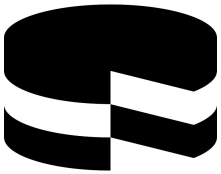
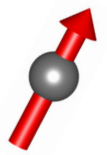
All sorts of metals

ab initio calculations



Li-ion batteries

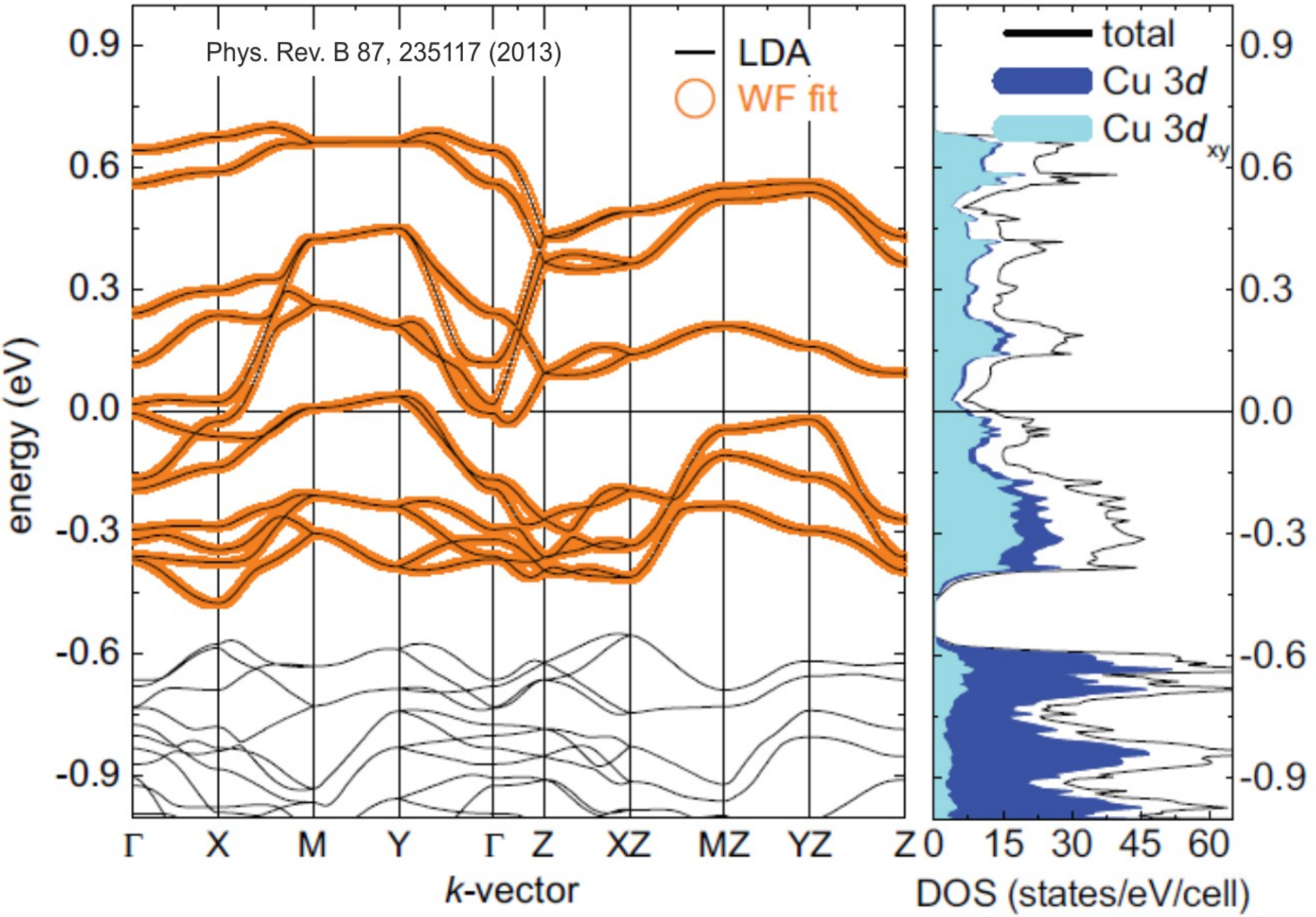
Marvin Cohen

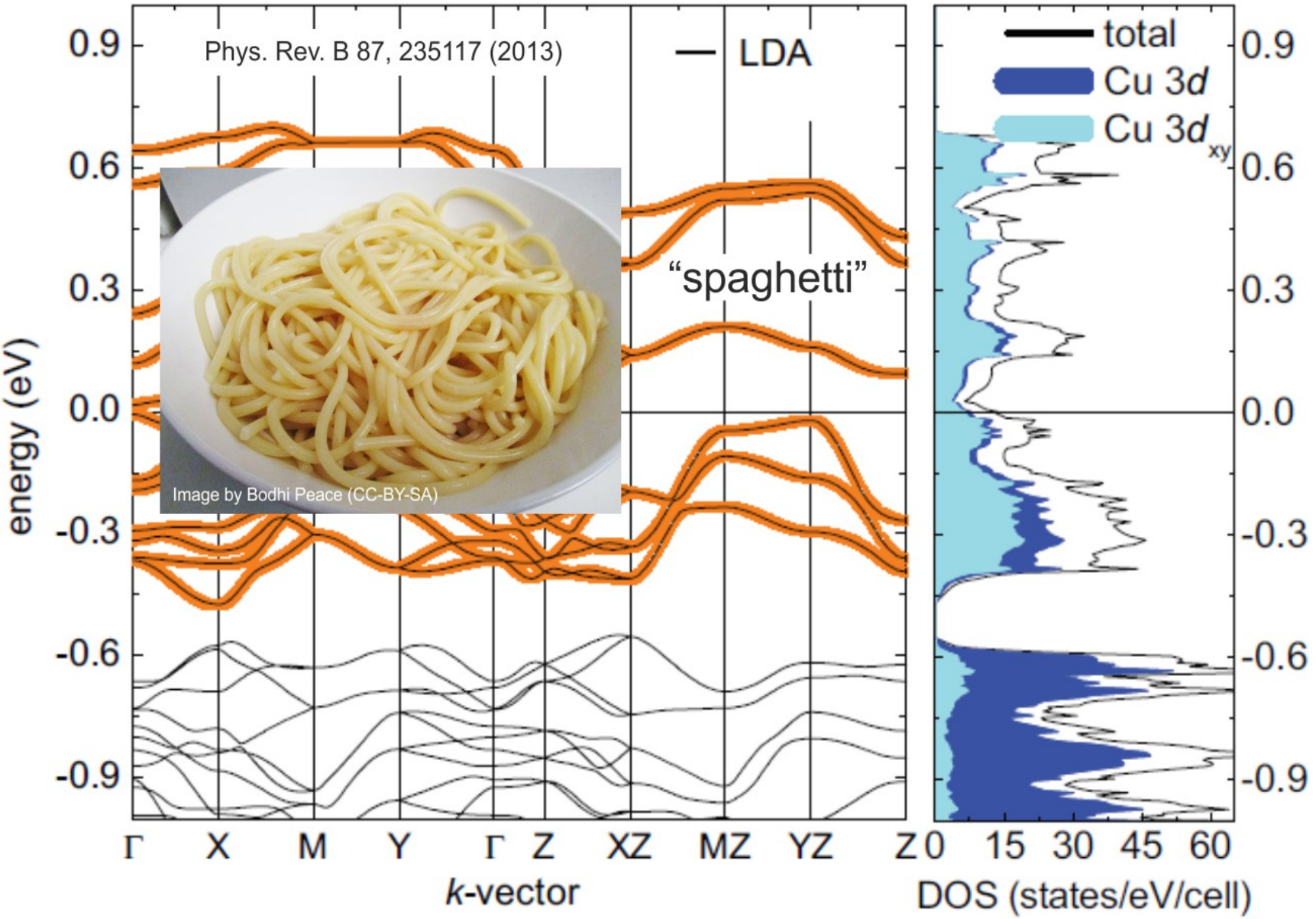


by Alexander Tsirlin, Leipzig University

Lecture 21: January 4, 2024

Bands vs. DOS


Phys. Rev. B 87, 235117 (2013)
LDA
WF fit
energy (eV)
0.9
0.6
0.3
0.0
-0.3
-0.6
-0.9
Γ X M Y Γ Z XZ MZ YZ Z
k-vector
total
Cu 3d
Cu 3d xy
0 15 30 45 60
DOS (states/eV/cell)


Phys. Rev. B 87, 235117 (2013)
LDA
"spaghetti"
Image by Bodhi Peace (CC-BY-SA)
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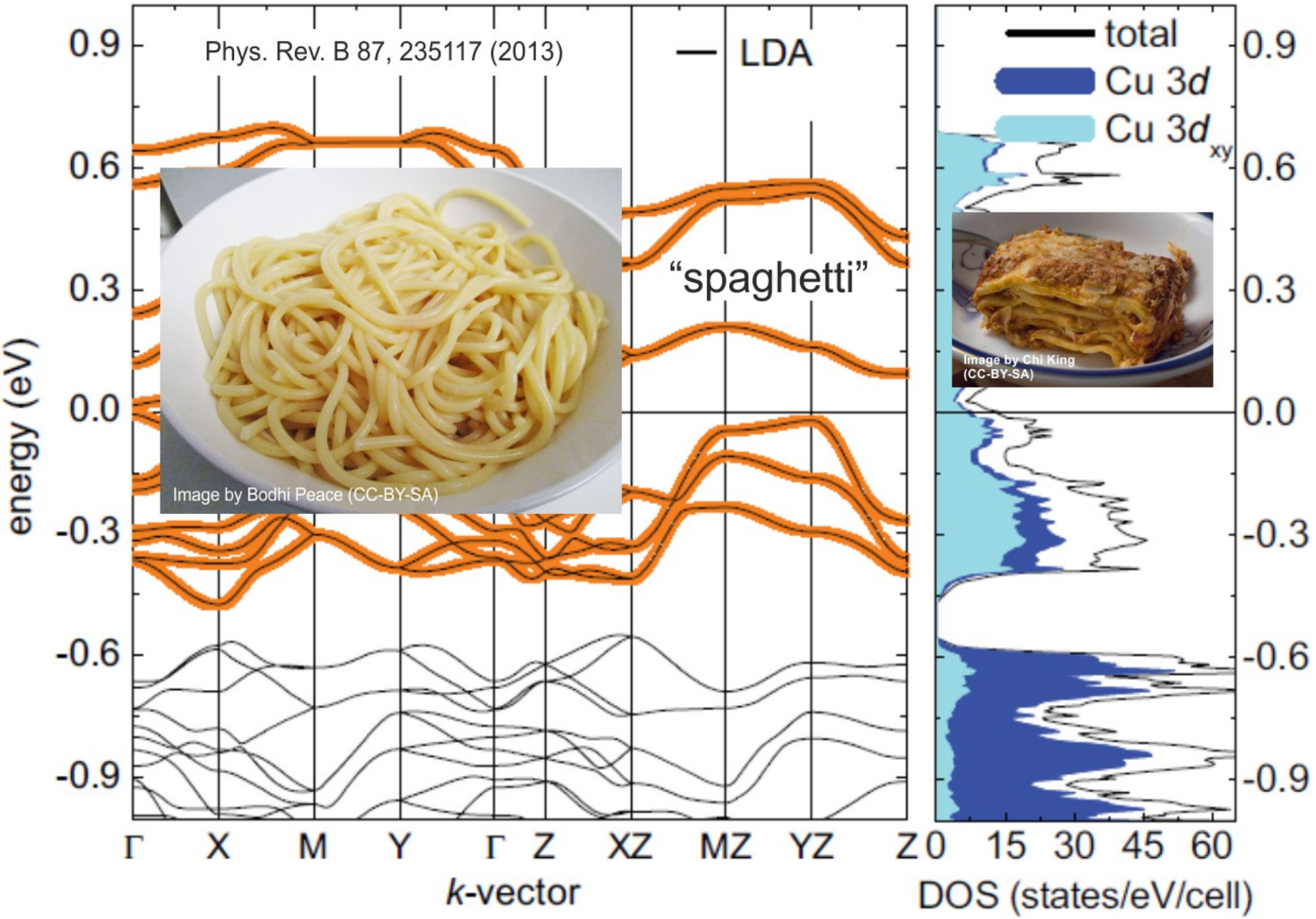
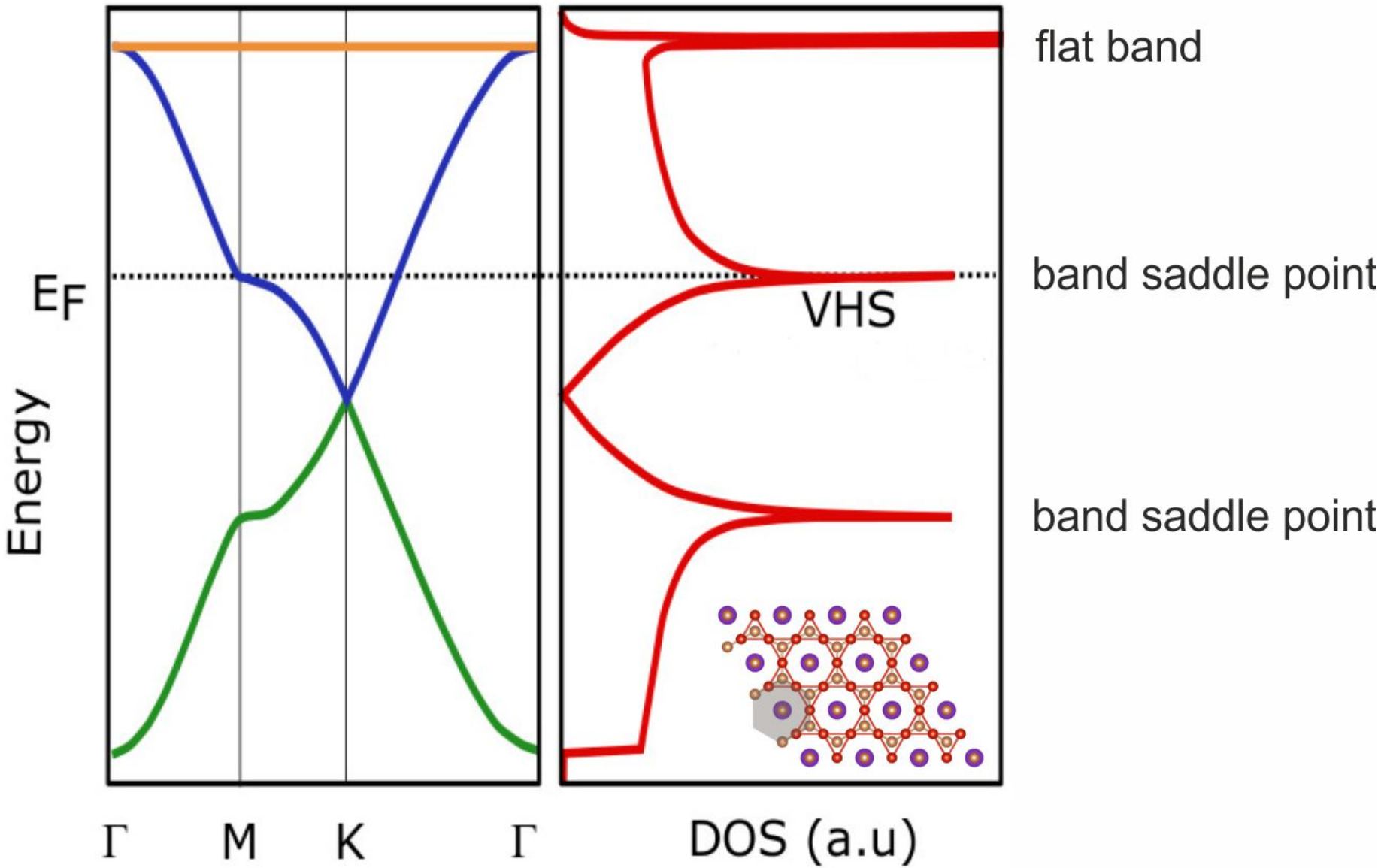
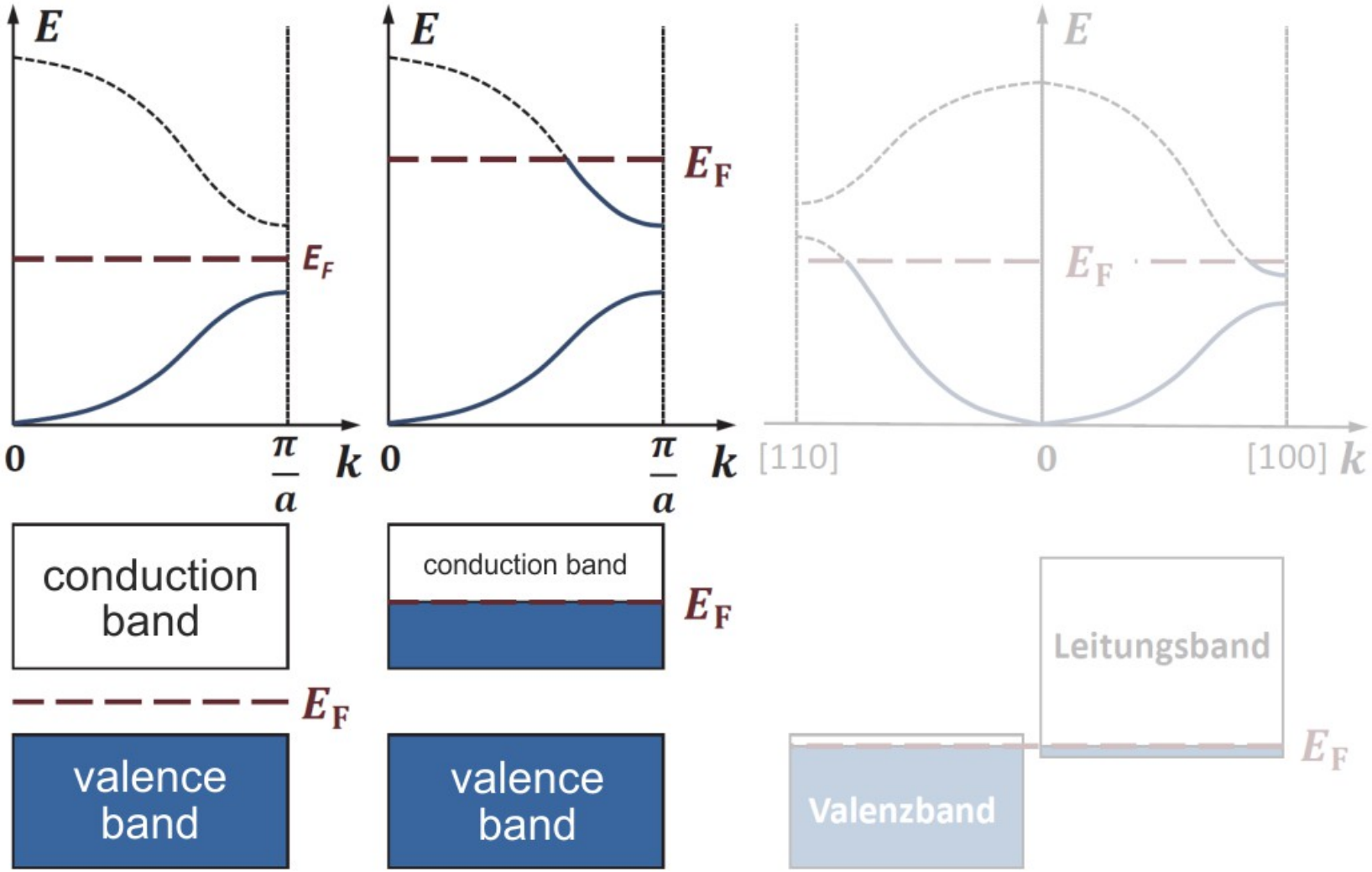

Phys. Rev. B 87, 235117 (2013)
LDA
"spaghetti"
Image by Bodhi Peace (CC-BY-SA)
total
Cu 3d
Cu 3d xy
Image by Chi King (CC-BY-SA)
energy (eV)
0.9
0.6
0.3
0.0
-0.3
-0.6
-0.9
Γ X M Y Γ Z XZ MZ YZ Z
k-vector
0 15 30 45 60
DOS (states/eV/cell)

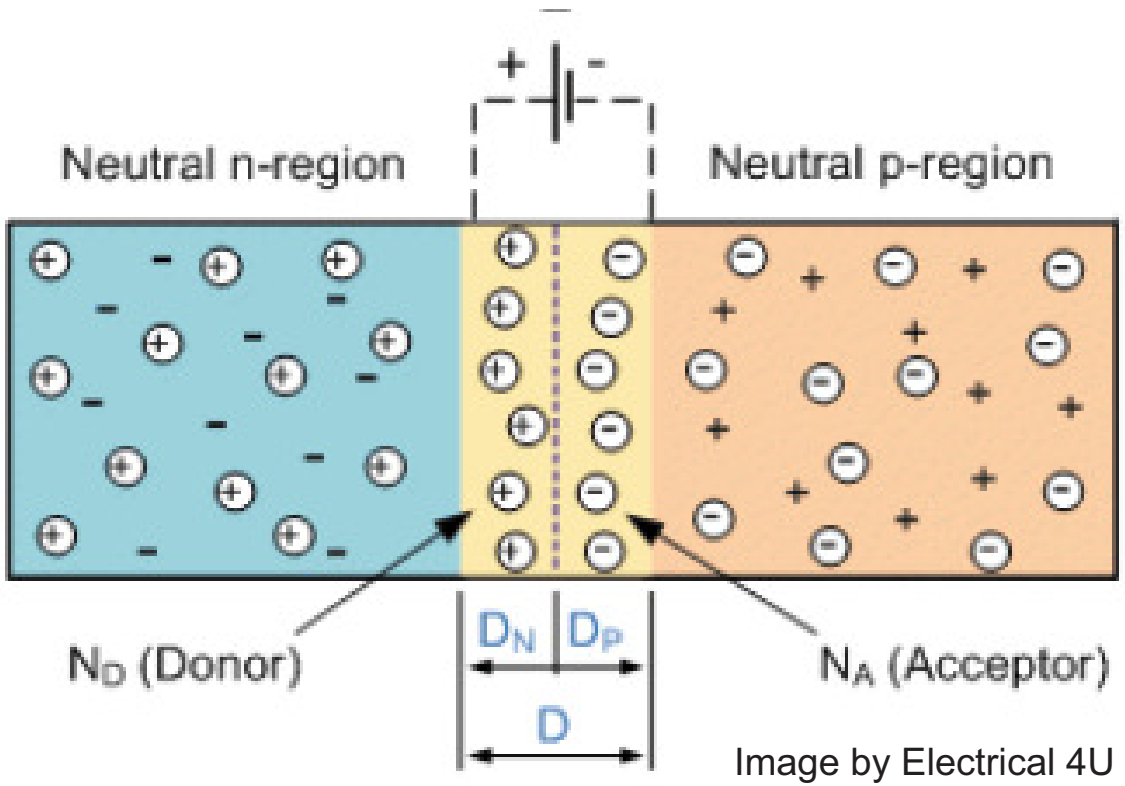
Van Hove singularities

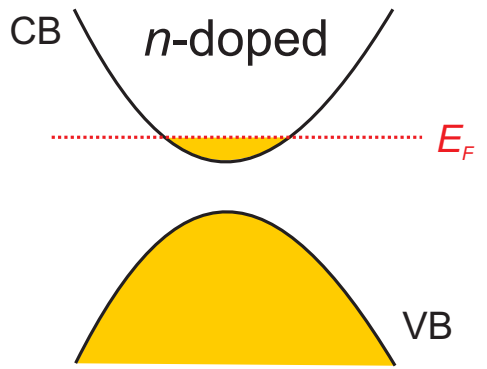


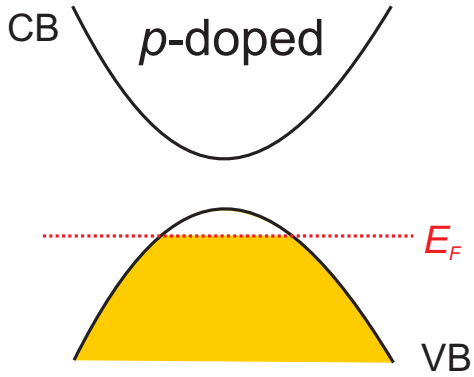
Metal vs. insulator



R. Gross, A. Marx, Festkörperphysik



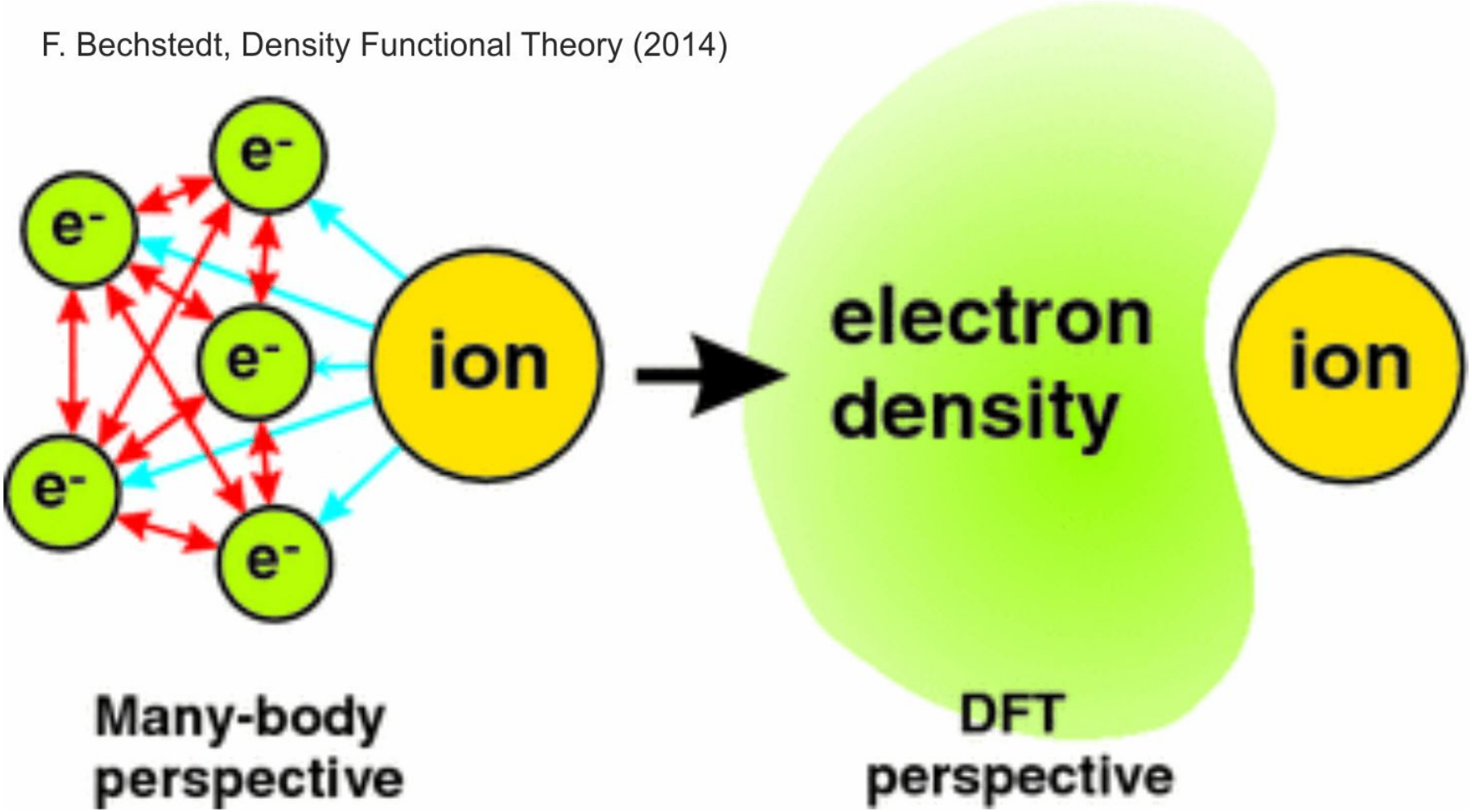




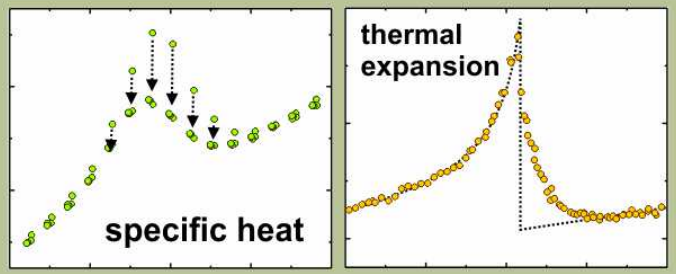
Band gap of a semiconductor can be larger or smaller, but it's crucial that **both types of doping** should be feasible and lead to sufficiently **high mobility** of the charge

Experimental technique

ab initio calculations


F. Bechstedt, Density Functional Theory (2014)
e-
e-
e-
e-
e-
ion
Many-body perspective
electron density
ion
DFT perspective

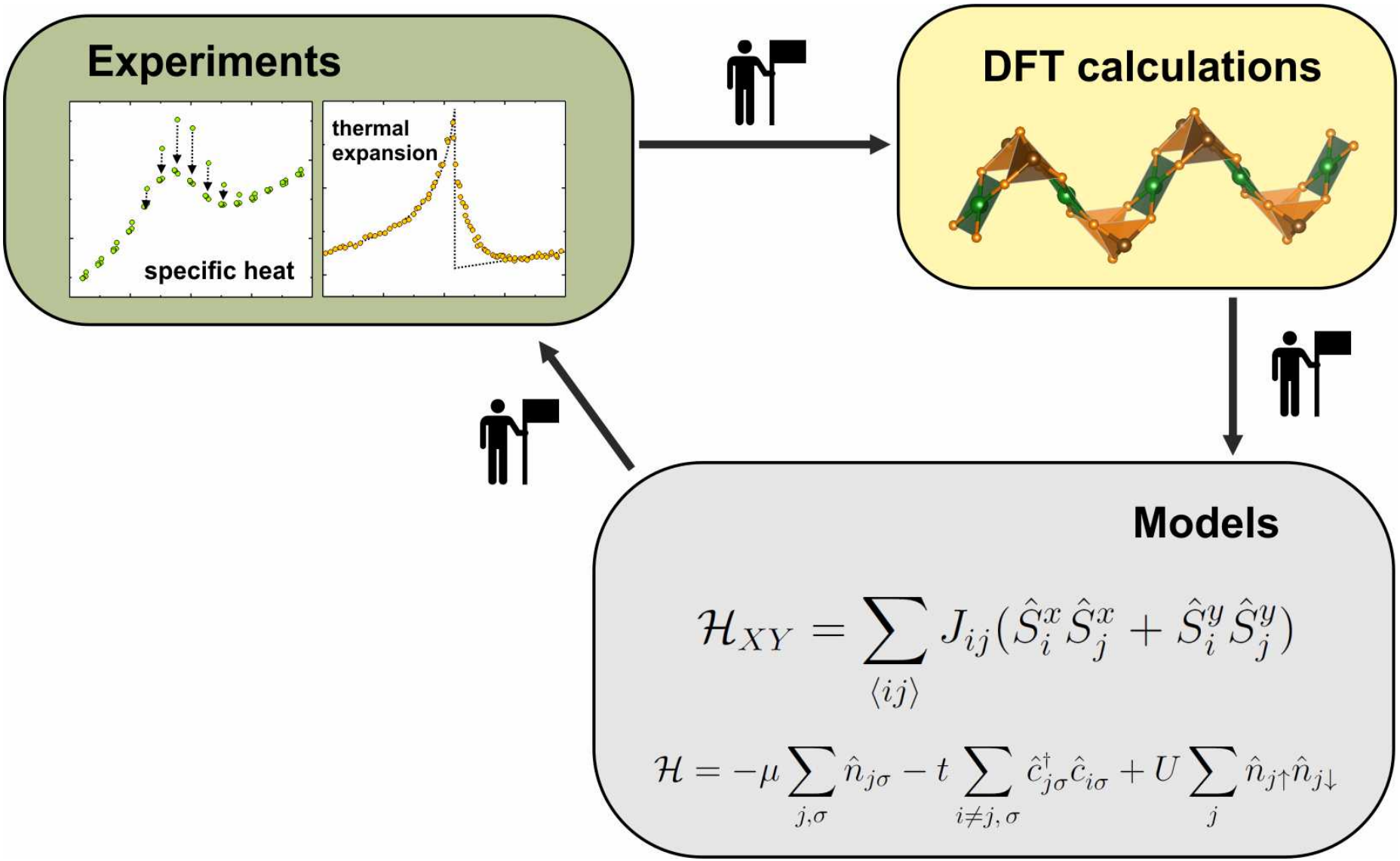
Experiments

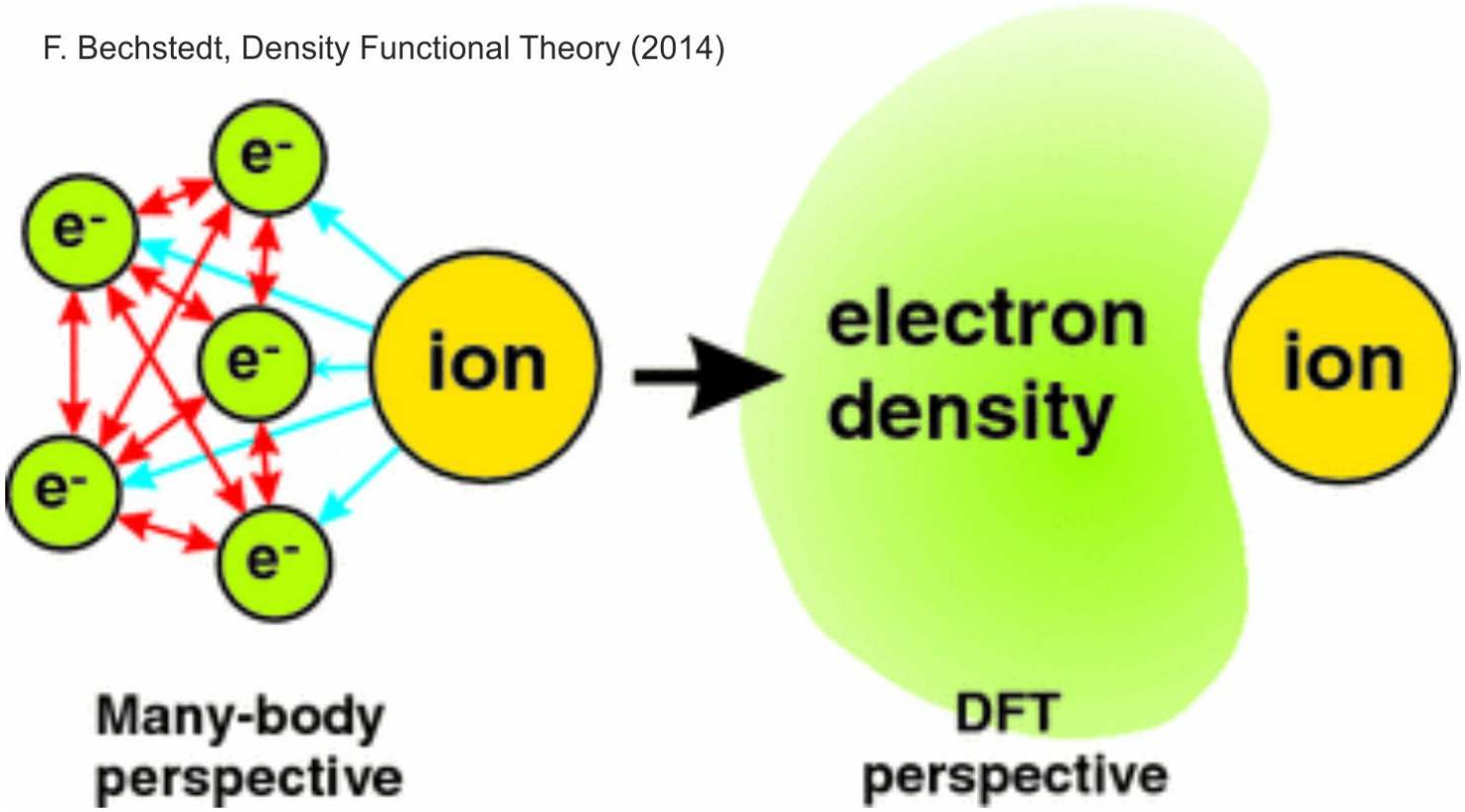


Models

$$\mathcal{H}_{XY} = \sum_{\langle ij \rangle} J_{ij} (\hat{S}_i^x \hat{S}_j^x + \hat{S}_i^y \hat{S}_j^y)$$

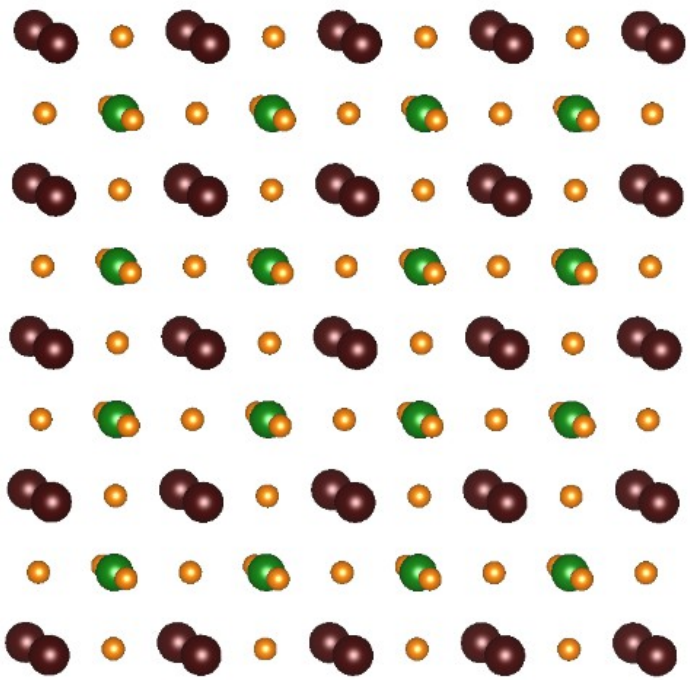
$$\mathcal{H} = -\mu \sum_{j,\sigma} \hat{n}_{j\sigma} - t \sum_{i \neq j,\,\sigma} \hat{c}_{j\sigma}^{\dagger} \hat{c}_{i\sigma} + U \sum_{j} \hat{n}_{j\uparrow} \hat{n}_{j\downarrow}$$

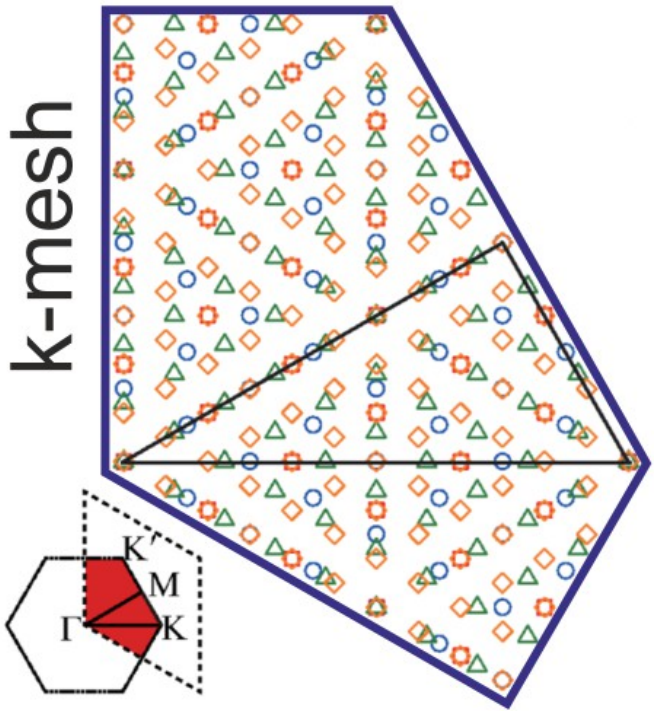

Experiments
specific heat
thermal expansion
DFT calculations
Models
$\mathcal{H}_{XY} = \sum_{\langle ij \rangle} J_{ij}(\hat{S}_i^x \hat{S}_j^x + \hat{S}_i^y \hat{S}_j^y)$
$\mathcal{H} = -\mu \sum_{j,\sigma} \hat{n}_{j\sigma} - t \sum_{i \neq j,\sigma} \hat{c}_{j\sigma}^\dagger \hat{c}_{i\sigma} + U \sum_j \hat{n}_{j\uparrow} \hat{n}_{j\downarrow}$



Electron-electron interactions are replaced
by an effective, **exchange-correlation potential** V_{xc}

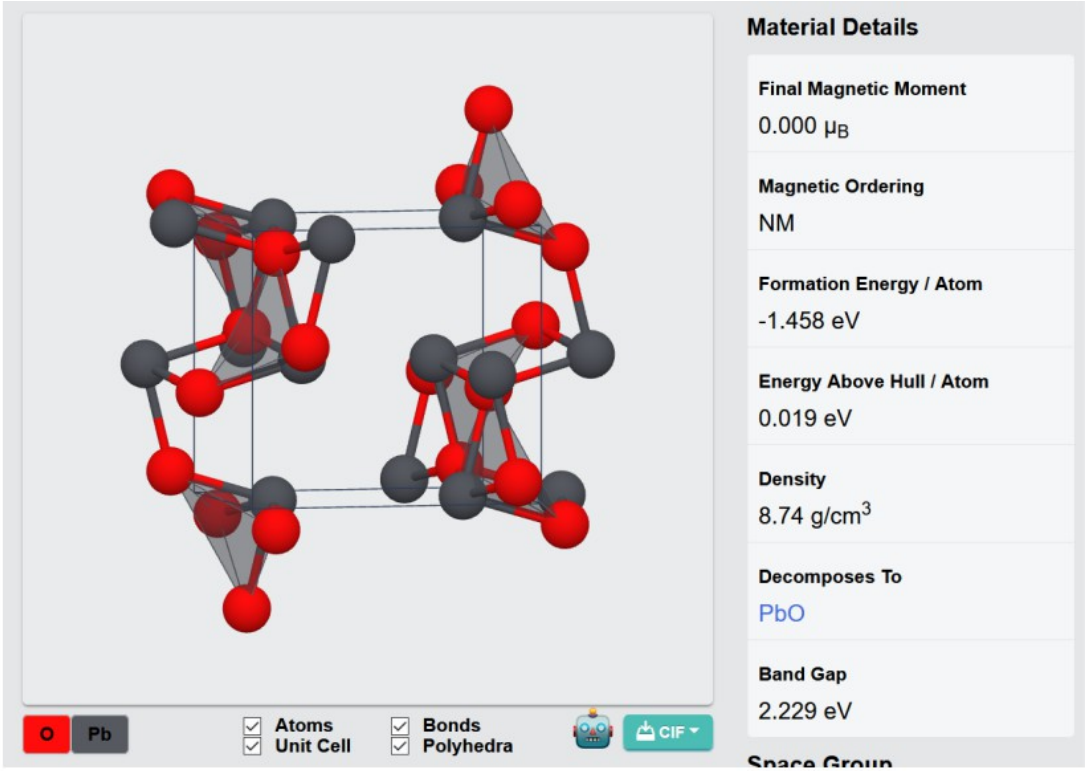
Problem: the exact form of V_{xc} is not known,
but sensible approximations exist





Bloch functions and band energies
are calculated on a mesh of k-points
within the first Brillouin zone (irreducible part)

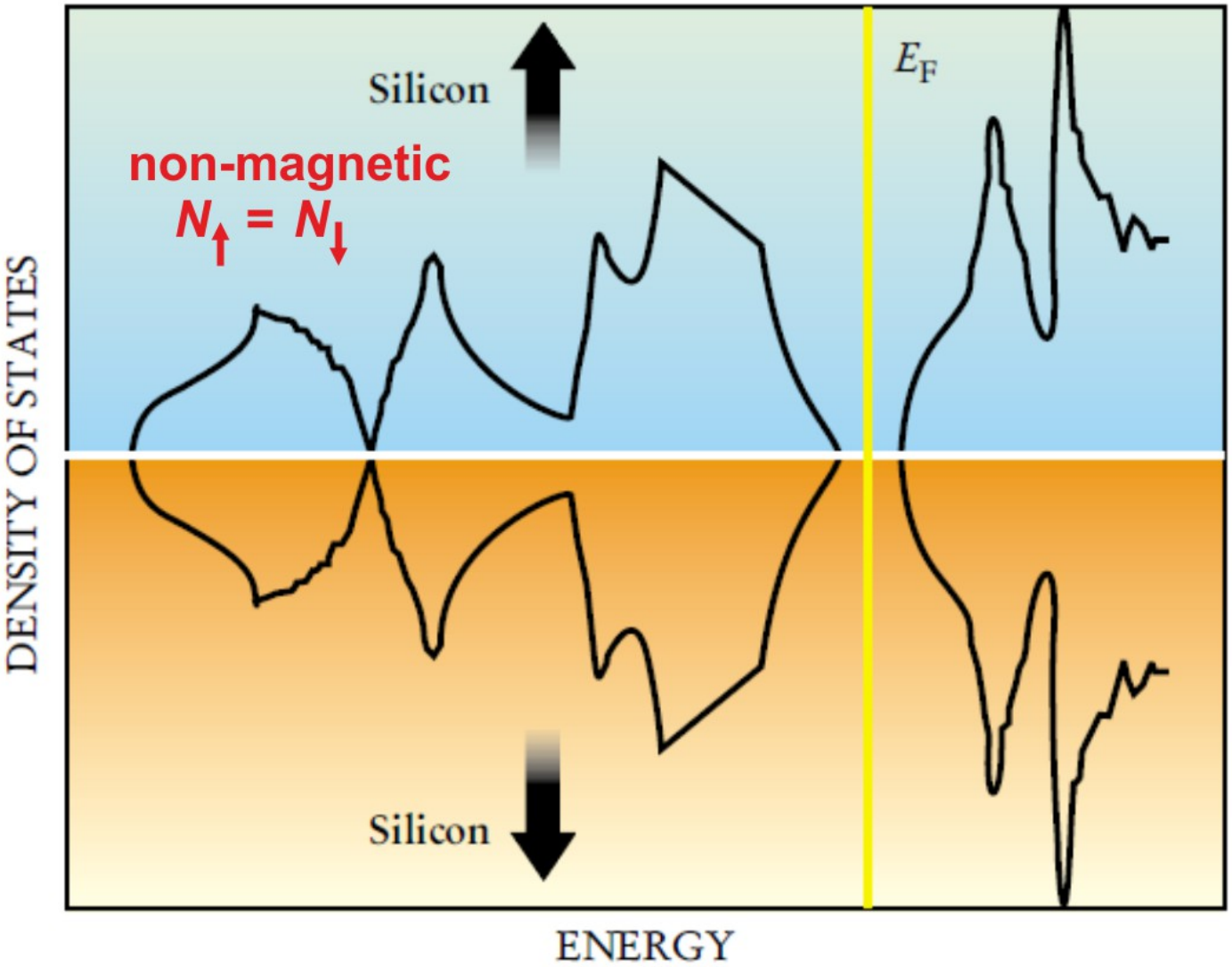
https://materialsproject.org



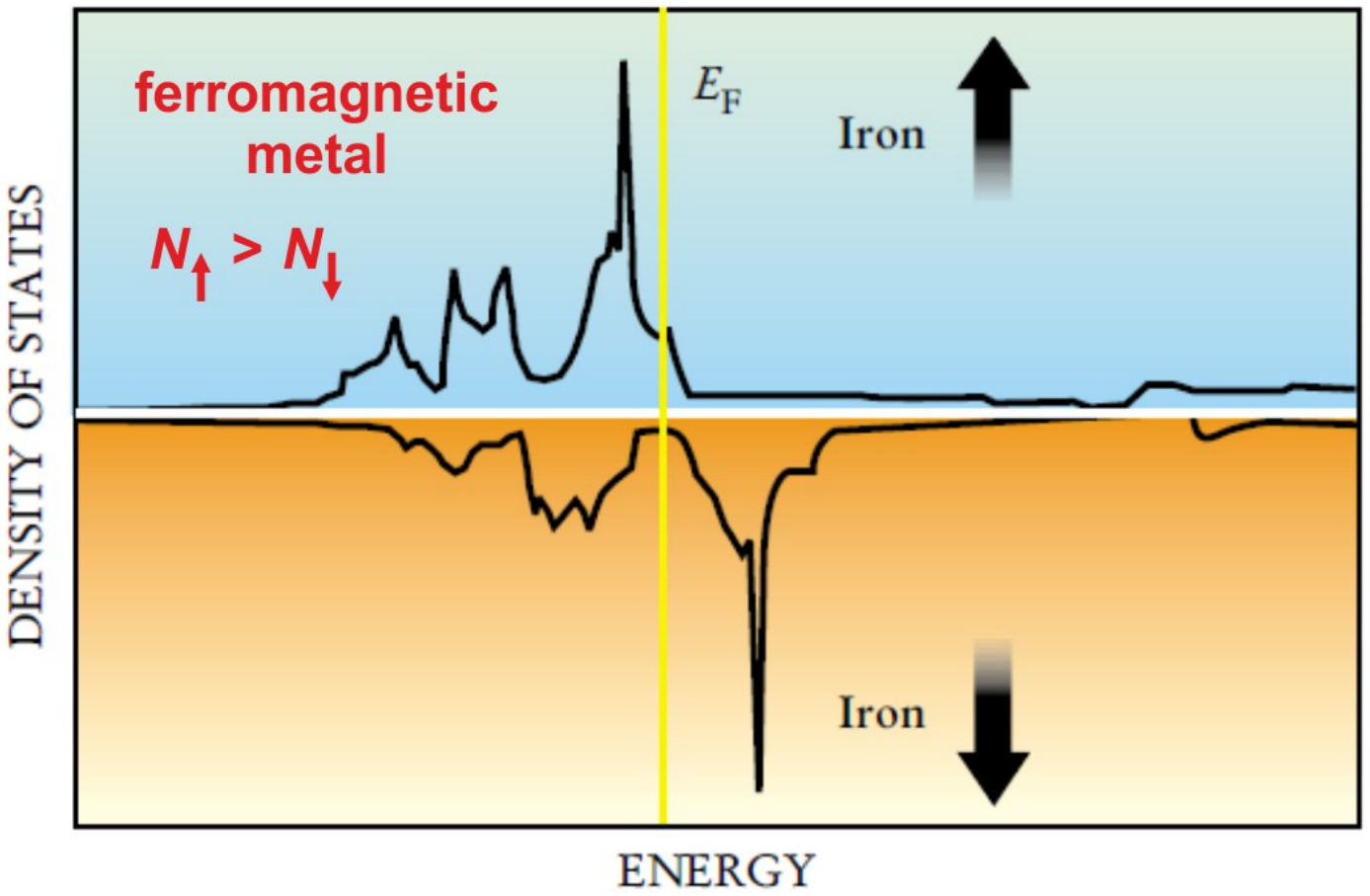
Multiple properties are calculated for all known materials and many hypothetical ones

Extensive search capabilities, prediction of thermodynamic properties, and a lot more

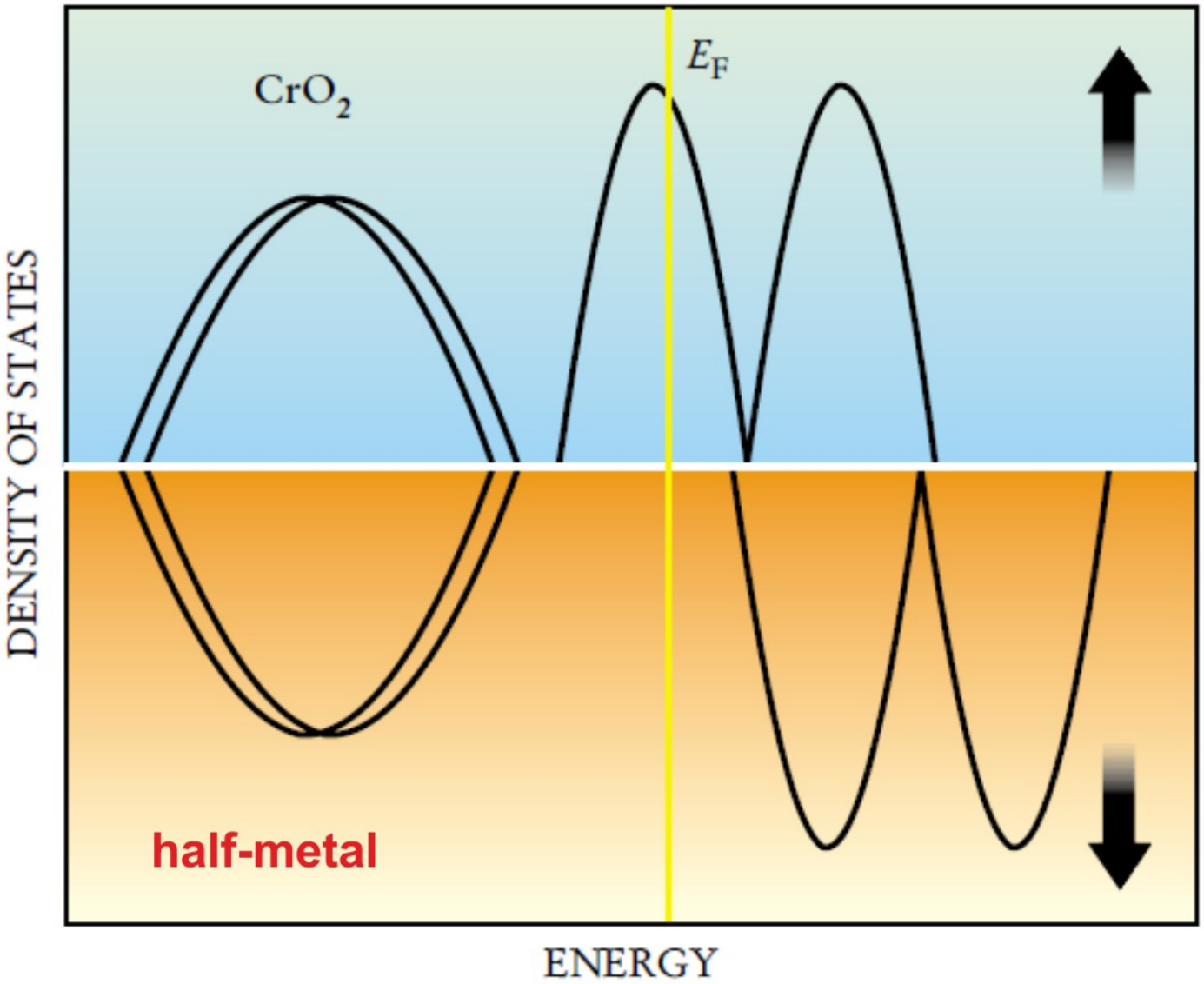
Caveat: most information is obtained from band-structure calculations
and may be inaccurate or even misleading



W.E. Pickett and J.S. Moodera, Physics Today 54(5), 39 (2001)



W.E. Pickett and J.S. Moodera, Physics Today 54(5), 39 (2001)



W.E. Pickett and J.S. Moodera, Physics Today 54(5), 39 (2001)

semi-sweet

Image by Makro

Half $\neq$ Semi

Half vs. semi

semi-sweet

Image by Makro

half-sweet

Image by Starbucks

Half $\neq$ Semi

Half vs. semi

semi-sweet

Image by Makro

half-sweet

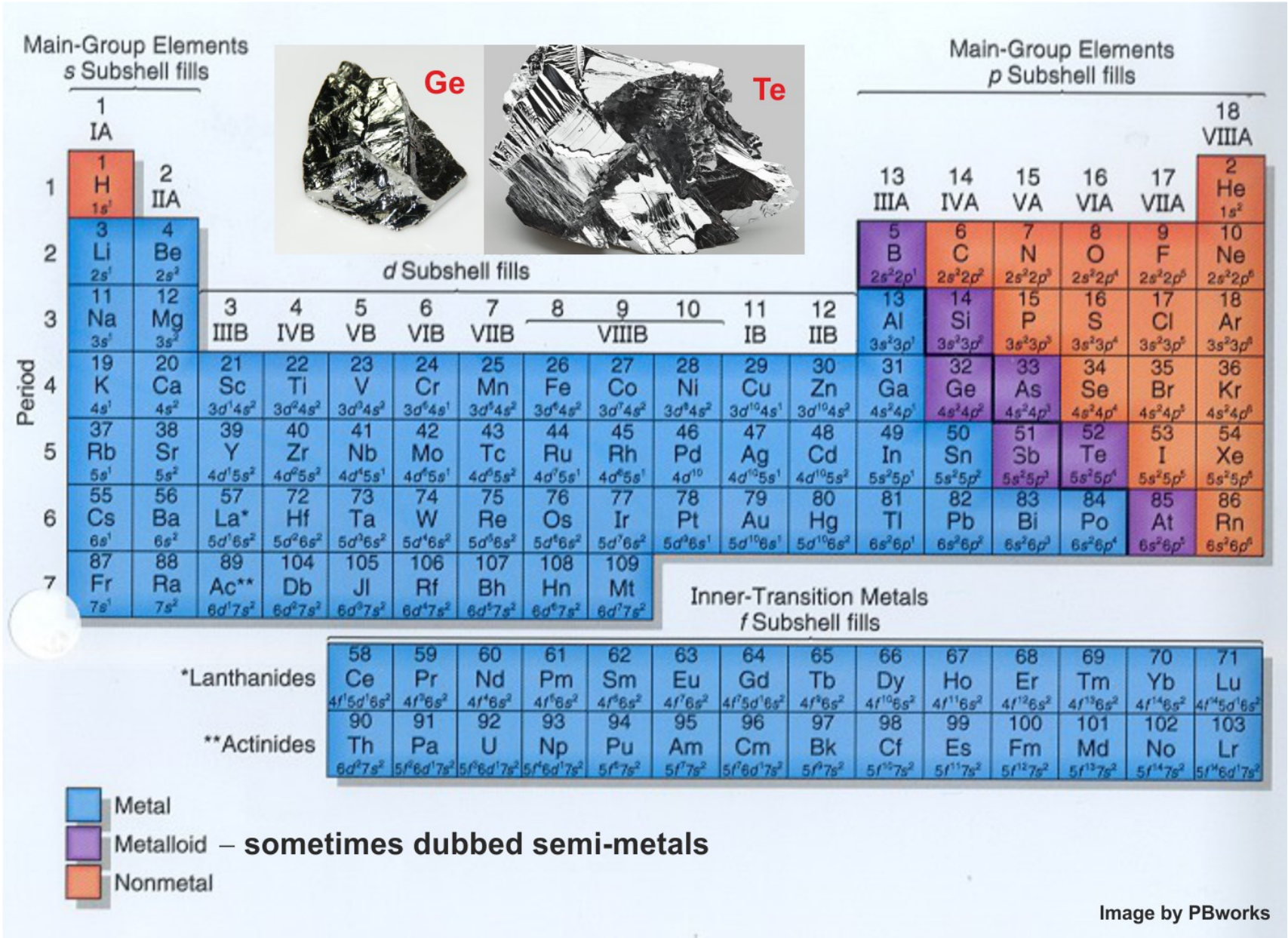
Image by Starbucks

half a pint!

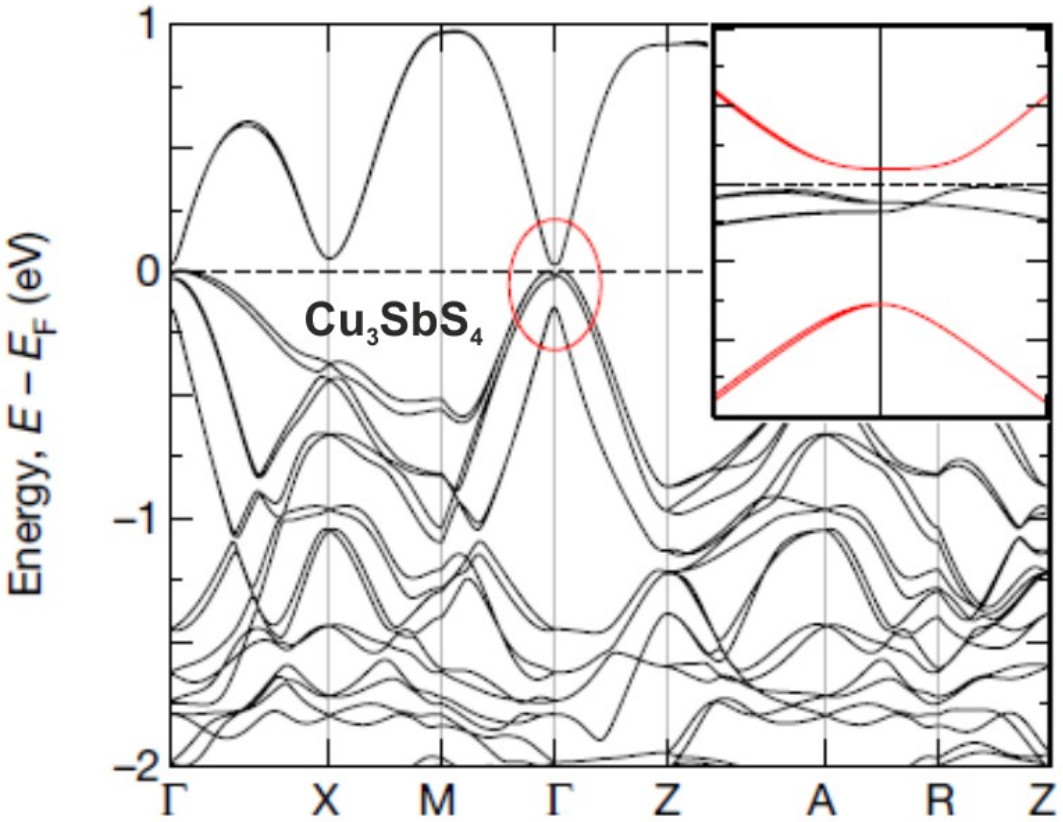
Image by KegWorks

Half $\neq$ Semi

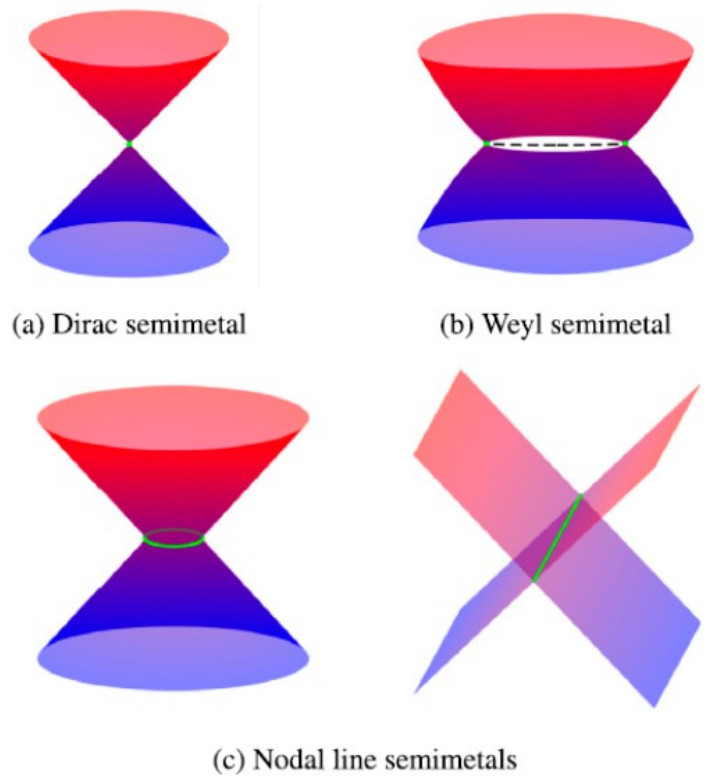
Semi-metals / Metalloids



Semi-metals (modern definition)

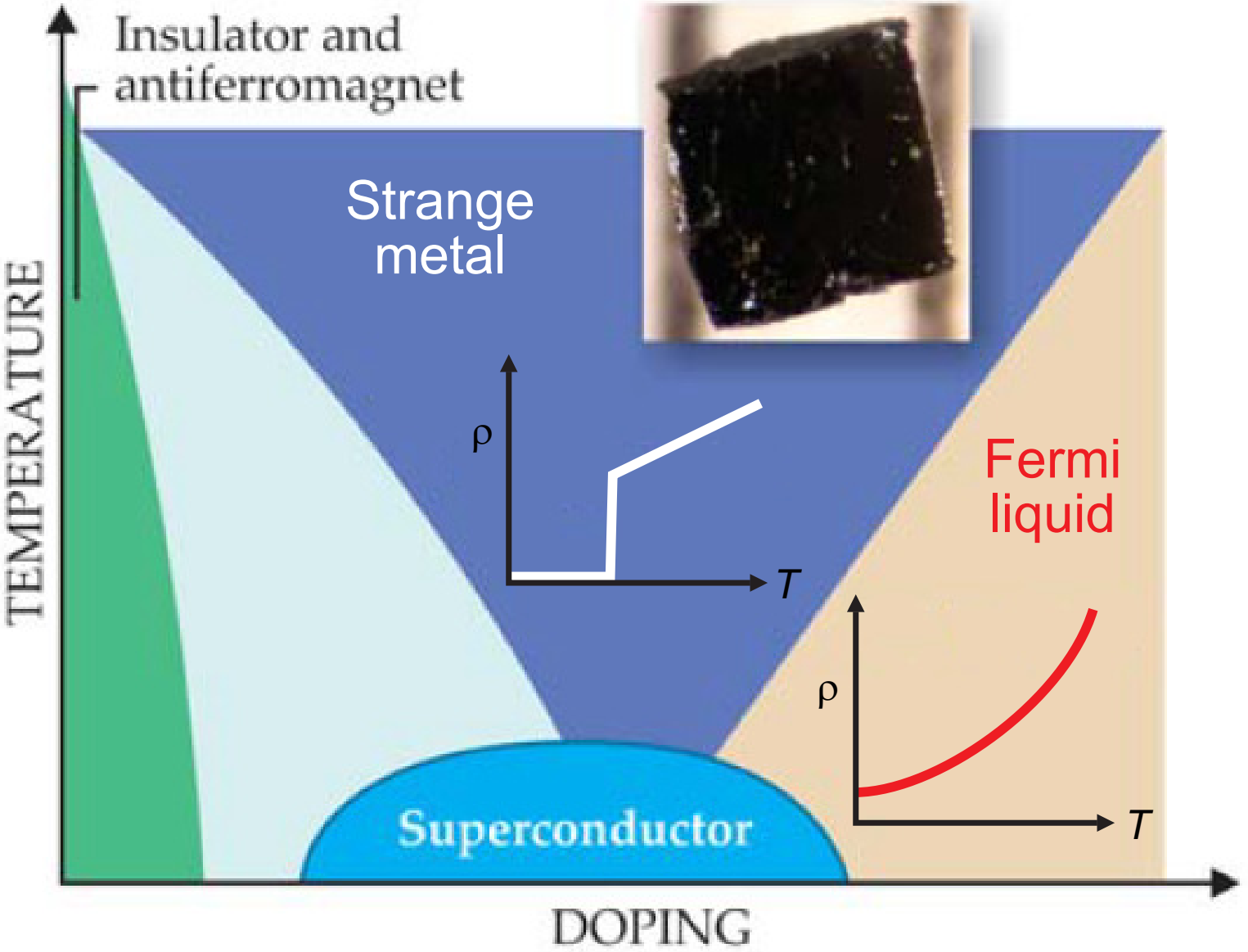


Nature 547, 298 (2017)



Adv. Phys. X 3, 1414631 (2018)

Electrons at the Fermi level may have very unusual properties caused by non-trivial band topology



$\rho \sim T$

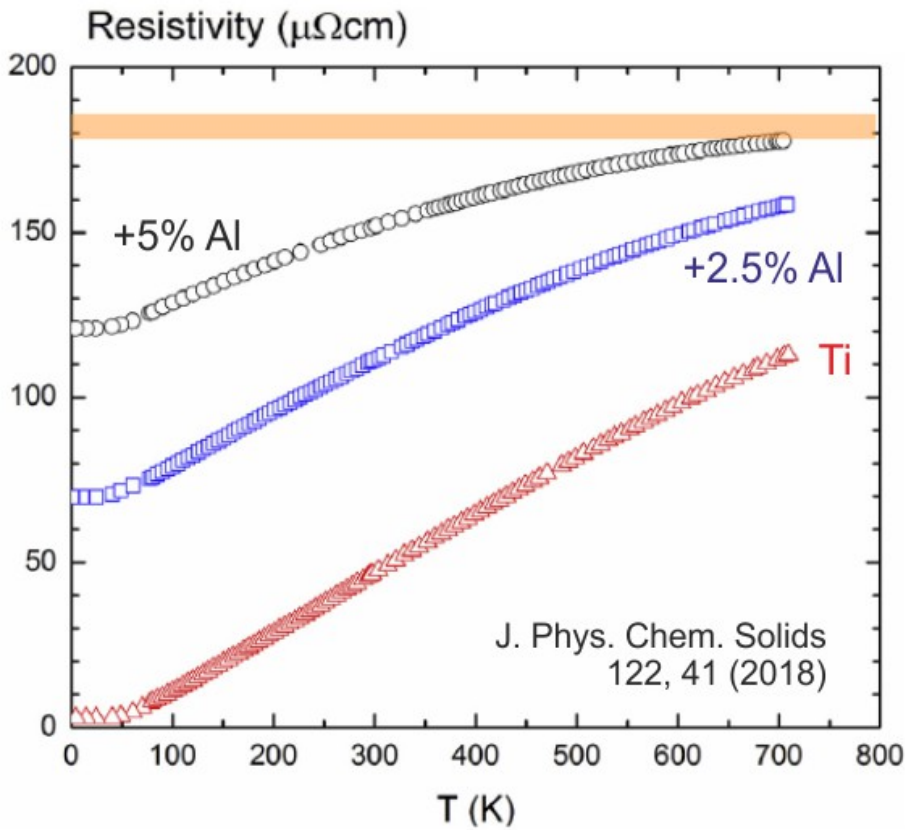
vs.

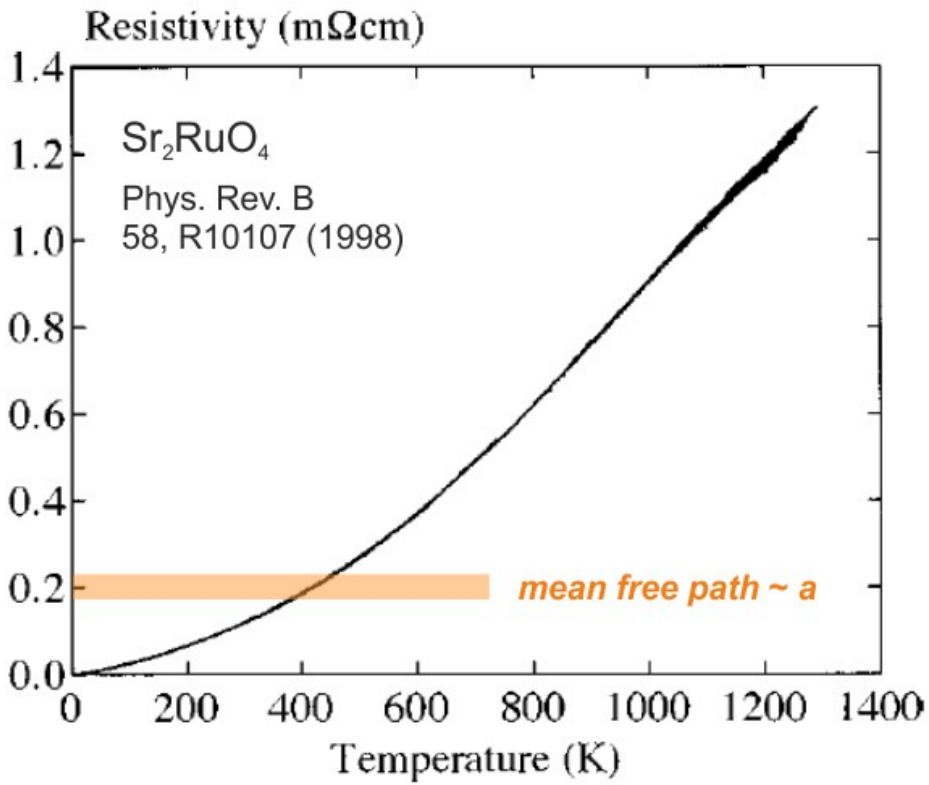
$\rho \sim T^2$

at low T's

H. Liu, Physics Today 65(6), 68 (2012)

Bad metals





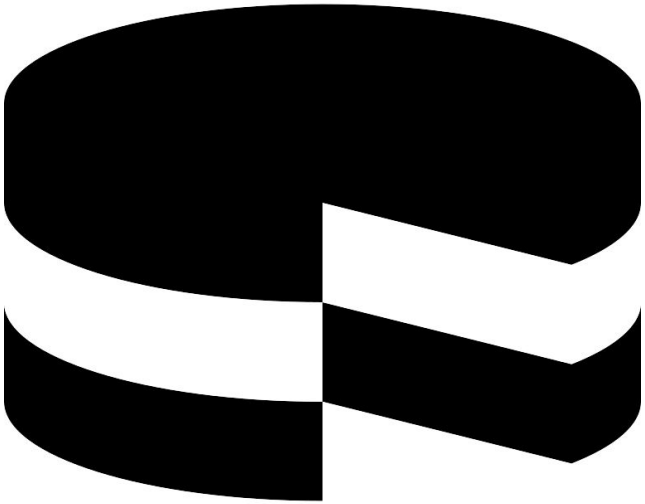
At high T, resistivity well exceeds the Mott-Ioffe-Regel limit ($l_{\mathrm{mean}} \sim a$)

But at low T, such "bad metals" can be still good metals (low ρ_{dc})

Each electron is dependent on other electrons in the system

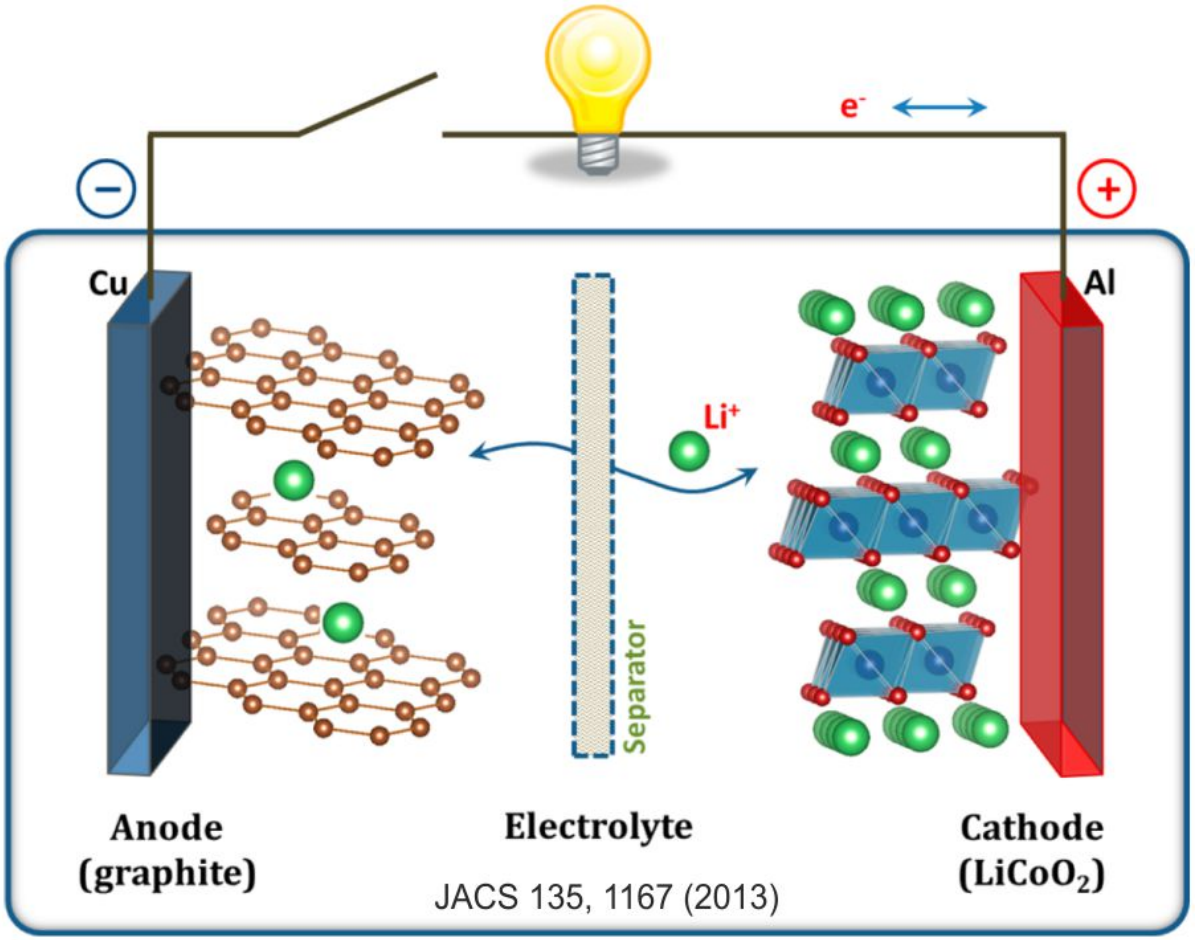
Many-body problem

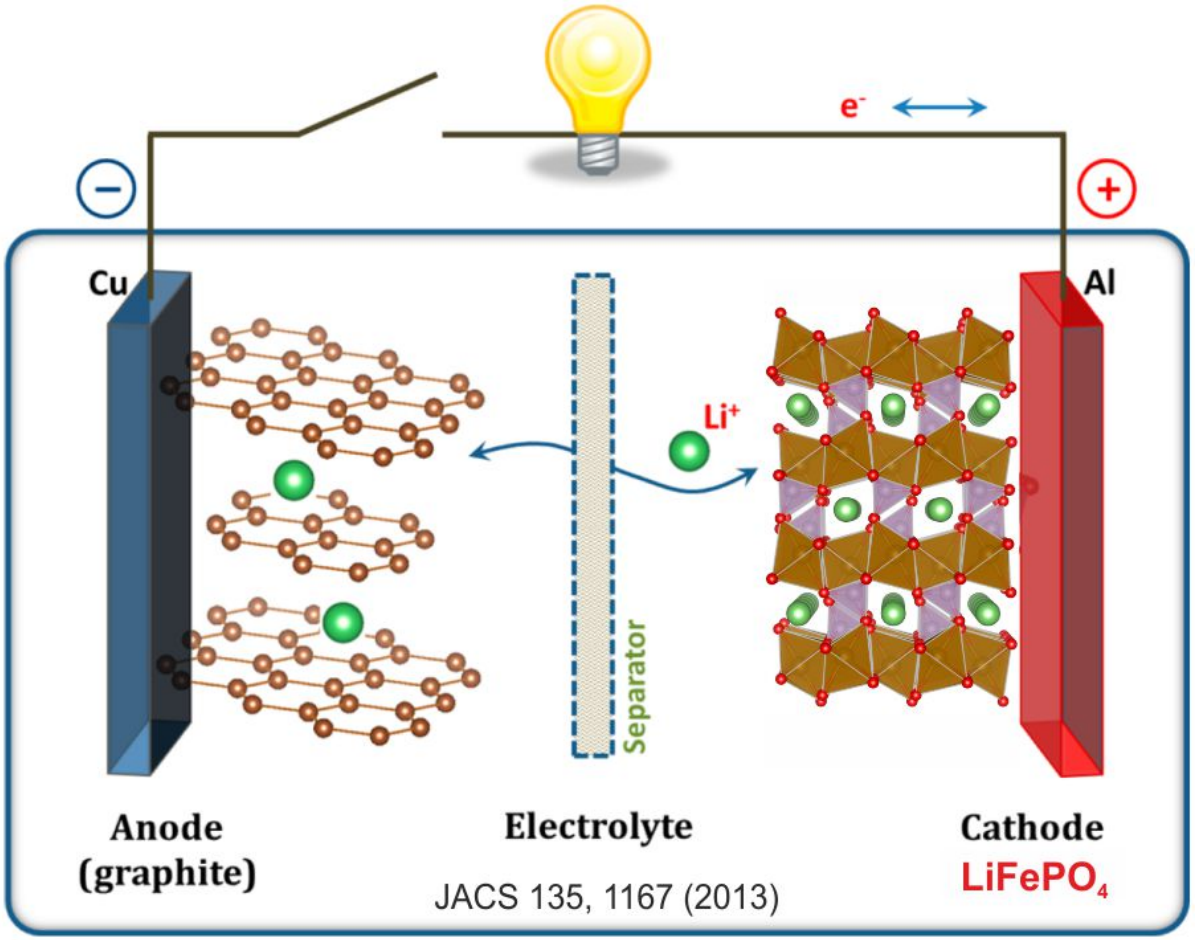
Significant repercussions for electronic properties
(high-temperature superconductors, battery materials...)

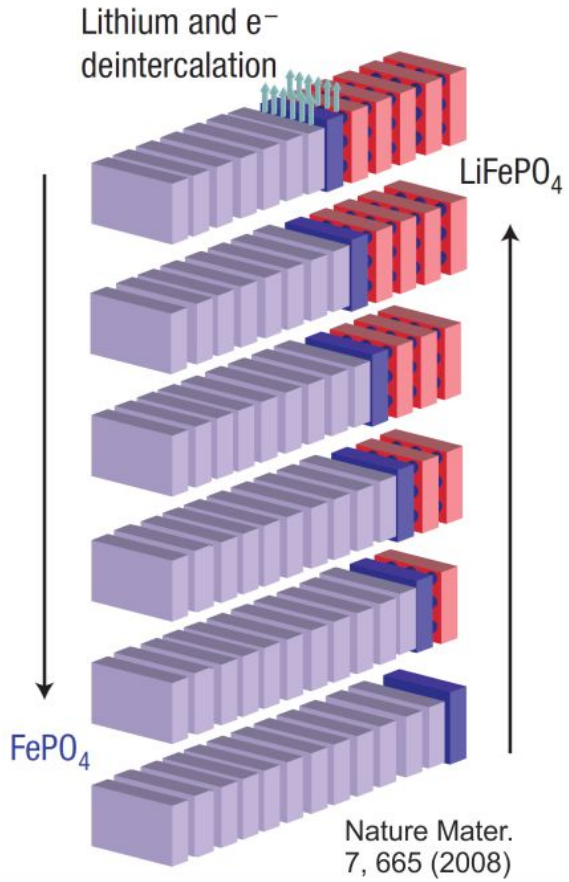


Material

Li-ion batteries


e⁻
Cu
Al
Li⁺
Separator
Anode
(graphite)
Electrolyte
Cathode
(LiCoO2)
JACS 135, 1167 (2013)





$LiFePO_4$ (olivine) – Nobel Prize in Chemistry 2019

but transformation is abrupt with no intermediate compositions

Most common correlated material

PHYSICAL REVIEW B **69**, 201101(R) (2004)

Phase separation in Li_xFePO_4 induced by correlation effects

F. Zhou*
Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

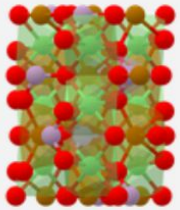
C. A. Marianetti, M. Cococcioni, D. Morgan, and G. Ceder†
Department of Material Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA
(Received 10 March 2004; published 12 May 2004)

We report on a significant failure of the local density approximation (LDA) and the generalized gradient approximation (GGA) to reproduce the phase stability and thermodynamics of mixed-valence Li_xFePO_4 compounds. Experimentally, Li_xFePO_4 compositions ($0 \leqslant x \leqslant 1$) are known to be unstable and phase separate into $LiFePO_4$ and $FePO_4$. However, first-principles calculations with LDA/GGA yield energetically favorable intermediate compounds and hence no phase separation. This qualitative failure of LDA/GGA seems to have its

Phase separation in batteries

is driven by electronic correlations

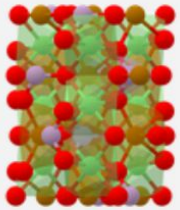
Straight-forward DFT calculations do not work



$LiFePO_4$

mp-19017

Energy Above Hull	0.000 eV/atom
Space Group	Pnma
Band Gap	3.92 eV
Predicted Formation Energy	-2.477 eV/atom
Magnetic Ordering	Ferromagnetic
Total Magnetization	4.00 μB/f.u.



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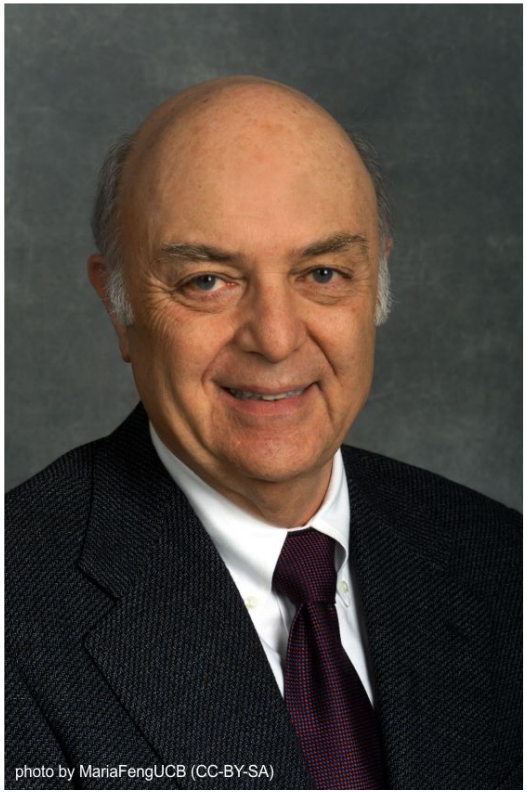
Person

Marvin Cohen

Marvin Cohen

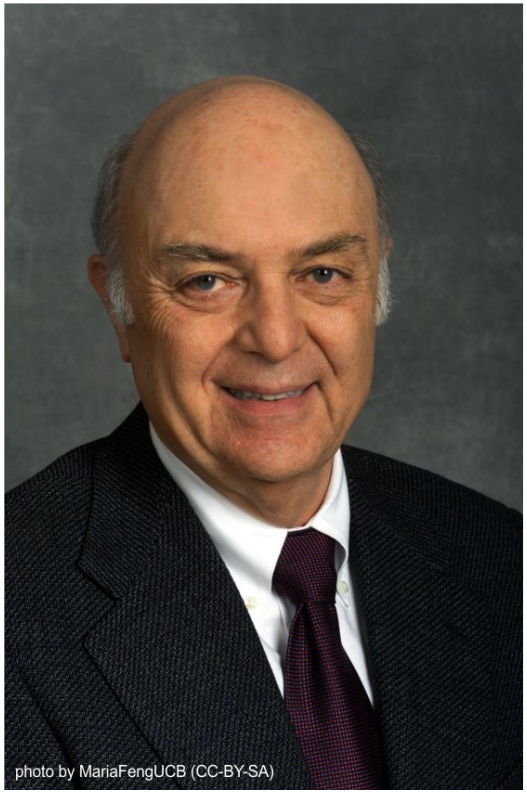


Marvin Cohen

born 1935

- 1953-1957: bachelor in Berkley,
  not accepted for master program
- 1958-1963: master and PhD in Chicago
  theory work based on electronic structure calculations
  for real materials
- 1963-1964: very short postdoc at Bell Labs
- since 1964: professor at Berkley
- 1960-70's: optical properties of semiconductors
- since 1970's: high-pressure transformations of solids
- 1980's: superconductors
- since 1990's: carbon allotropes, nanotubes

Marvin Cohen



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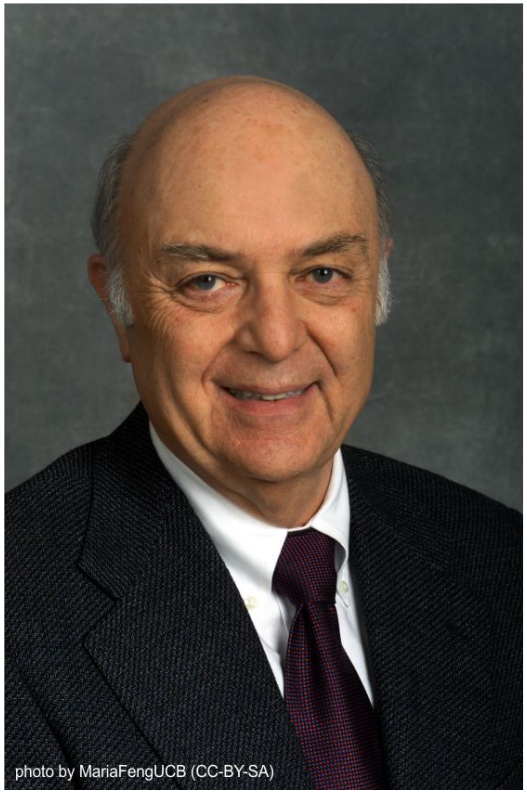

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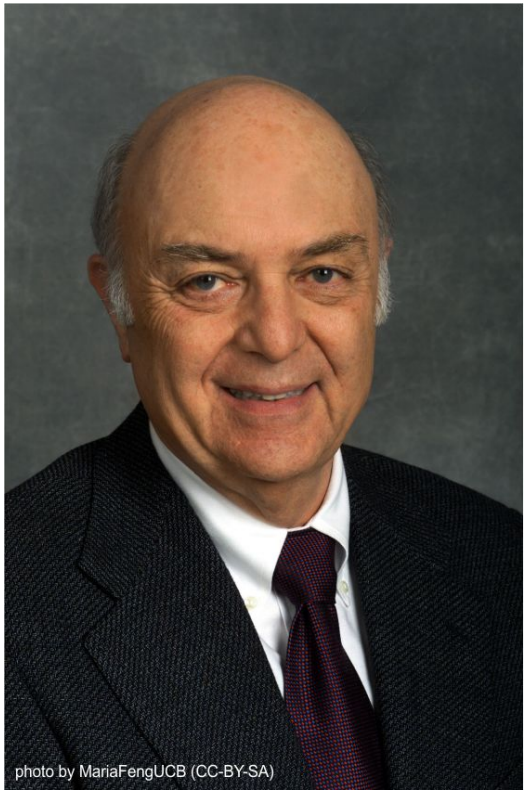

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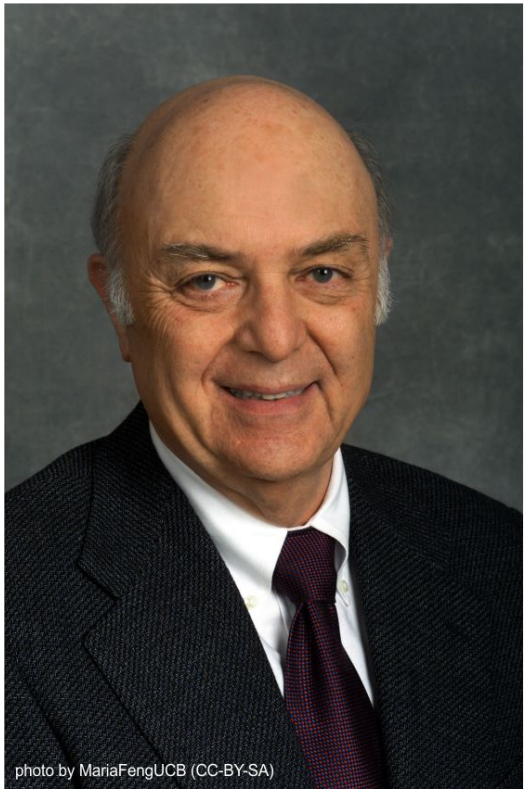
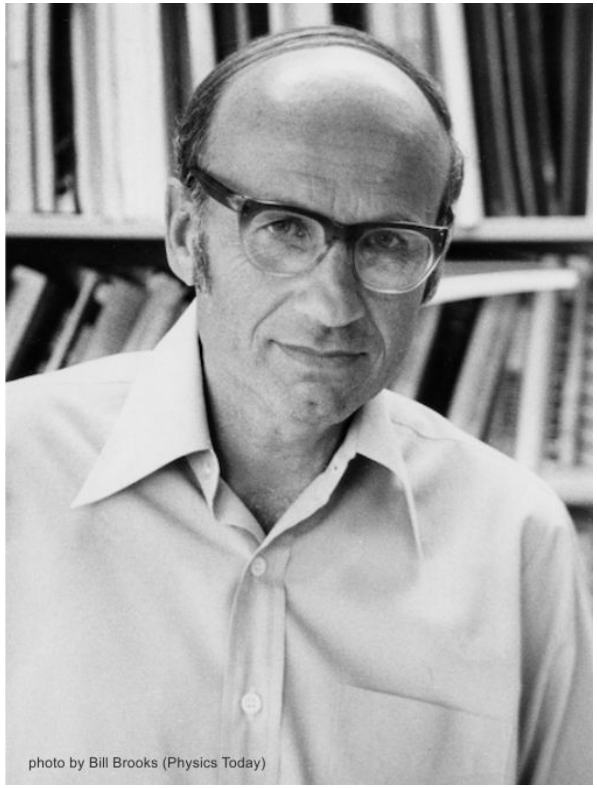
Cohen vs. Kohn



Marvin Cohen

pseudopotentials

pioneer of electronic-structure and DFT methods in solids



Walter Kohn

density-functional theory

Nobel Prize in Chemistry 1998

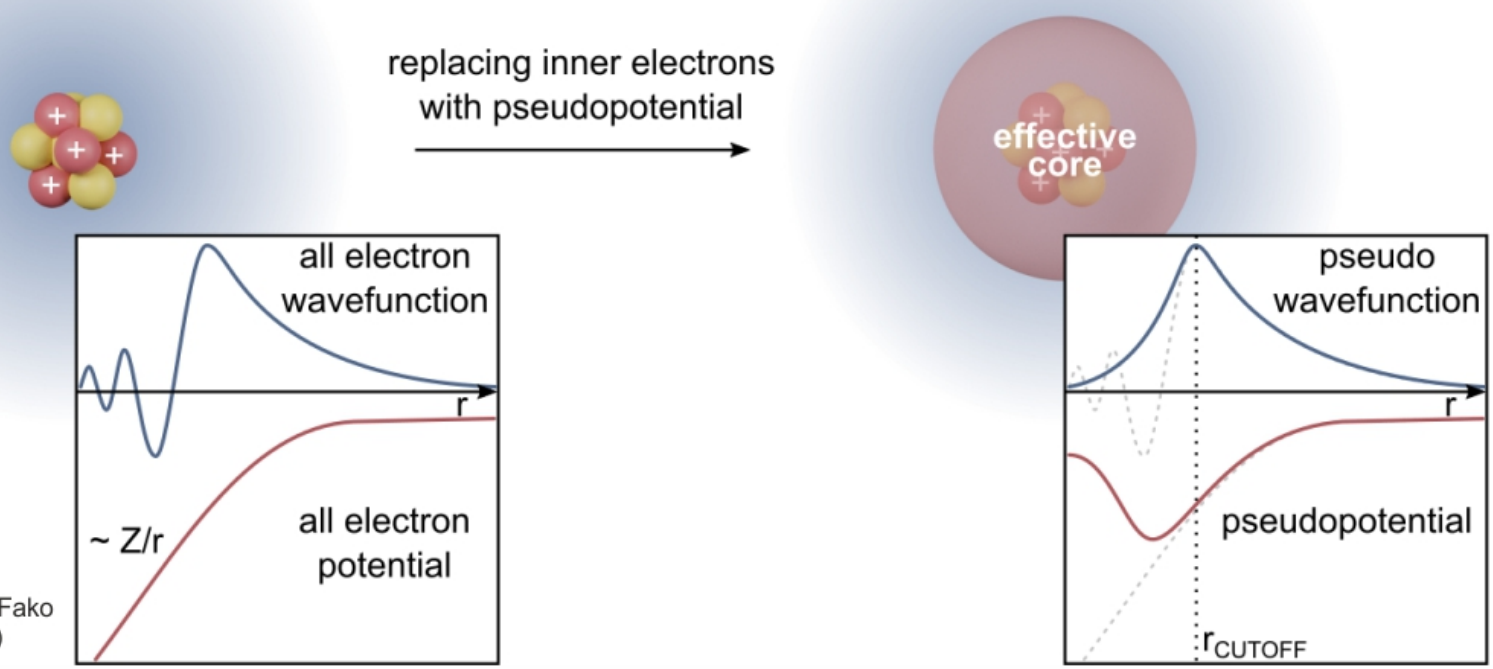
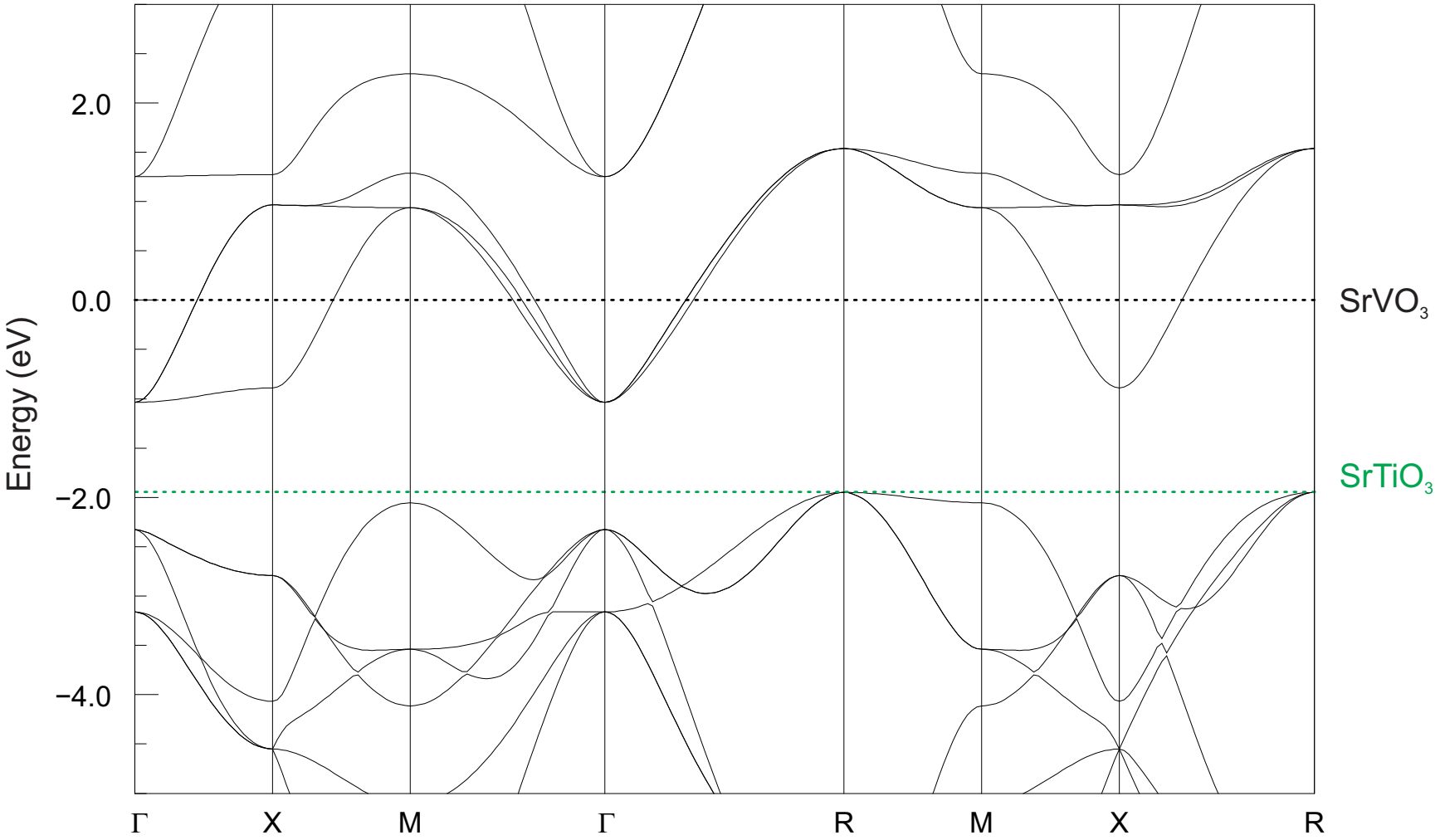


image by Edvin Fako
(CC-BY-SA)

M.L. Cohen
Phys. Scr. T1, 5 (1982)

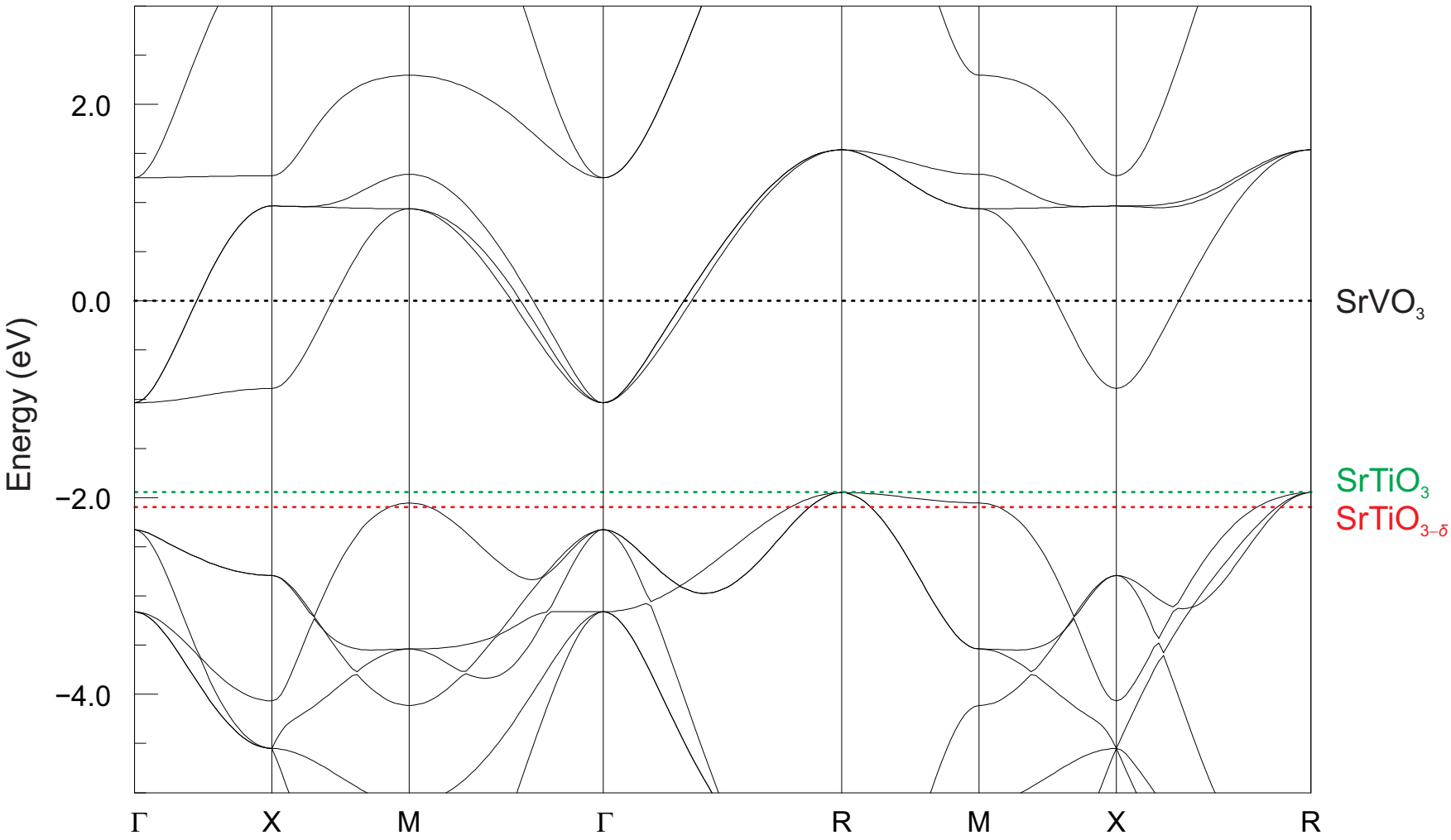
	lattice constant (Å)	cohesive energy (eV)	bulk modulus (Mbar)
Si			
Calc.	5.45	4.67	0.98
Expt.	5.43	4.63	0.99
% Diff.	0.4%	1%	−1%
Ge			
Calc.	5.66	4.02	0.73
Expt.	5.65	3.85	0.77
% Diff.	0.1%	4%	−5%

Superconducting semiconductor



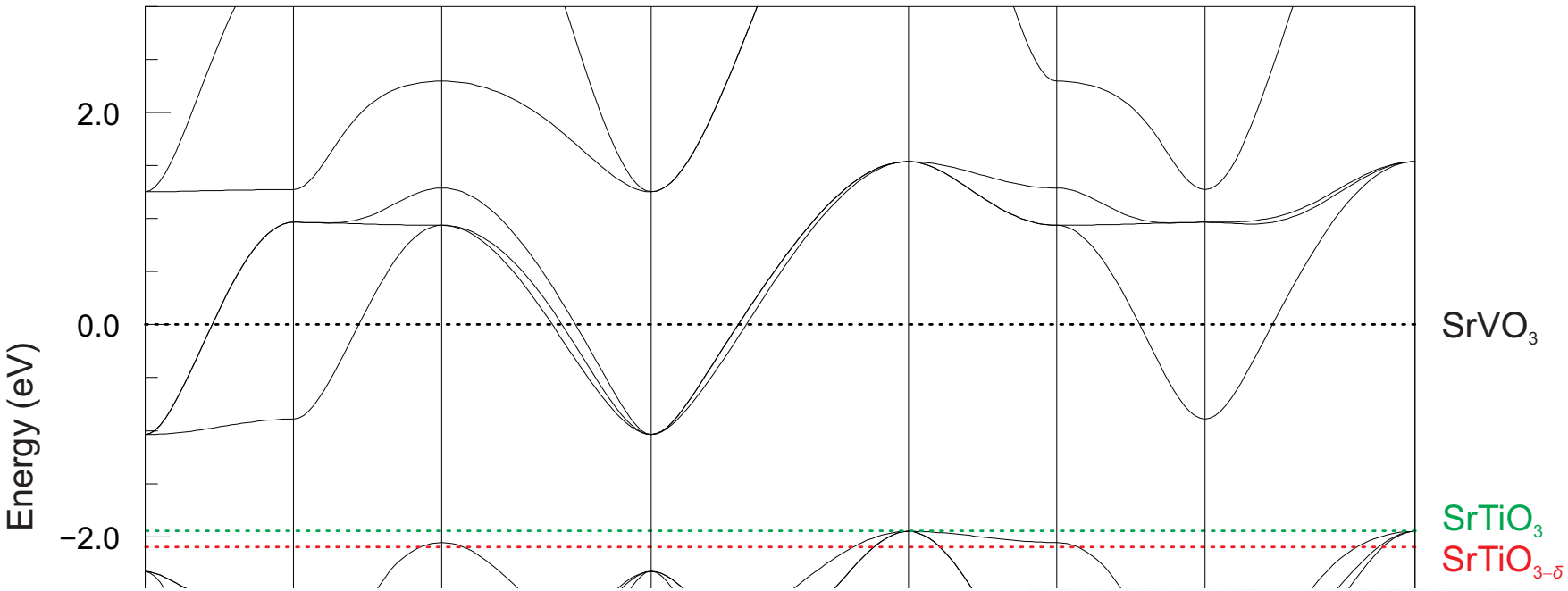
$SrTiO_3$ is a mundane wide-gap semiconductor

Superconducting semiconductor



$SrTiO_3$ is a mundane wide-gap semiconductor
but $SrTiO_{3-\delta}$ should be metallic and may become superconducting

Superconducting semiconductor



PHYSICAL REVIEW LETTERS

SUPERCONDUCTIVITY IN SEMICONDUCTING $SrTiO_3$

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