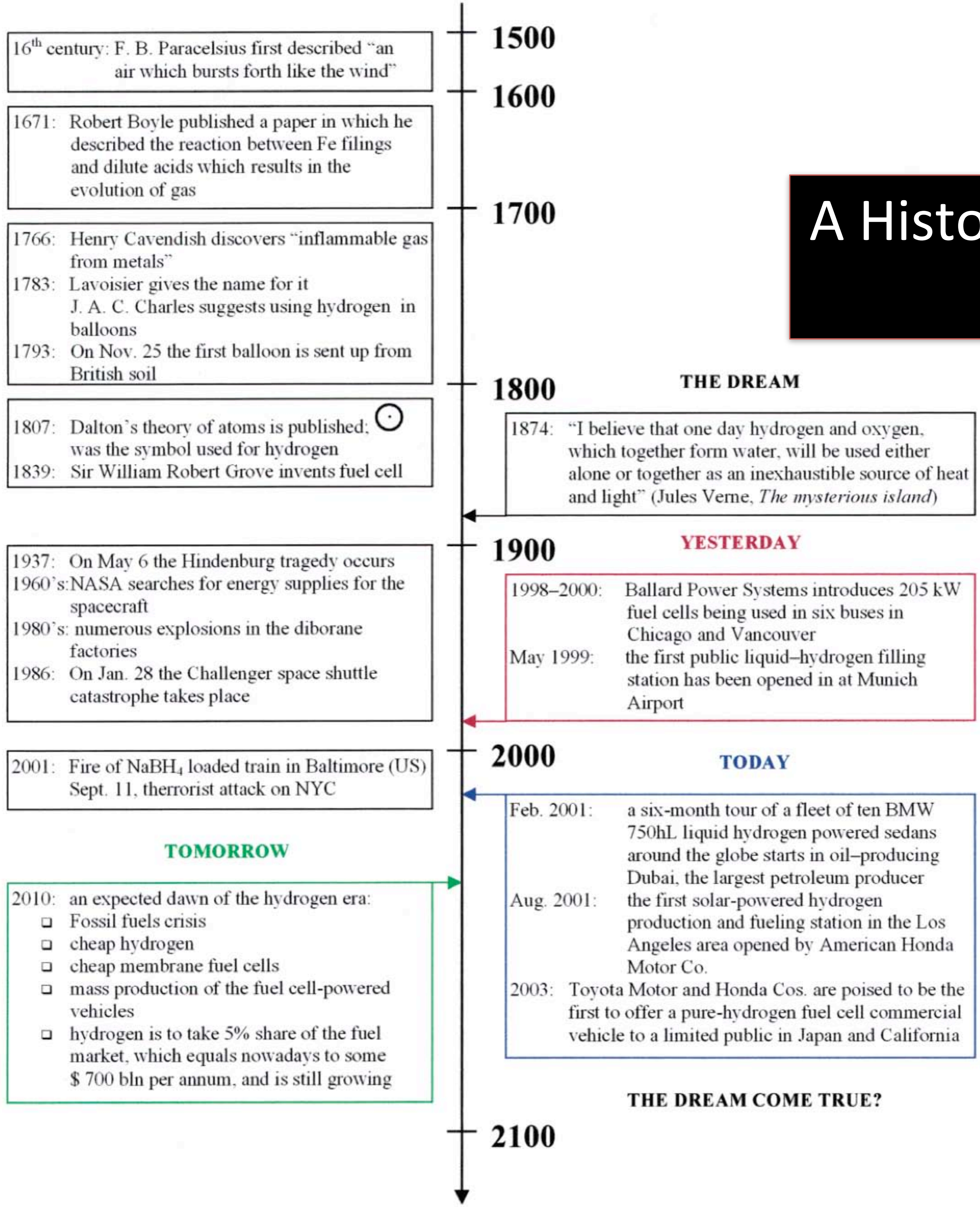


BREAKING NEWS Renault Fluence EV to be assembled in Turkey

# Obama, DOE slash hydrogen fuel cell funding in new budget

by **Sebastian Blanco** (**RSS feed**) on May 8th 2009 at 7:55AM **BREAKING**

# A History of Hydrogen as a Fuel




Chemical Reviews, 2004, Vol. 104, No. 3, Grochala and Edwards

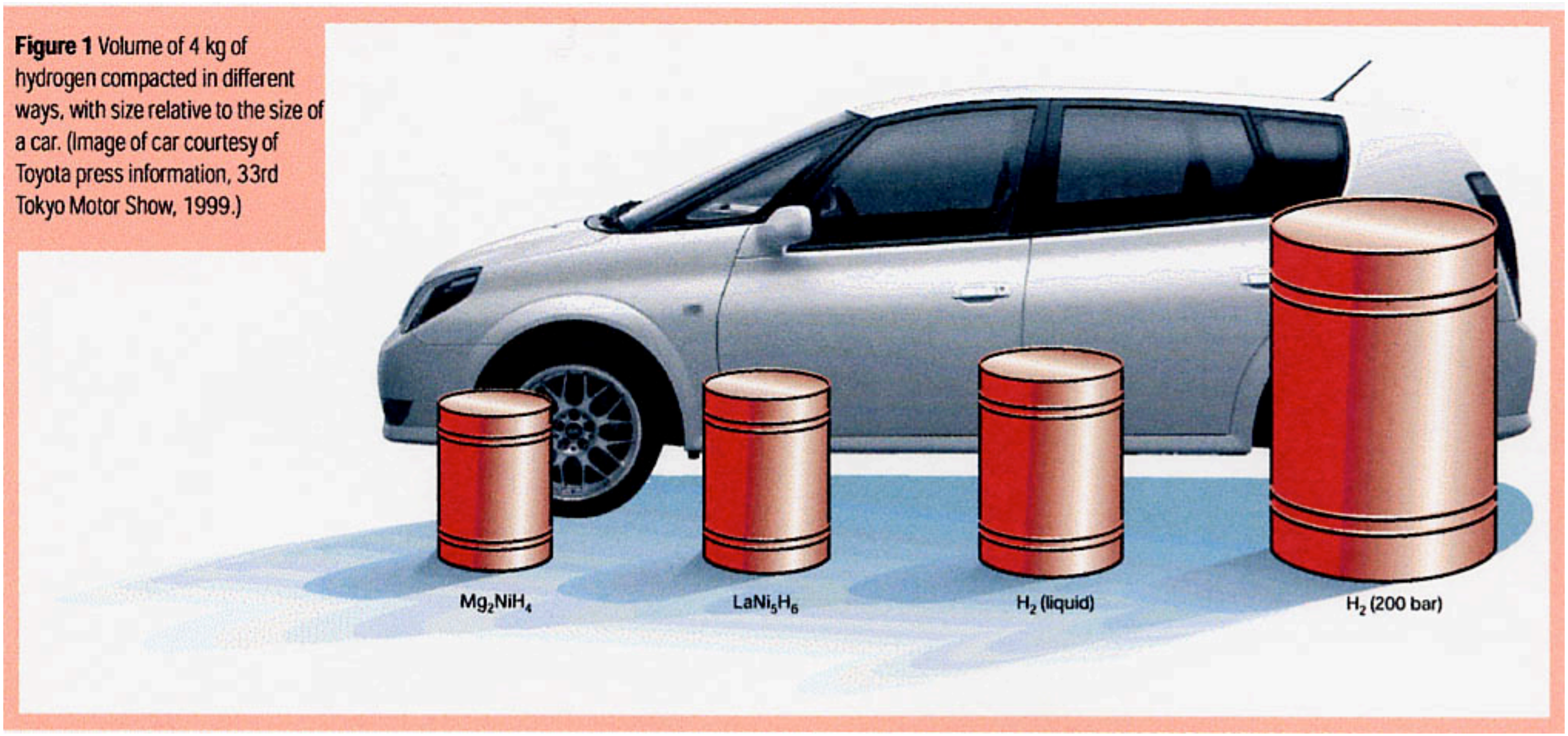
# The Hydrogen Fuel Challenge

- The low volumetric density of gaseous fuels requires a storage method which densifies the fuel.
  - This is particularly true for hydrogen because of its lower energy density relative to hydrocarbon fuels
  - 3 MJ/l (5000 psi $H_2$), 8 MJ/l ($LH_2$) vs. 32 MJ/l (gasoline)
- Storing enough hydrogen on vehicles to achieve greater than 300 miles driving range is difficult.
- Storage system adds an additional weight and volume above that of the fuel.

How do we achieve adequate stored energy in an efficient, safe and cost-effective system?

# How large of a gas tank do you want?

Volume Comparisons for 4 kg Vehicular $H_2$ Storage




Schlapbach & Züttel, Nature, 15 Nov. 2001

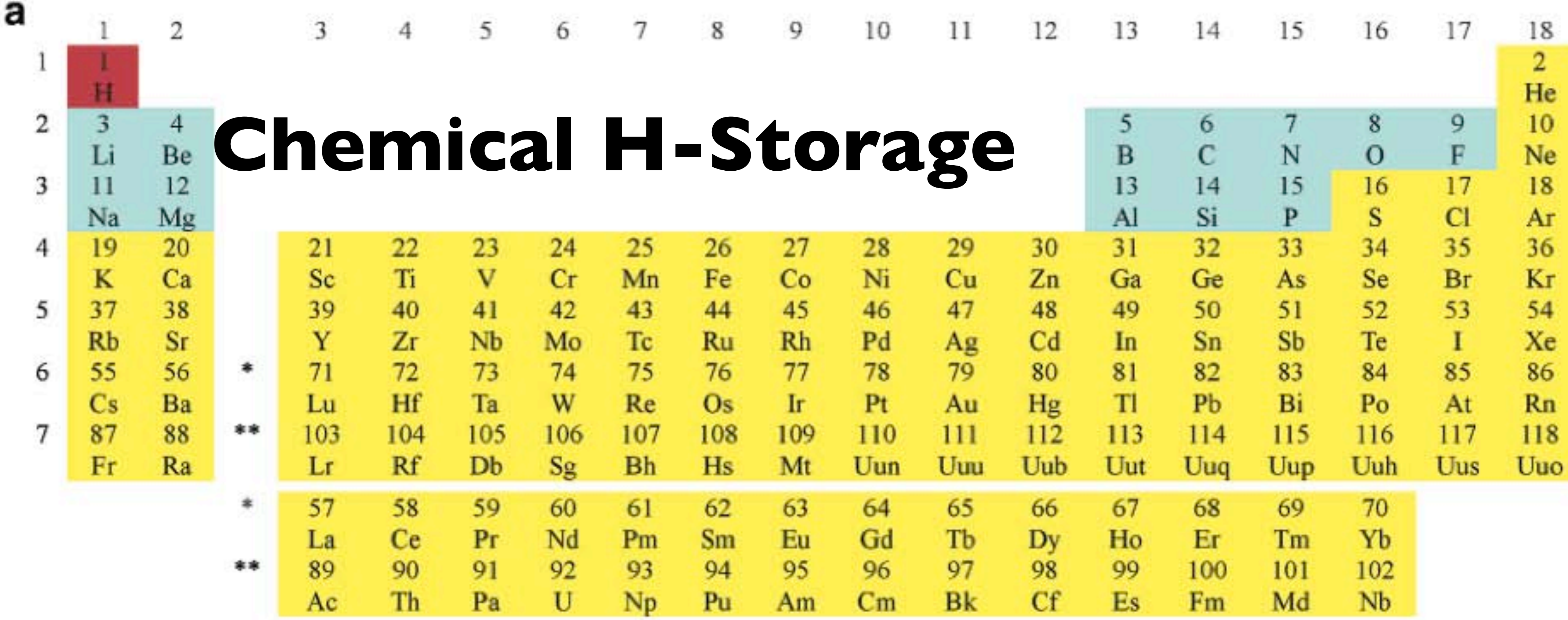
# Compressed/Liquid Hydrogen Storage


**Figure:** Drop Test from 90 feet (27m) stimulates an impact of 52mph

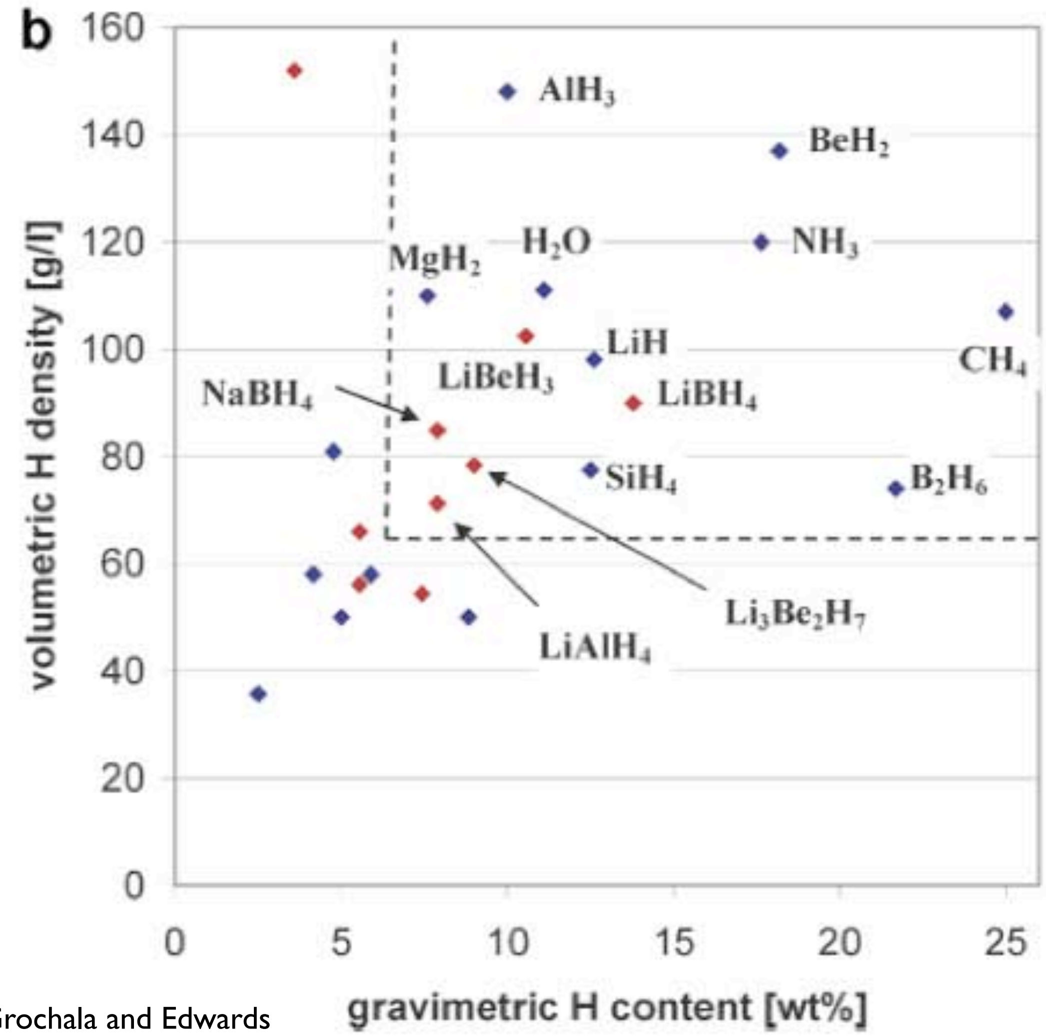


***Packaging volume and safety are key issues***

# Chemical H-Storage




- Only the light elements.
- Short list: Li, Be, B, C, N, O, F, Na, Mg, Al, Si, and P.
- No toxicity!




- List becomes only eight elements.
- Not a lot of room to do chemistry!

Chemical Reviews, 2004, Vol. 104, No. 3, Grochala and Edwards

# Lots of Materials Choices

Crystalline Nanoporous Materials

Polymer Microspheres

Self-Assembled Nanocomposites

Advanced Hydrides

Inorganic – Organic Compounds

BN Nanotubes

Hydrogenated Amorphous Carbon

Mesoporous Materials

Bulk Amorphous Materials (BAMs)

Iron Hydrolysis

Nanosize Powders

Metallic Hydrogen

Hydride Alcoholysis

From Patrovic & Milliken (2003)

# Lots of Materials Choices

| Formula | Formula wt.% Hydrogen |
|---|---|
| $CH_4$ | 25 |
| $H_3BNH_3$ | 19.5 |
| $LiBH_4$ | 18.3 |
| $(CH_3)_4NBH_4$ | 18 |
| $NH_3$ | 17.7 |
| $Al(BH_4)_3$ | 16.8 |
| $Mg(BH_4)_2$ | 14.8 |
| $LiH$ | 12.6 |
| $CH_3OH$ | 12.5 |
| $H_2O$ | 11.2 |
| $LiAlH_4$ | 10.6 |
| $NaBH_4$ | 10.6 |
| $AlH_3$ | 10.0 |
| $MgH_2$ | 7.6 |
| $NaAlH_4$ | 7.4 |

# Example: BN Nanotubes

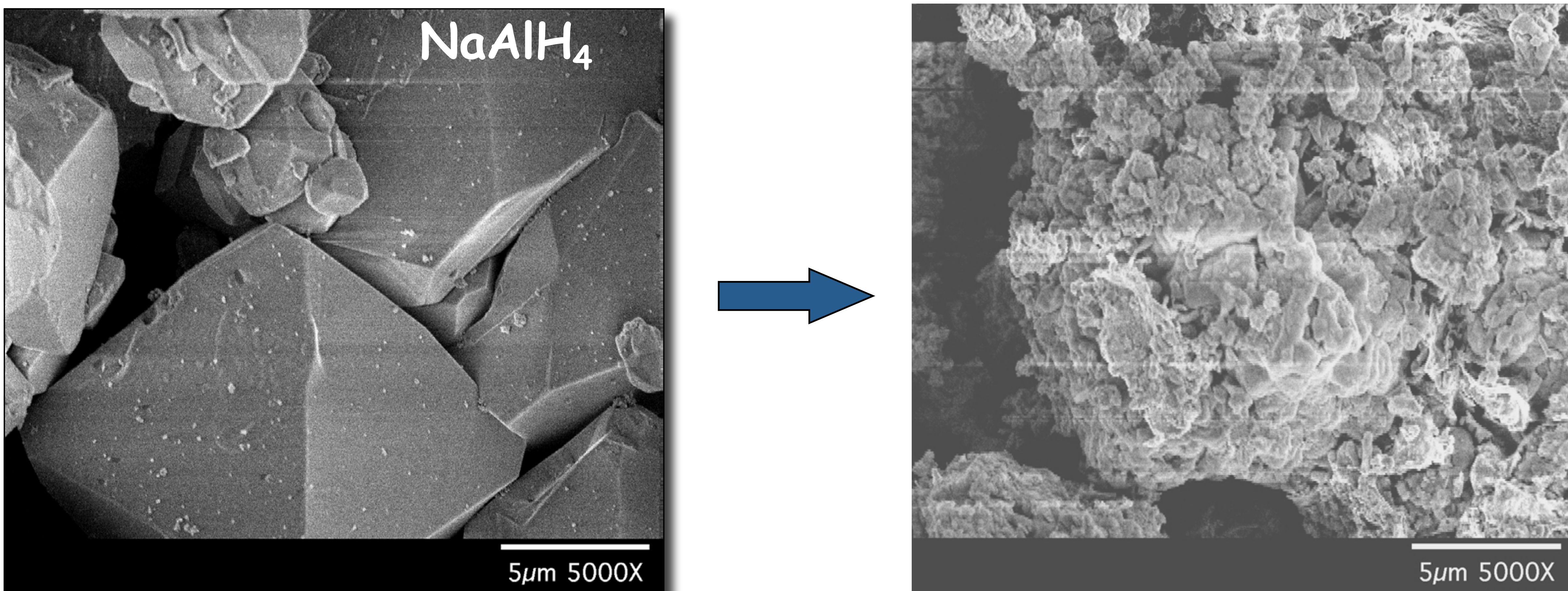
Figure 1 The morphologies of BN nanotubes: (a) multiwall nanotubes and (b) bamboo-like nanotubes. Scale bar: 100 nm.

Figure 2 The hydrogen adsorption as a function of pressure in multiwall BN nanotubes and bamboo nanotubes at 10 MPa is 1.8 and 2.6 wt %, respectively, in sharp contrast to the 0.2 wt % in bulk BN powder. The values reported here have an error of <0.3 wt %.



R. Ma, Y. Bando, H.Zhu, T. Sato, C. Xu, and D. Wu, "Hydrogen Uptake in Boron Nitride Nanotubes at Room Temperature", J. Am. Chem. Soc., 124, 7672-7673 (2002).

# Example: NaAl






*Sodium alanate doped with Ti is a reversible material hydrogen storage approach.*

$$3NaAlH_4 \longrightarrow Na_3AlH_6 + 2Al + 3H_2 \longrightarrow 3NaH + Al + 3/2H_2$$

**3.7 wt%** **1.8 wt%**

**Low hydrogen capacity and slow kinetics are issues**

# Metal Hydrides

- Some metals absorb hydrogen to form metal hydrides

- These release the hydrogen gas when heated at low pressure and relatively high temperature

- Thus the metals soak up and release hydrogen like a sponge

- Hydrogen becomes part of the chemical structure of the metal itself and therefore does not require high pressures or cryogenic temperatures for operation

BUT: irreversibility problem!

Image removed due to copyright restrictions. Table 1 From: Grochala, W., and Peter P. Edwards. *Chemical Reviews* 104 (2004): 1283-315.

# There is no ONE material yet.

- There is, as yet, no material known to meet simultaneously all of the key requirements and criteria.

- Palladium metal has long been viewed as an attractive hydrogen-storage medium, exhibiting reversible behavior at quite low temperature. However, its poor storage efficiency (less than 1 wt %) and the high cost of palladium ($1000 per ounce) eliminate it from any realistic consideration

- On the other hand, the composite material "Li3Be2H7" is a highly efficient storage medium (ca. 8.7 wt % of reversibly stored H), but it is highly toxic and operates only at temperatures as high as 300 °C.

# There is no ONE material yet.

- Or take $AlH_3$: the compound is a relatively low temperature (150 °C), highly efficient (10.0 wt %) storage material and contains cheap Al metal ($1300 per tonne), but, unfortunately, its hydrogen uptake is almost completely irreversible.

- Similarly, an alkaline solution of $NaBH_4$ in $H_2O$ constitutes a super-efficient storage system (9.2 wt % hydrogen), and full control may be gained over $H_2$ evolution by use of a proper catalyst, but the starting material cannot be simply (economically) regenerated.

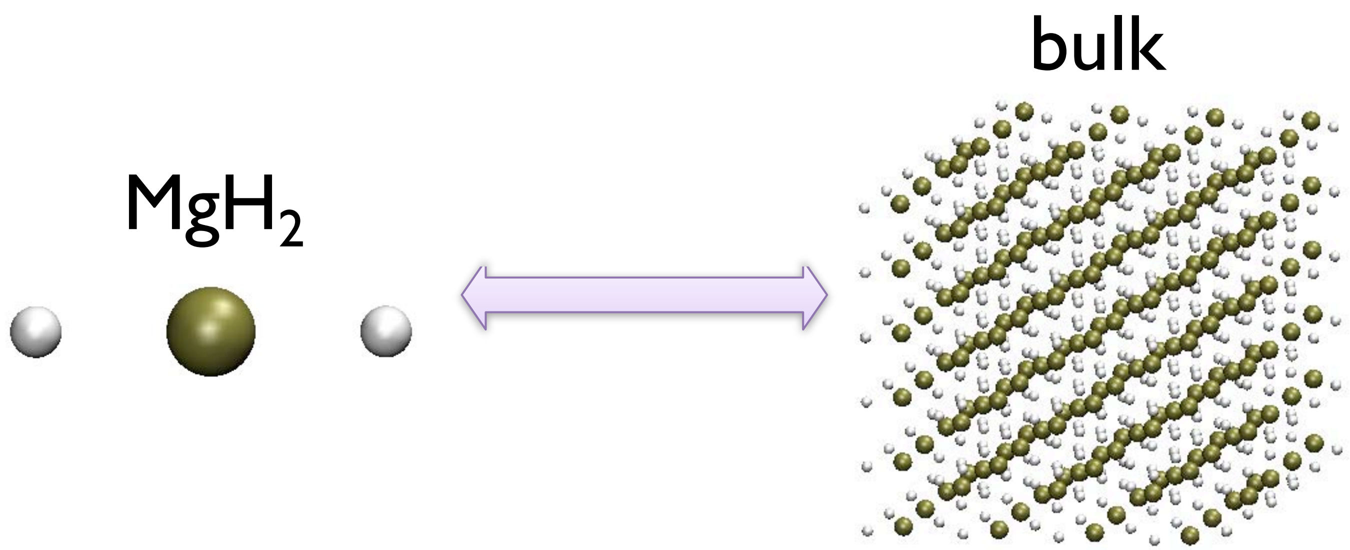
- Finally, pure water contains 11.1 wt % of H, but its decomposition requires much thermal, electric, or chemical energy.

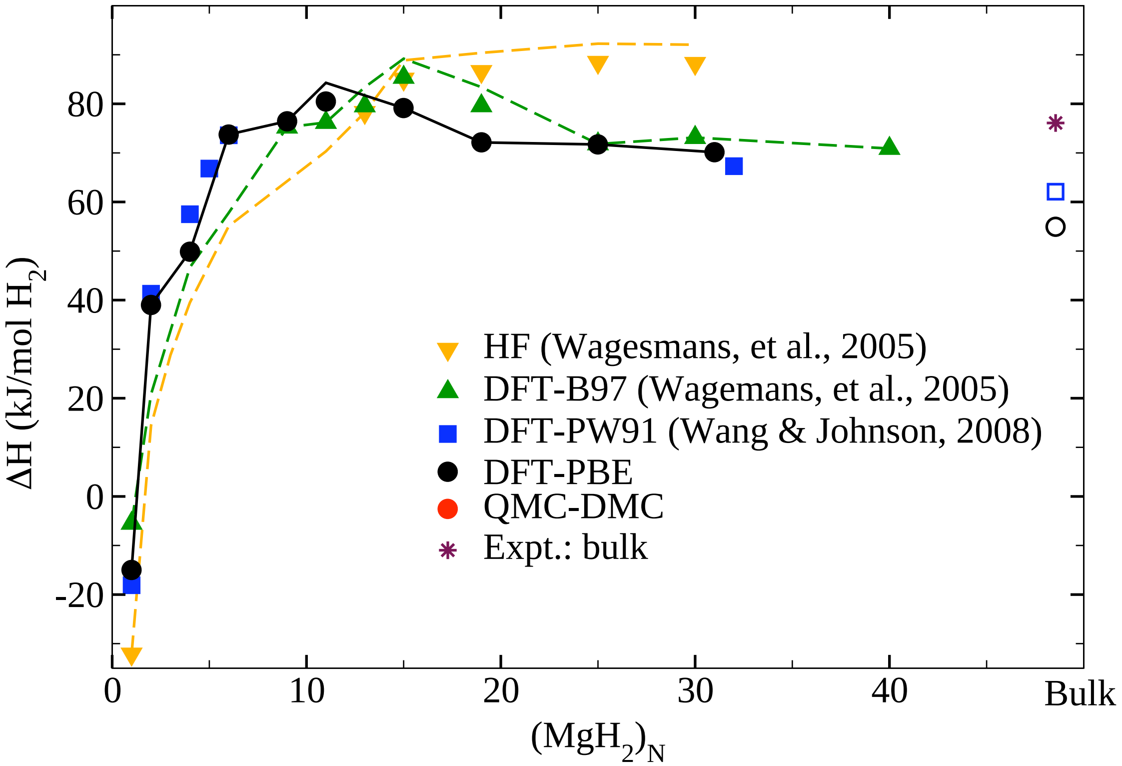
- Recently advanced technology of hydrogen storage in nitrides and imides allows for effective (6.5-7.0 wt % H) but high- temperature (around 300 °C) storage.

# PERFECT Problem for Computational Quantum Mechanics!


Image is in the public domain.

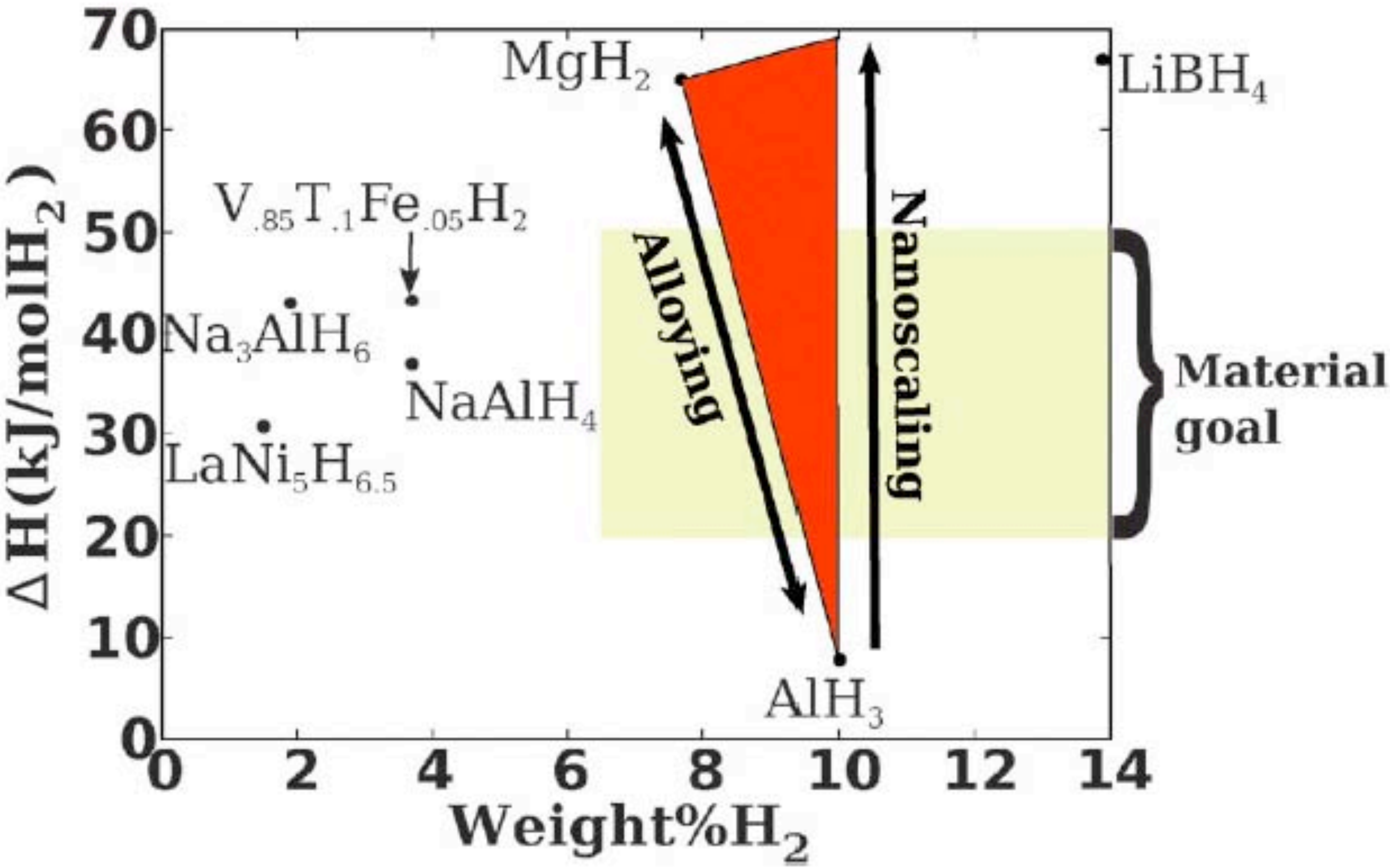
- Hydrogen storage: store hydrogen in a lightweight and compact manner for mobile applications.
- Bulk materials are often too stable.
  - E.g. $MgH_2$: 7.7wt%, $\Delta H^0_d$ = 75 kJ/mol, $T_d$ ~ 300 °C
- Desirable $\Delta H^0_d$ = **20 – 50** kJ/mol
- $\Delta H^0_d$ can be **tuned** by the size of nanoparticles.




Wu, Allendorf, and JCG, JACS (2009)

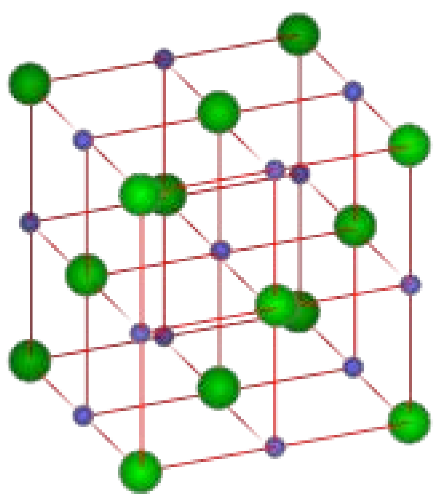
# Alloying and Nanostructuring May be the Key, but Phase Space is Enormous






Wagner, Allendorf, and JCG, PCCP (2012)

# From Atoms to Solids




# From atoms to solids

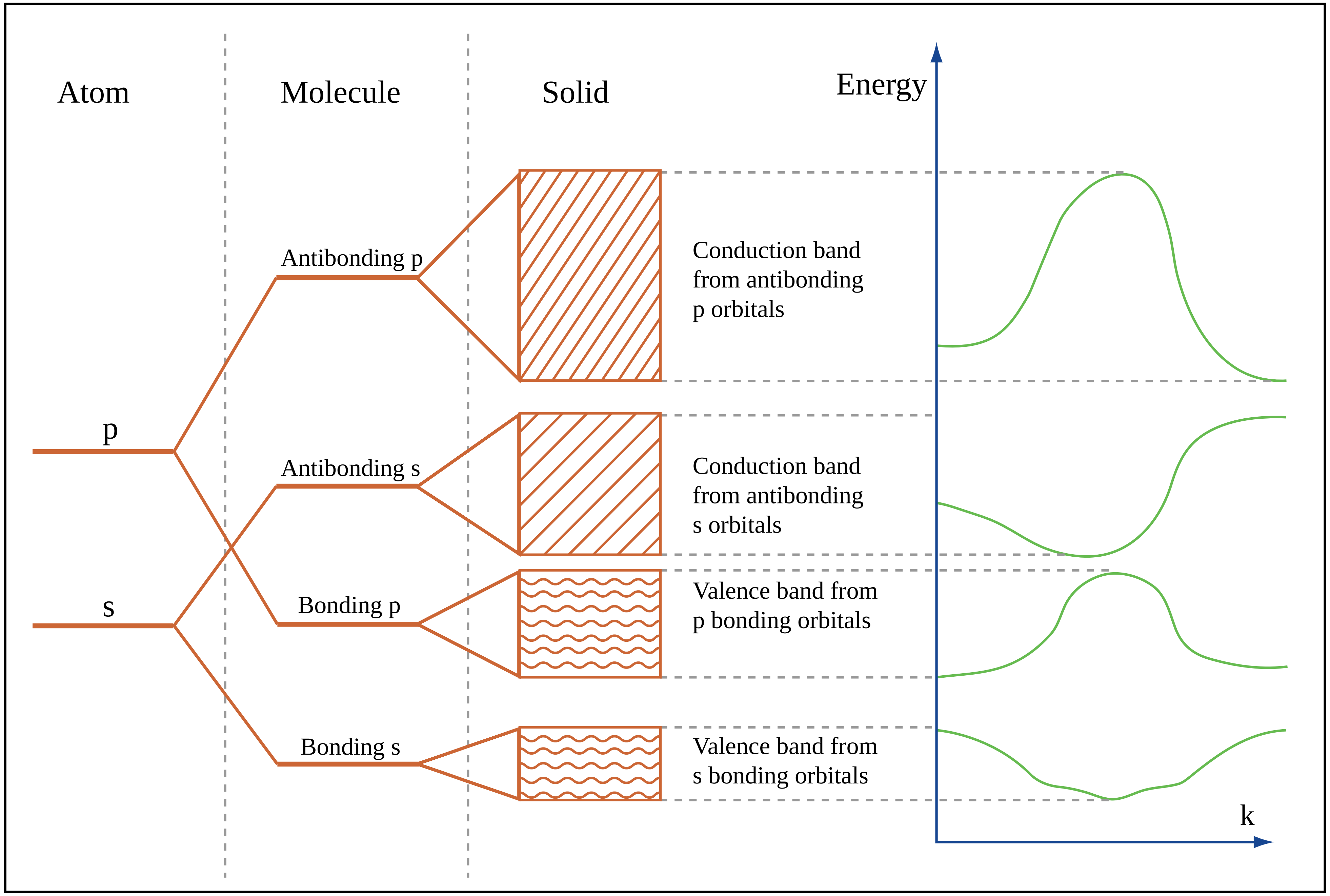
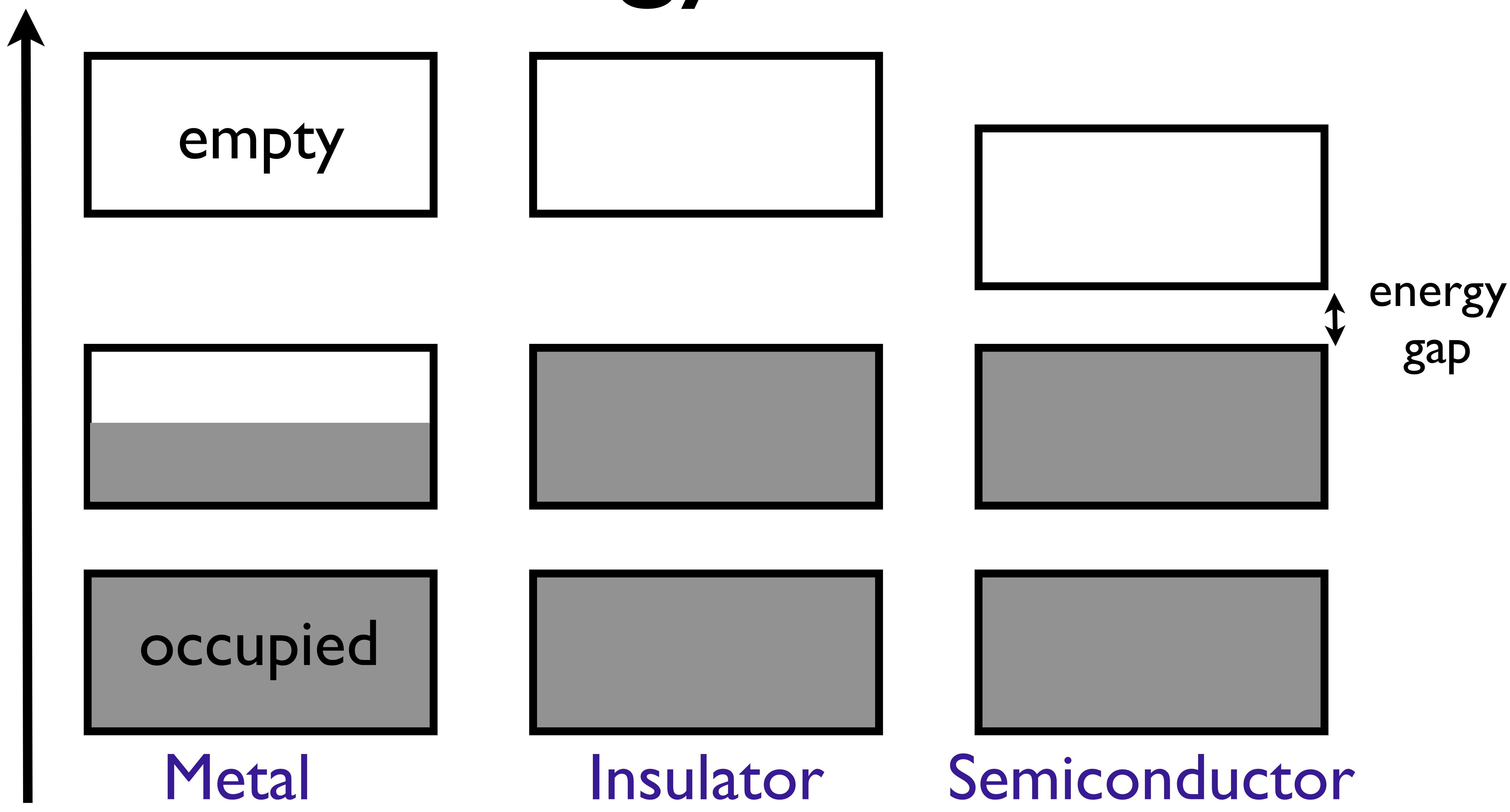



Image by MIT OpenCourseWare.

The ground state electron configuration of a system is constructed by putting the available electrons, two at a time (Pauli principle), into the states of lowest energy

# Energy bands




NB: boxes = allowed energy regions

# Crystal symmetries

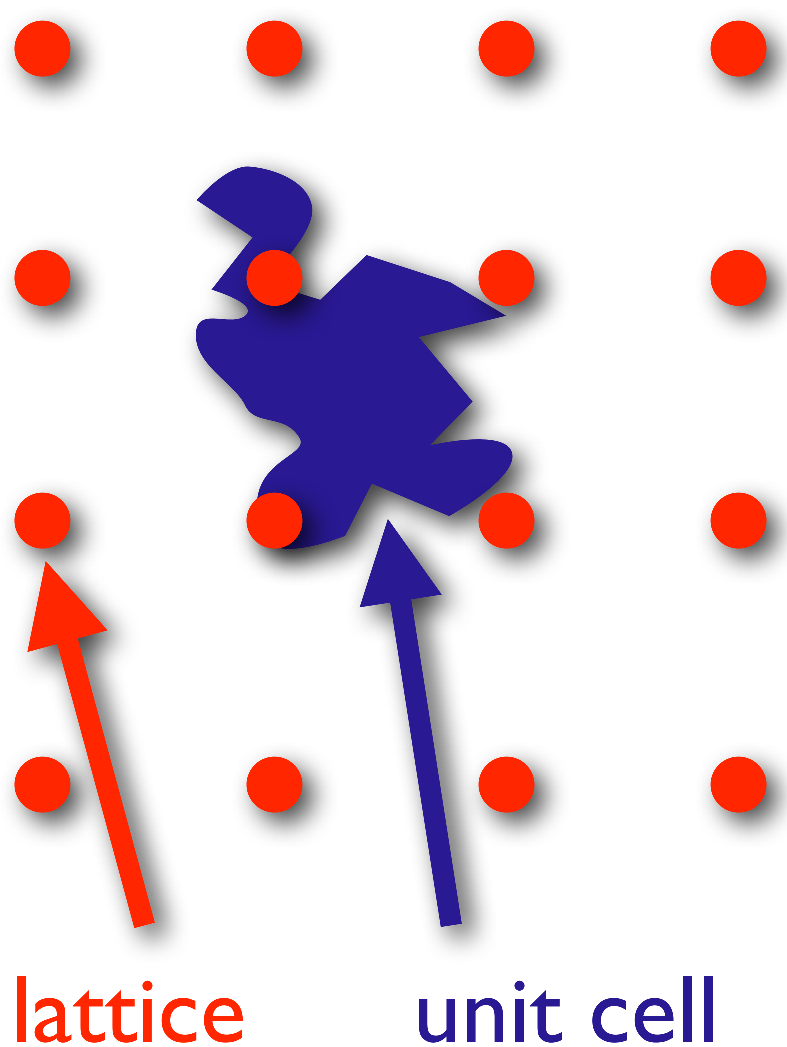
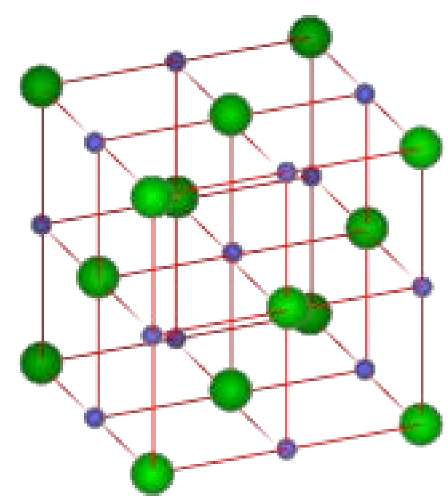



Image of Sketch 96 (Swans) by M.C. Escher removed due to copyright restrictions.

A crystal is built up of a unit cell and periodic replicas thereof.

# Crystal symmetries

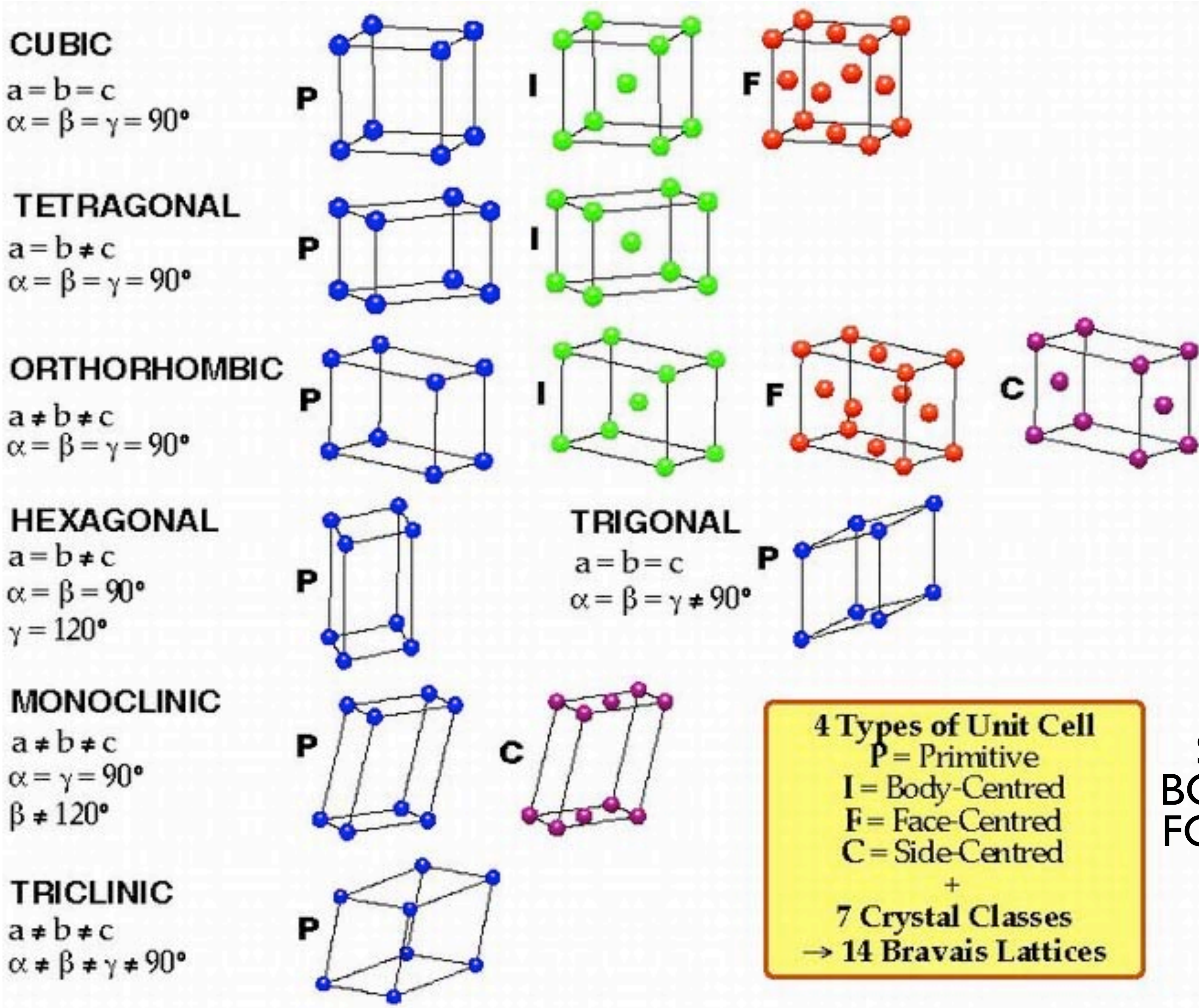

crystal/solid



$10^{23}$ particles per $cm^3$

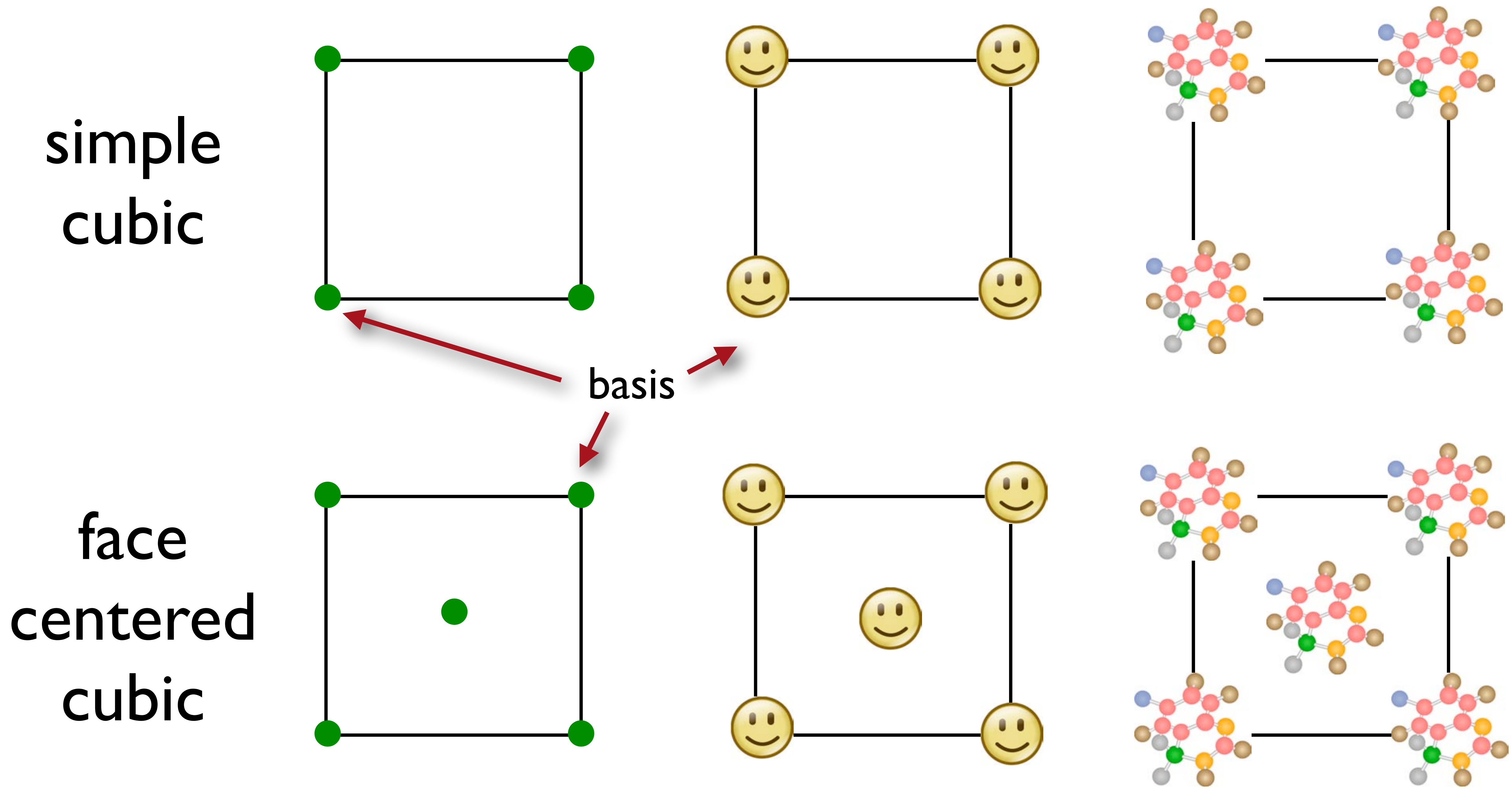
Since a crystal is periodic, maybe we can get away with modeling only the unit cell?

# Crystal symmetries




S = simple
BC = body centered
FC = face centered

# Lattice and basis




Images by MIT OpenCourseWare.

# The inverse (or “reciprocal”) lattice

Associated with each real space lattice, there exists something we call a reciprocal lattice.

The reciprocal lattice is the set of wave-vectors which are commensurate with the real space lattice.

It is defined by a set of vectors a*, b*, and c* such that a* is perpendicular to b and c of the Bravais lattice, and the product a* x a is 1.

# The inverse lattice

The real space lattice is described by three basis vectors:

$$\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$$

The inverse lattice is described by three basis vectors:

$$\vec{G} = m_1\vec{b}_1 + m_2\vec{b}_2 + m_3\vec{b}_3$$

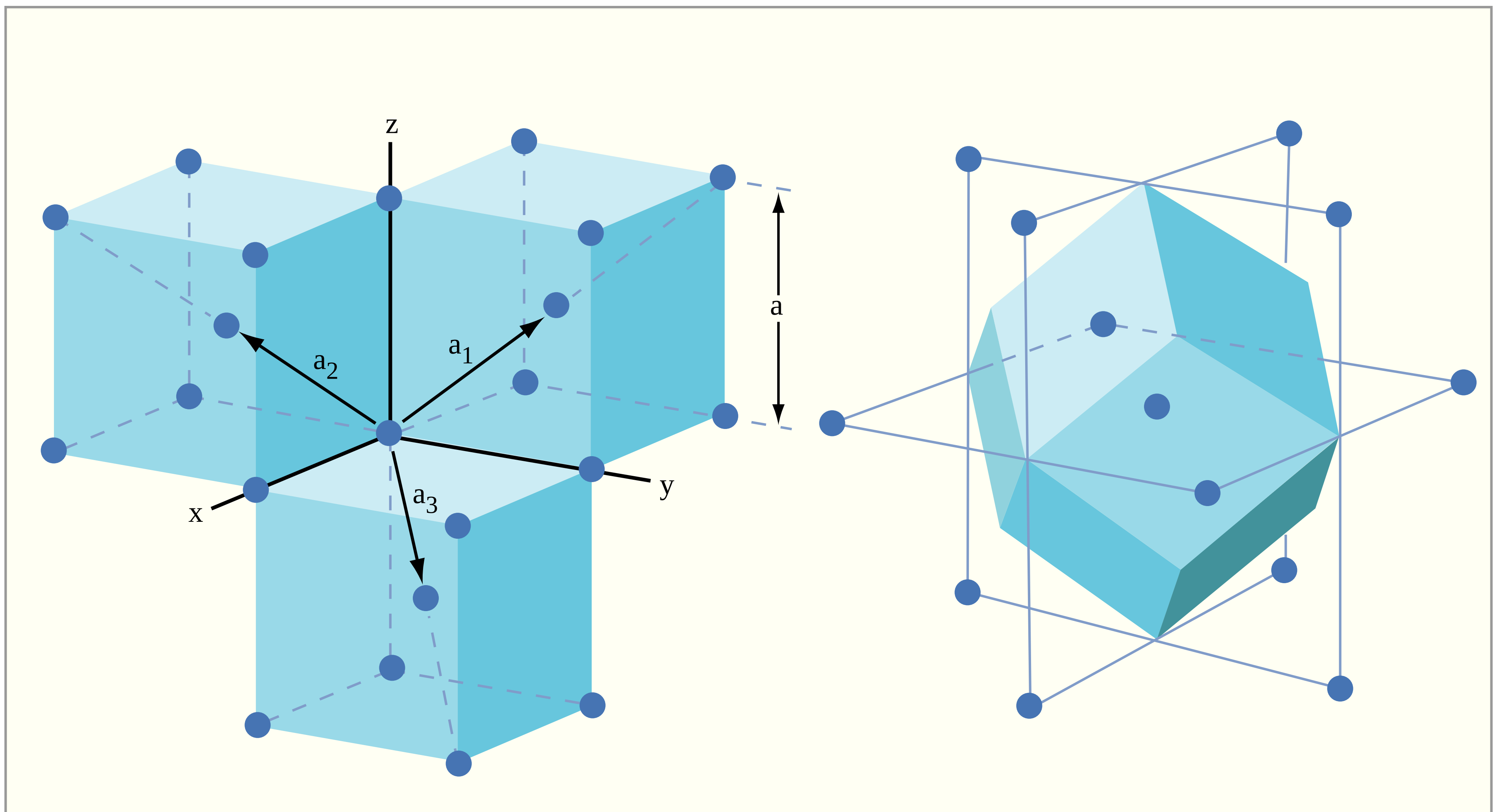
$$\mathbf{b}_1 = 2\pi\frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \qquad \mathbf{b}_2 = 2\pi\frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_2 \cdot (\mathbf{a}_3 \times \mathbf{a}_1)} \qquad \mathbf{b}_3 = 2\pi\frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_3 \cdot (\mathbf{a}_1 \times \mathbf{a}_2)}$$

$$e^{i\vec{G}\cdot\vec{R}} = 1 \longrightarrow \psi(\vec{r}) = \sum_j c_j e^{i\vec{G}_j\cdot\vec{r}}$$

automatically periodic in R!

# The inverse lattice

real space lattice (BCC) inverse lattice (FCC)

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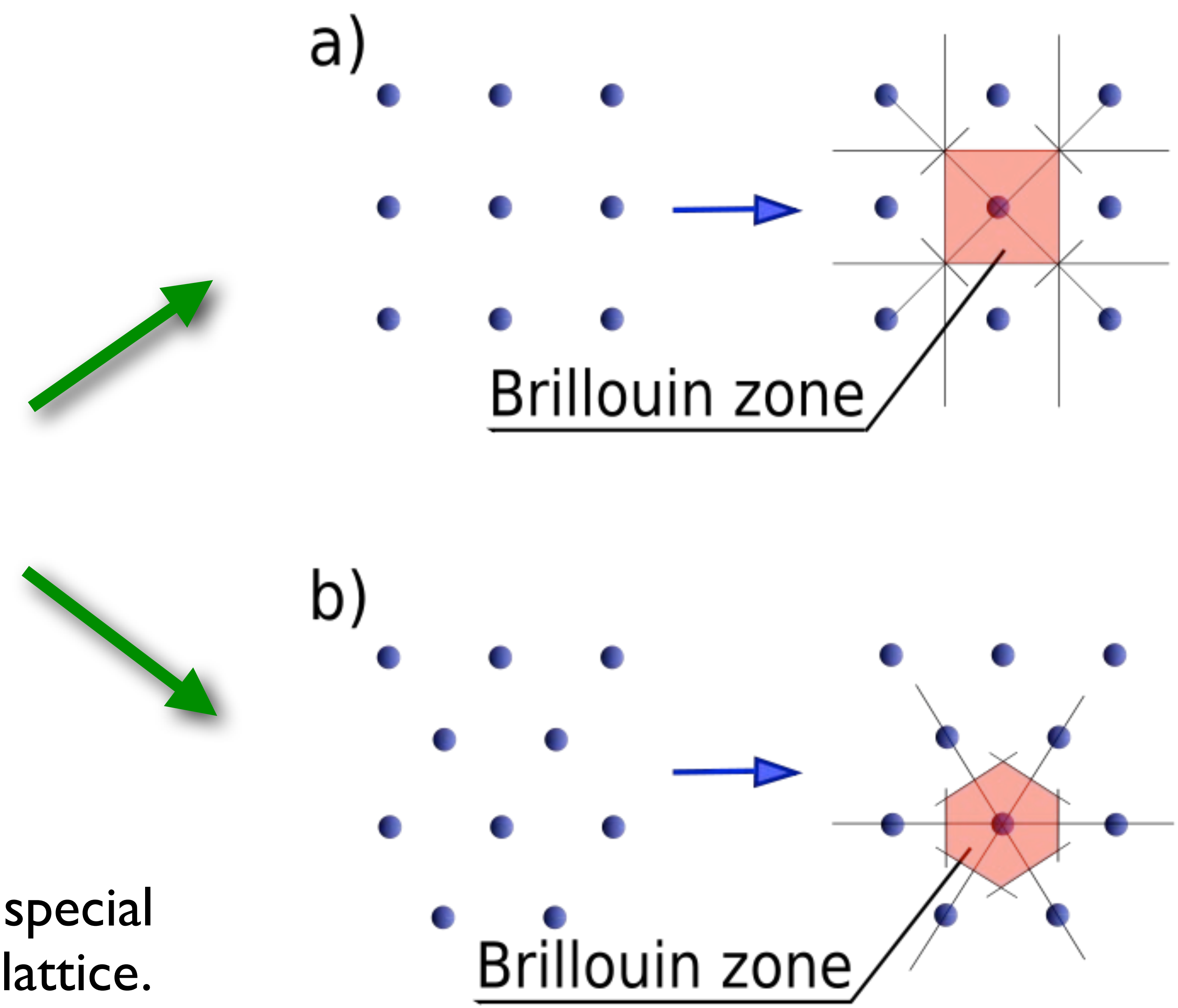
# The Brillouin zone

inverse lattice



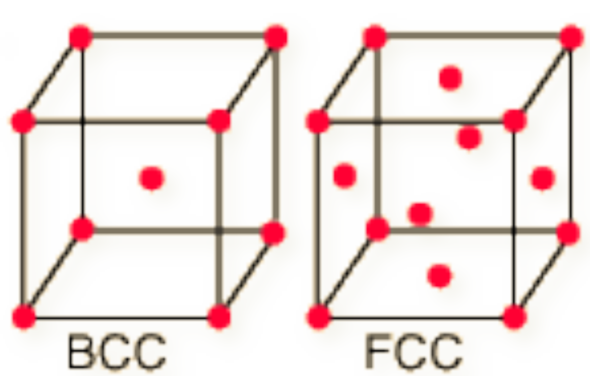

The Brillouin zone is a special unit cell of the inverse lattice.

# Reciprocal Lattice & Brillouin Zone

It is defined by a set of vectors a*, b*, and c* such that a* is perpendicular to b and c of the Bravais lattice, and the product a* x a is 1.

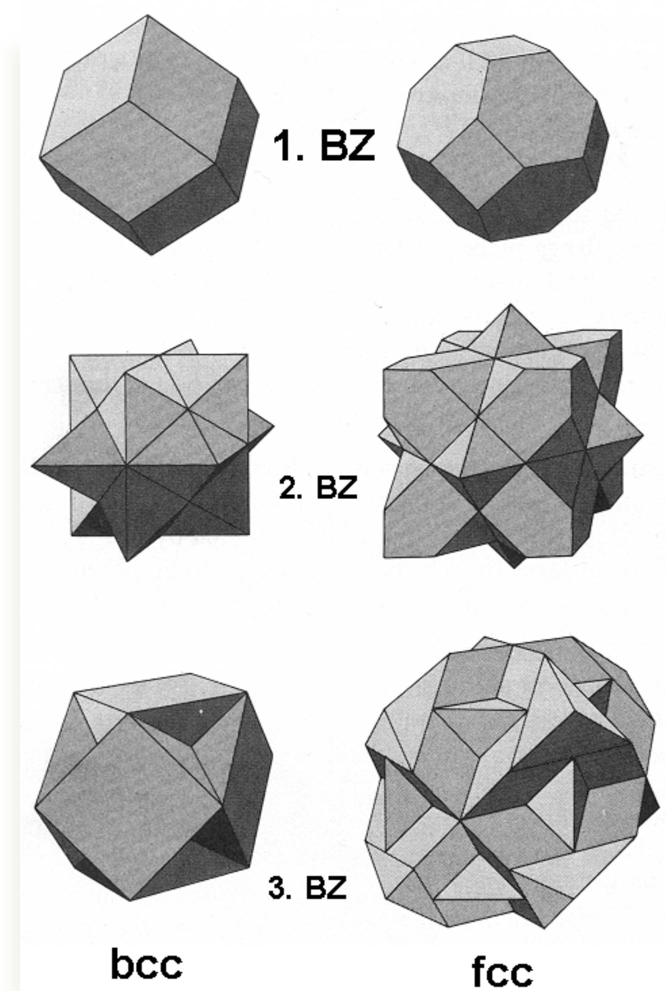
In particular: $$\mathbf{a}^* = \frac{\mathbf{b}\times\mathbf{c}}{\mathbf{a}\cdot\mathbf{b}\times\mathbf{c}}$$

Image is in the public domain.




Brillouin

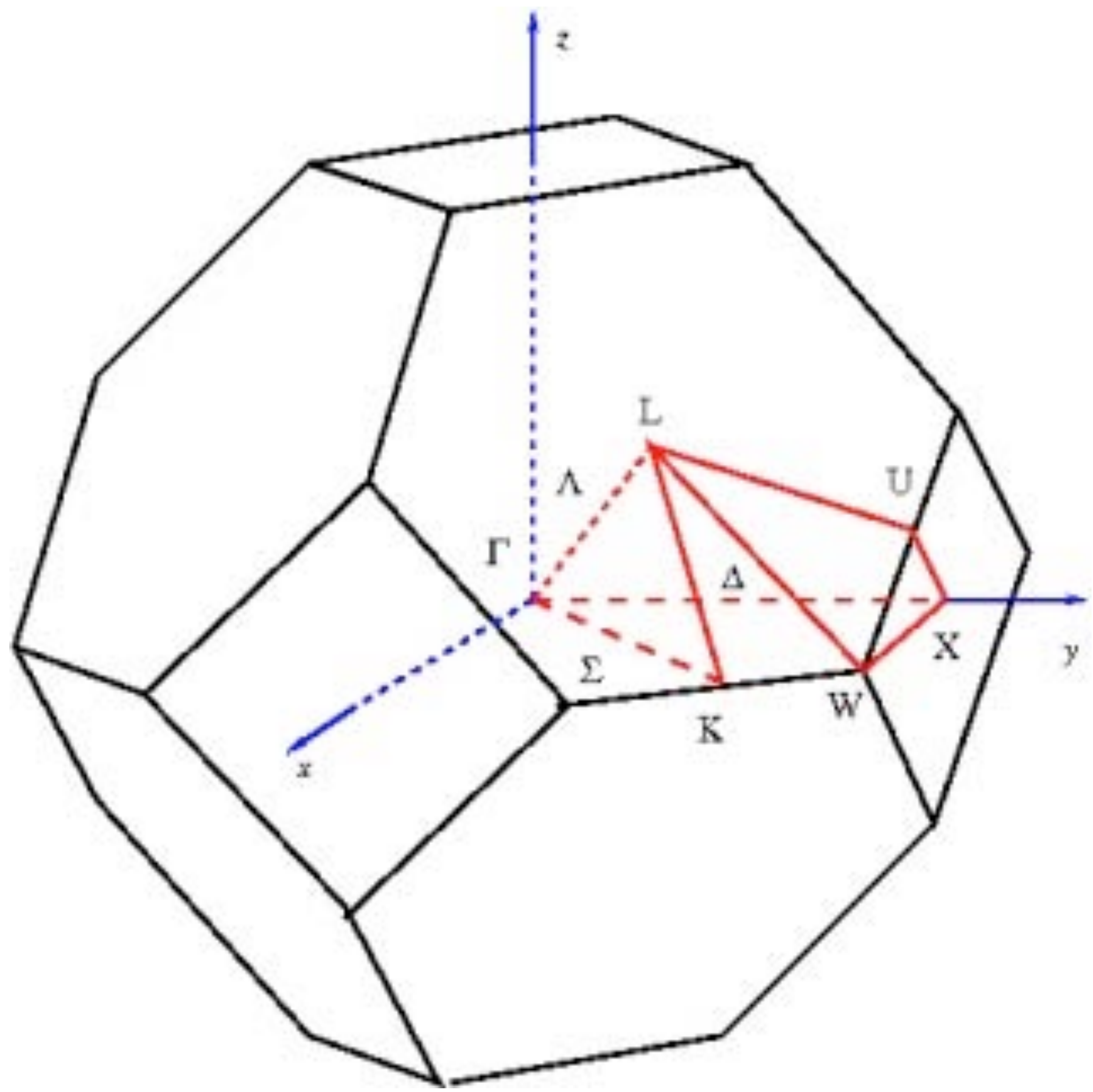
$$\longrightarrow \quad \mathbf{a}^* = \frac{\mathbf{b}\times\mathbf{c}}{\mathbf{a}\cdot\mathbf{b}\times\mathbf{c}} \quad \longrightarrow$$






Surfaces of the first, second, and third Brillouin zones for body-centered cubic and face-centered cubic crystals. Images are in the public domain.

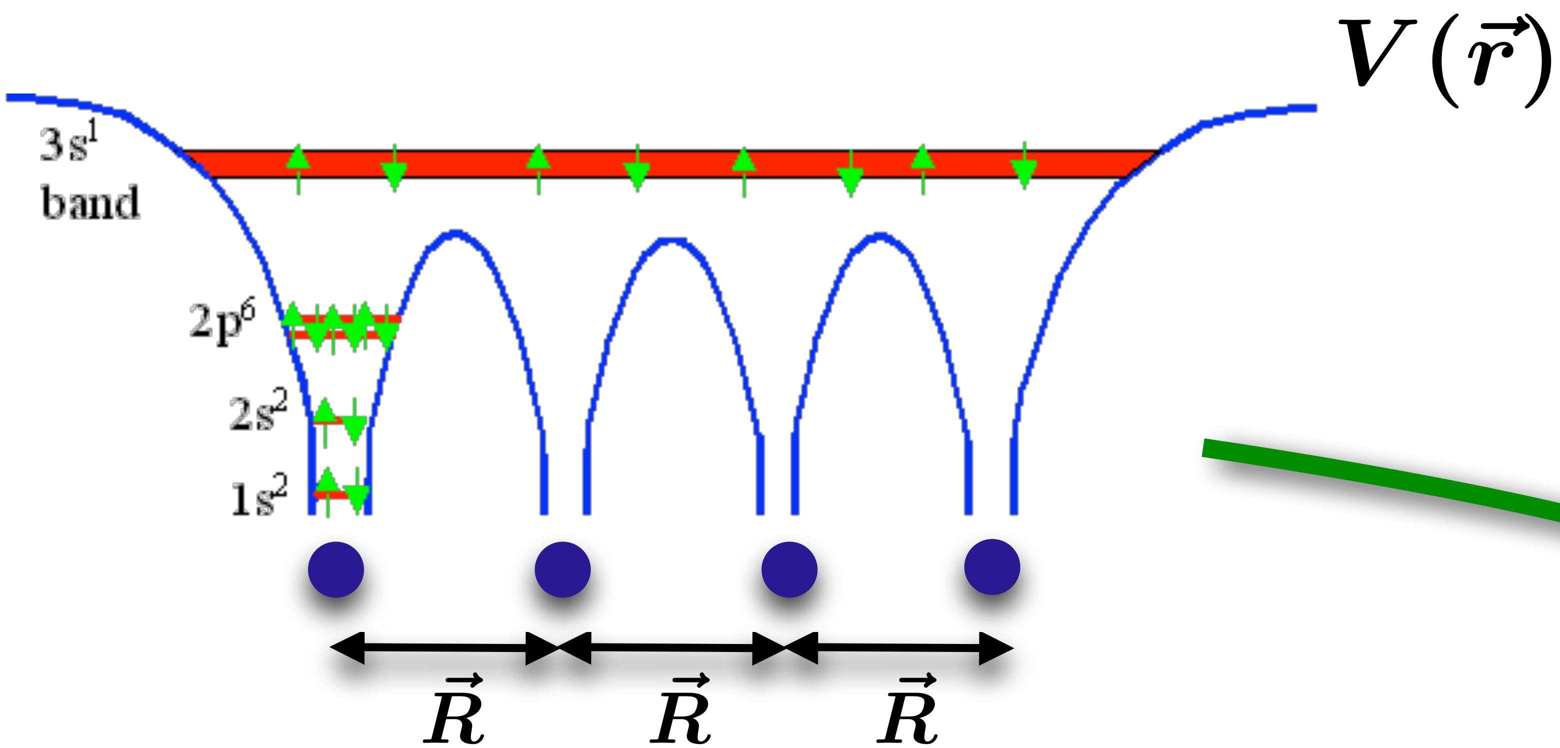
# The Brillouin zone




Brillouin zone of the FCC lattice

# Periodic potentials

metallic sodium




$$\left[-\frac{\hbar}{2m}\nabla^2 + V(\vec{r})\right]\psi = E\psi$$

# Periodic potentials

It becomes much easier if you use the periodicity of the potential!

lattice vector

$$V(\vec{r}) = V(\vec{r} + \vec{R})$$

Results in a VERY important new concept.

Bloch's Theorem

# Bloch's Theorem

Reciprocal lattice vectors have special properties of particular value for calculations of solids.

We write the reciprocal lattice vector:

$$\mathbf{G} = 2\pi n\mathbf{a}^* + 2\pi m\mathbf{b}^* + 2\pi o\mathbf{c}^*$$

We added the 2 simply for convenience, and the n, m, o, are integers.

Now consider the behavior of the function exp(iGr).

# Bloch's Theorem

$$\exp(i\mathbf{G}\cdot\mathbf{r}) = \exp\left[i(2\pi n\mathbf{a}^* + 2\pi m\mathbf{b}^* + 2\pi o\mathbf{c}^*)\cdot(\alpha\mathbf{a} + \beta\mathbf{b} + \gamma\mathbf{c})\right]$$

$$= \exp\left[i(2\pi n\alpha + 2\pi m\beta + 2\pi o\gamma)\right]$$

$$= \cos(2\pi n\alpha + 2\pi m\beta + 2\pi o\gamma) + i\sin(2\pi n\alpha + 2\pi m\beta + 2\pi o\gamma)$$

As **r** is varied, lattice vector coefficients (α,β,γ) change between 0 and 1 and the function exp(i**G**.**r**) changes too.

However, since n, m, and o are integral, exp(i**G**.**r**) will always vary with the periodicity of the real-space lattice.

$$e^{i\vec{G}\cdot\vec{R}} = 1 \longrightarrow \psi(\vec{r}) = \sum_j c_j e^{i\vec{G}_j\cdot\vec{r}}$$

automatically periodic in R!

# Bloch's Theorem

The periodicity of the lattice in a solid means that the values of a function (e.g., density) will be identical at equivalent points on the lattice.

The wavefunction, on the other hand, is periodic but only when multiplied by a phase factor.

NEW quantum number k that lives in the inverse lattice!

This is known as Bloch's theorem.

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r})$$

$$u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r} + \vec{R})$$

# Periodic potentials

Results of the Bloch theorem:



$$\psi_{\vec{k}}(\vec{r}+\vec{R}) = \psi_{\vec{k}}(\vec{r})e^{i\vec{k}\cdot\vec{R}}$$

$$|\psi_{\vec{k}}(\vec{r}+\vec{R})|^2 = |\psi_{\vec{k}}(\vec{r})|^2$$

charge density
is lattice periodic

if solution $\psi_{\vec{k}}(\vec{r}) \longrightarrow \psi_{\vec{k}+\vec{G}}(\vec{r})$ also solution

with $E_{\vec{k}} = E_{\vec{k}+\vec{G}}$

# Periodic potentials

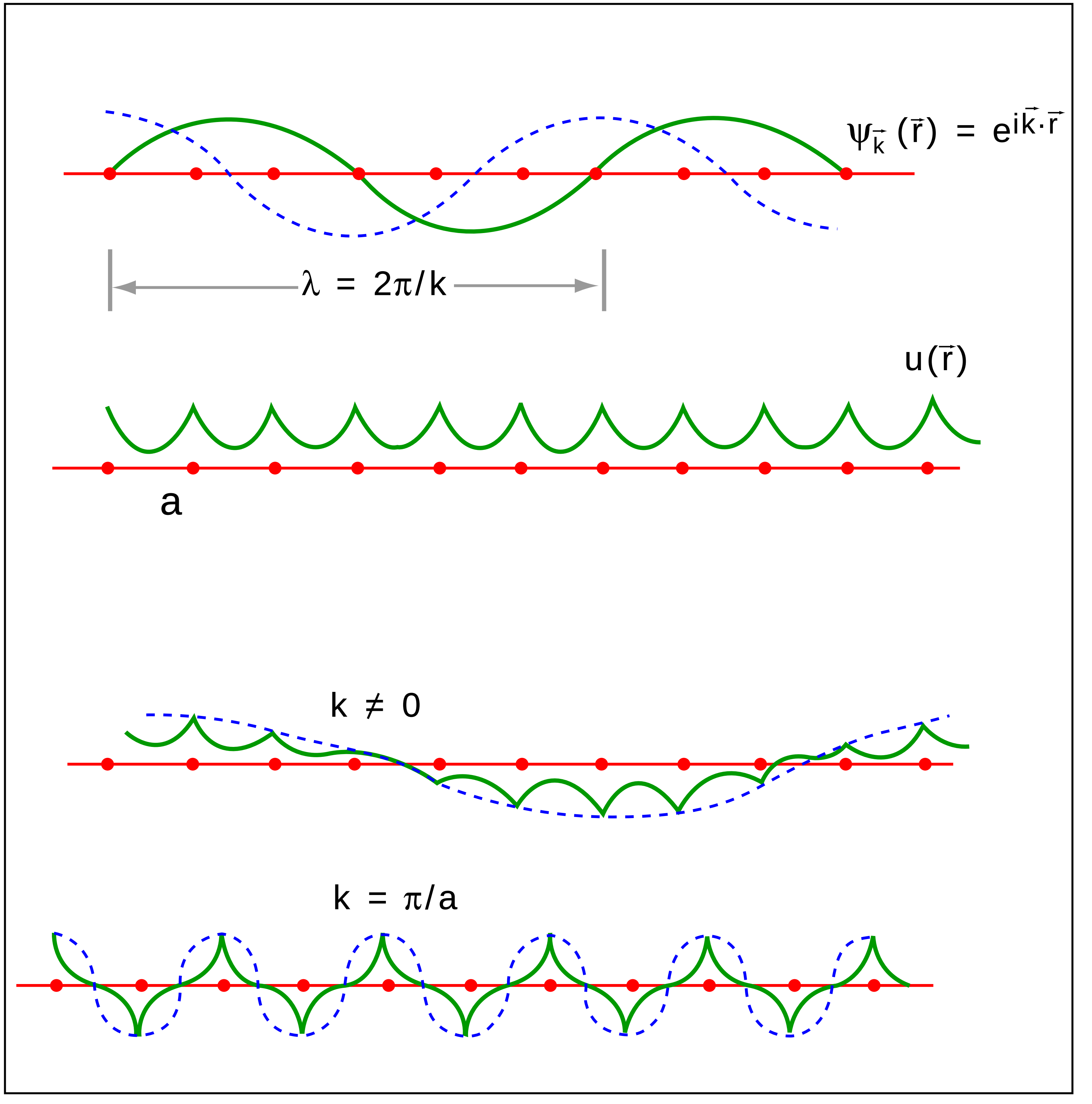
| Schrödinger equation | certain symmetry | quantum number |
|---|---|---|
| hydrogen atom | spherical symmetry $[H, L^2] = HL^2 - L^2H = 0$ $[H, L_z] = 0$ | $\psi_{n,l,m}(\vec{r})$ |
| periodic solid | translational symmetry $[H, T] = 0$ | $\psi_{n,\vec{k}}(\vec{r})$ |

# Periodic potentials

## Bloch's theorem

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r})$$

$$u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r} + \vec{R})$$

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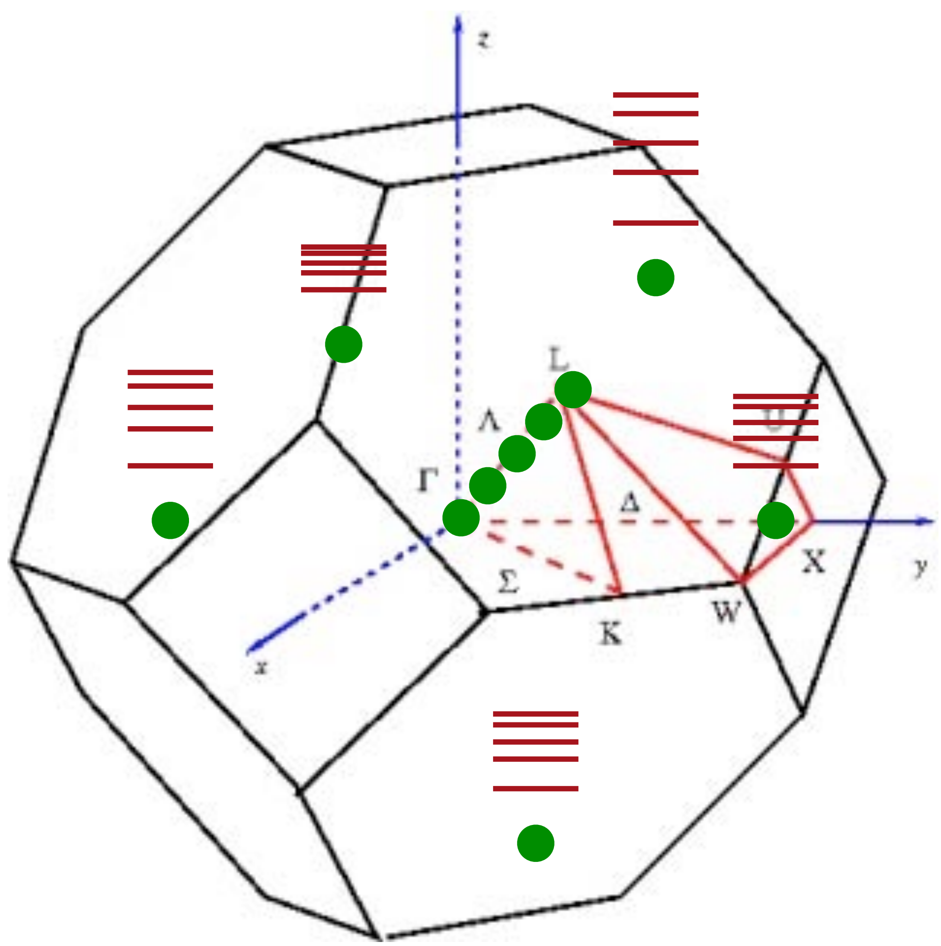
# The band structure

Different wave functions can satisfy the Bloch theorem for the same ***k***: eigenfunctions and eigenvalues labelled with ***k*** and the index n

$$[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})]\psi_{\vec{k}}(\vec{r}) = \epsilon_{\vec{k}}\psi_{\vec{k}}(\vec{r}) \longrightarrow \begin{array}{c} \psi_{n,\vec{k}}(\vec{r}) \\ \epsilon_{n,\vec{k}} \end{array}$$

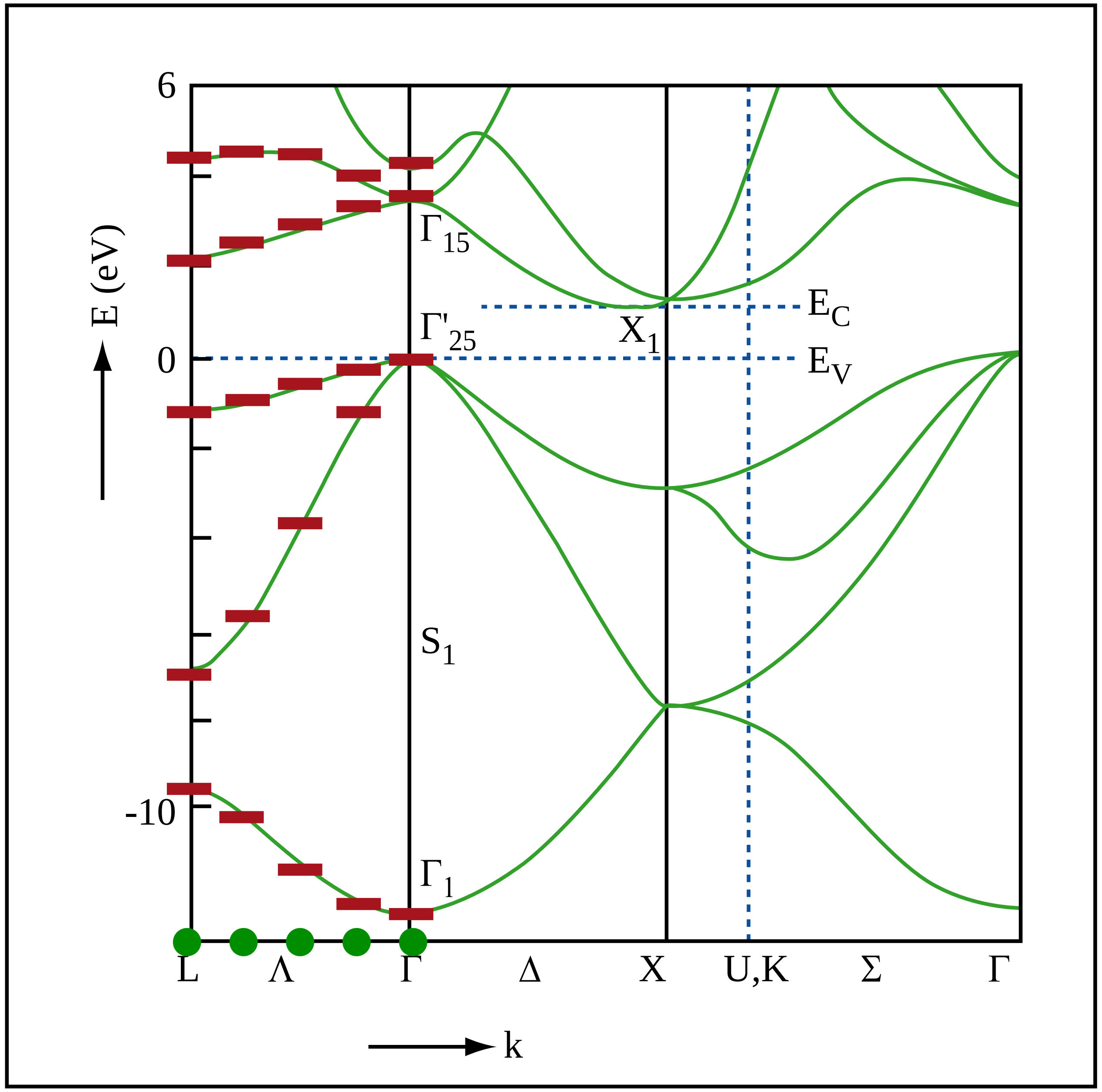
energy bands

# The band structure




energy levels
in the Brillouin zone

Silicon

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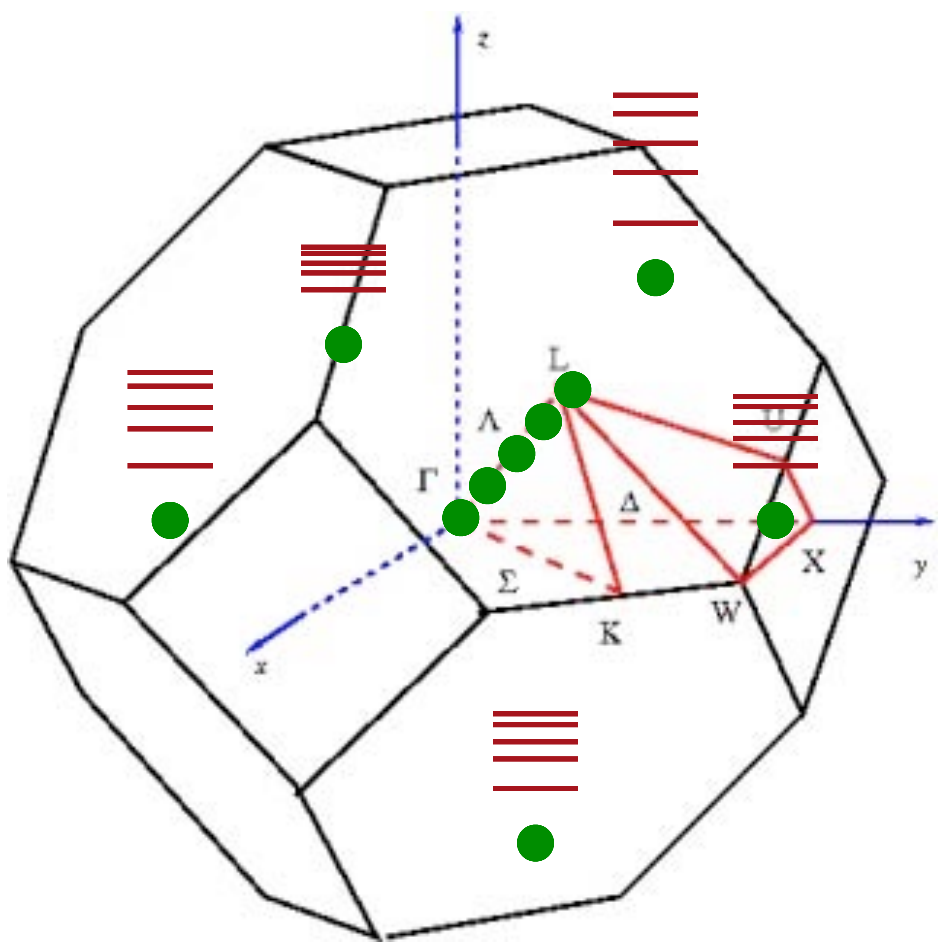
# The band structure




energy levels
in the Brillouin zone

Silicon

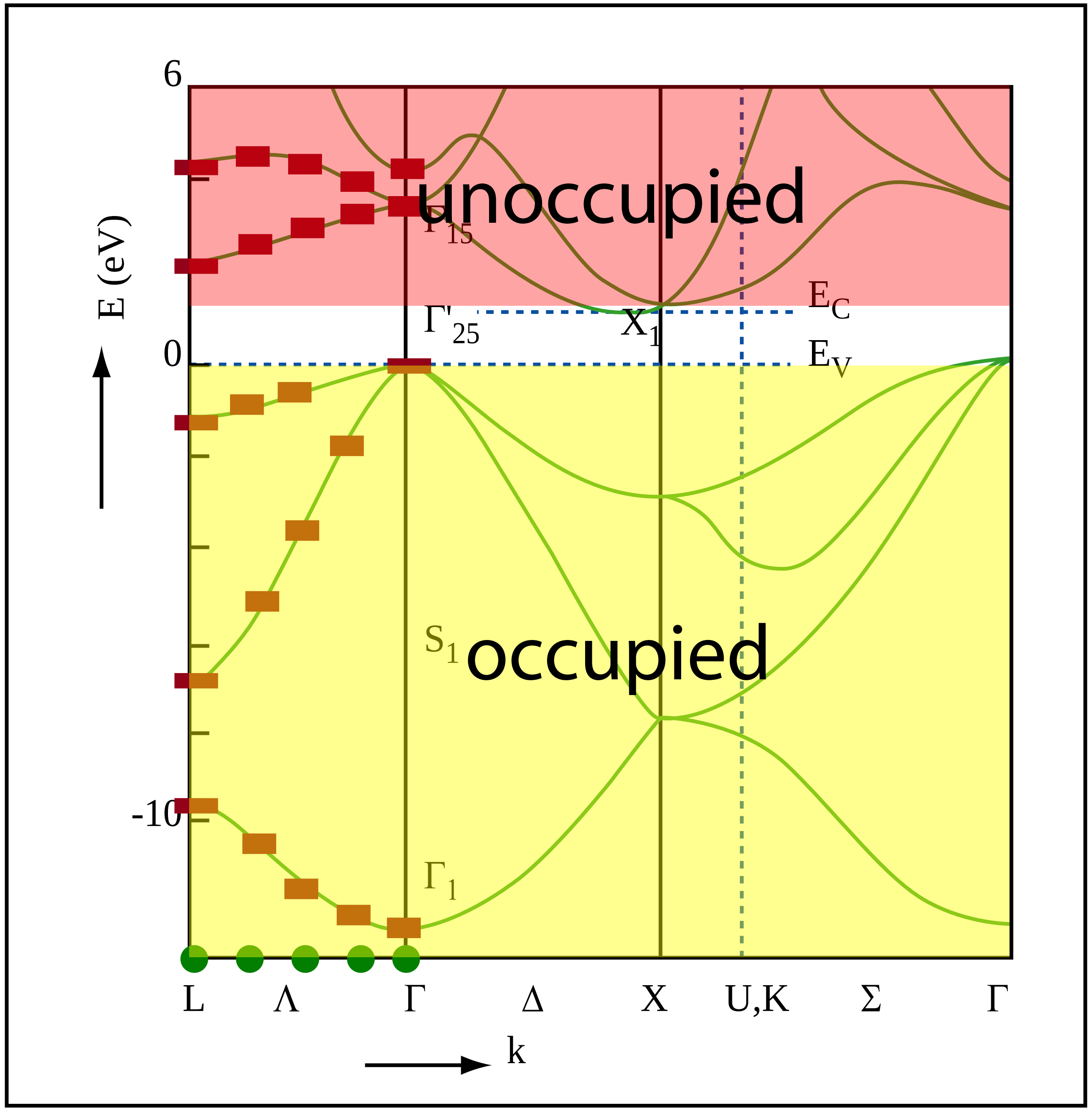



Image by MIT OpenCourseWare.

# Literature

- Charles Kittel, Introduction to Solid State Physics
- Richard M. Martin, Electronic Structure
- wikipedia, "solid state physics", "condensed matter physics", ...
- Simple band structure simulations: http://phet.colorado.edu/simulations/sims.php?sim=Band_Structure