Chemical Bonding, LOBSTER, and all that…

Richard Dronskowski

Overlap Populations in Molecules and Solids, COOP and COHP

Tellurium, Iron, Phase-Change Materials

Linear-Muffin-Tin Orbital Theory (LMTO) and Pseudopotentials

Bonding Information projected from Plane Waves

The **LOBSTER** computer program

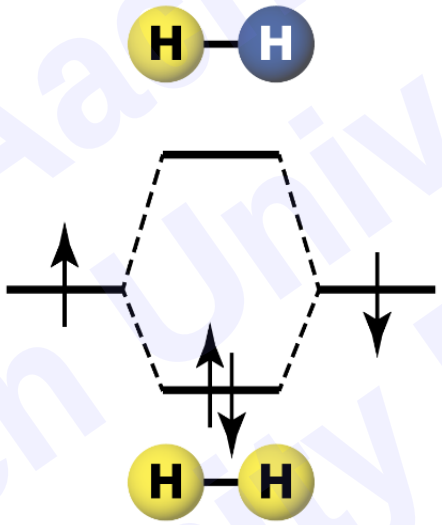
C & Nanotube & Ti & amorphous GeTe & GeO_2 surfaces & H bonding & CuN_3 & TiO & MnNCN/MnO & Ge_4Se_3Te & Carbons & Na_2He

Chair of Solid-State and Quantum Chemistry | RWTH AACHEN UNIVERSITY

Skoltech

H_2: Population Analysis by Robert S. Mulliken

$$\int \psi^* \psi d\tau = \underbrace{\int \psi^2 d\tau}_{\equiv 1} = c_1^2 \underbrace{\int \phi_1^2 d\tau}_{\equiv 1} + c_2^2 \underbrace{\int \phi_2^2 d\tau}_{\equiv 1} + 2c_1 c_2 \underbrace{\int \phi_1 \phi_2 d\tau}_{S_{12}}$$



R. S. Mulliken,
J. Chem. Phys. **1955**, *23*, 1833

… plus population analyses by Roby, Löwdin, Davidson, Jug, Ahlrichs, and others…

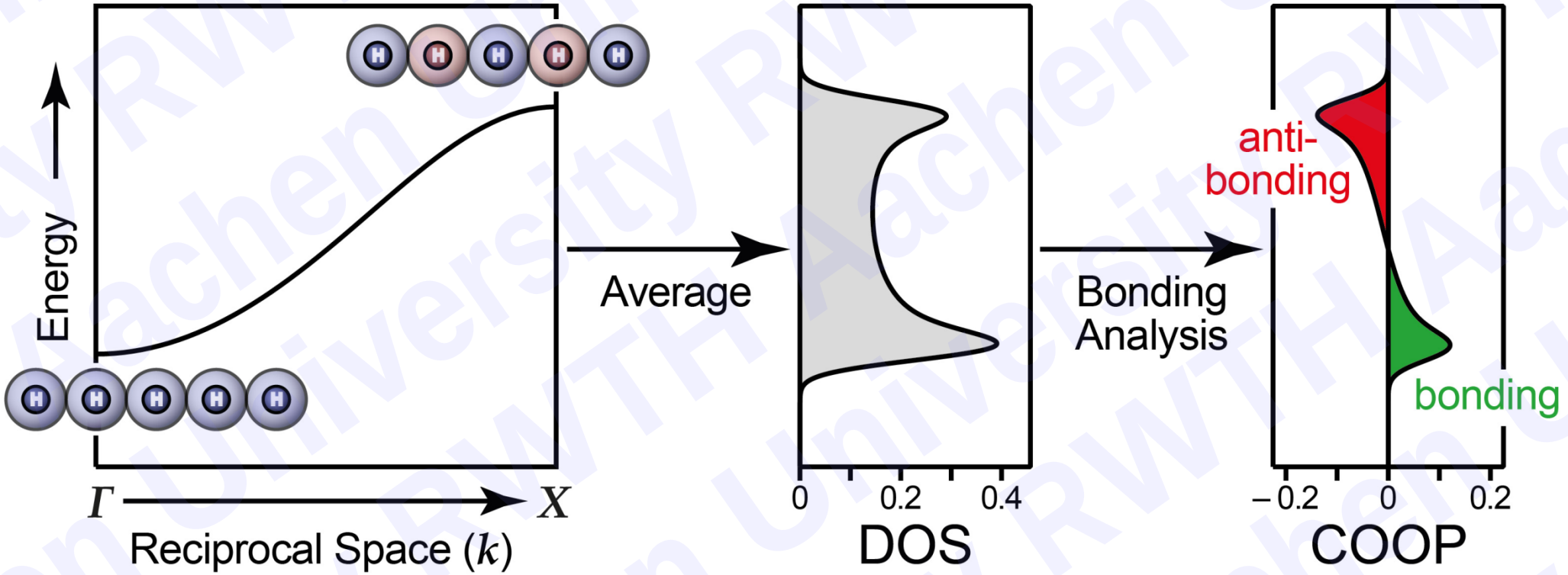
Simplest Population Analysis for σ_g-MO of H_2

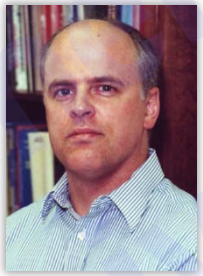
$$1 = \underbrace{\frac{1}{2(1+S_{12})}}_{=0.305} + \underbrace{\frac{1}{2(1+S_{12})}}_{=0.305} + \underbrace{\frac{2}{2(1+S_{12})}S_{12}}_{=0.390}$$

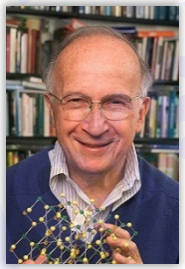
the two hydrogen atoms share 0.78 electrons

1dim H-chain: Band Structure, DOS, COOP

without any doubt (I guess) the icon of solid-state quantum chemistry:







T. Hughbanks, R. Hoffmann,
J. Am. Chem. Soc. **1983**, *105*, 3528

Crystal Orbital Overlap Population, COOP

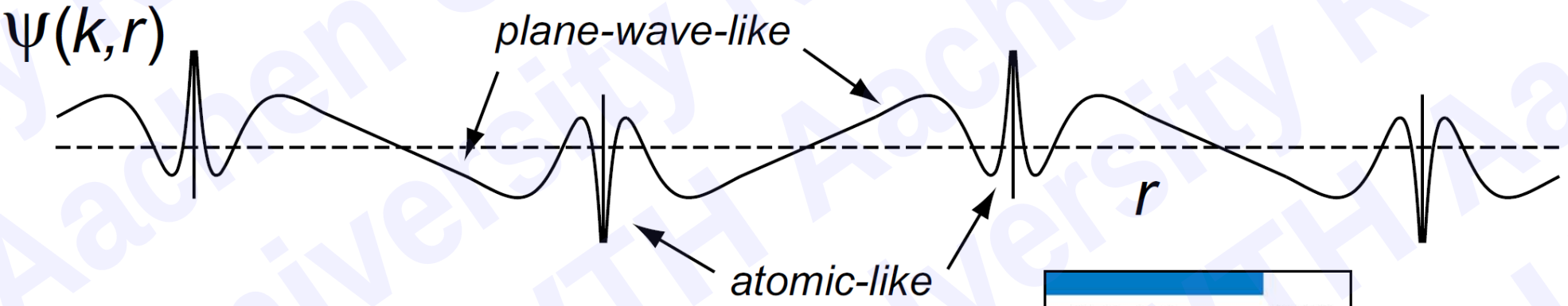
$$N = \underbrace{\int^{\varepsilon_F} \sum_A \sum_{\substack{\mu \\ \mu \in A}} P_{\mu\mu}(E)\, dE}_{\text{net populations}} + \underbrace{\int^{\varepsilon_F} 2 \sum_A \sum_{B>A} \sum_{\substack{\mu \\ \mu \in A}} \sum_{\substack{\nu \\ \nu \in B}} \mathrm{Re}[P_{\mu\nu}(E) S_{\mu\nu}]\, dE}_{\text{overlap populations}}$$

$$= \underbrace{\int^{\varepsilon_F} \sum_A \sum_{\substack{\mu \\ \mu \in A}} \left(P_{\mu\mu}(E) + \sum_{B \neq A} \sum_{\substack{\nu \\ \nu \in B}} \mathrm{Re}[P_{\mu\nu}(E) S_{\mu\nu}] \right) dE,}_{\text{gross populations}}$$

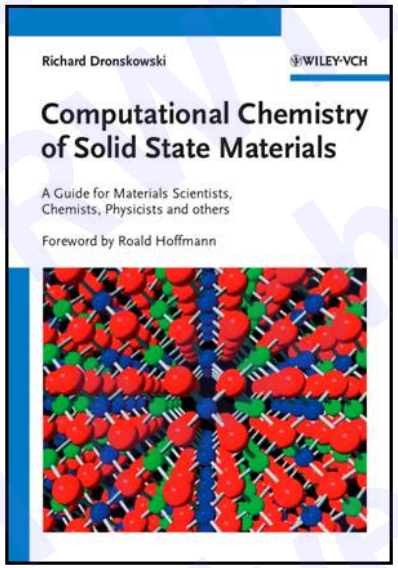
$$= \int^{\varepsilon_F} \sum_A \sum_{\substack{\mu \\ \mu \in A}} \sum_B \sum_{\substack{\nu \\ \nu \in B}} P_{\mu\nu}(E) S_{\mu\nu}\, dE.$$

Schrödinger's Equation in the Solid State

$$\hat{H}\,\Psi(k,r) = E\,\Psi(k,r)$$



Bloch function of a one-dimensional Na crystal at the X point of reciprocal space

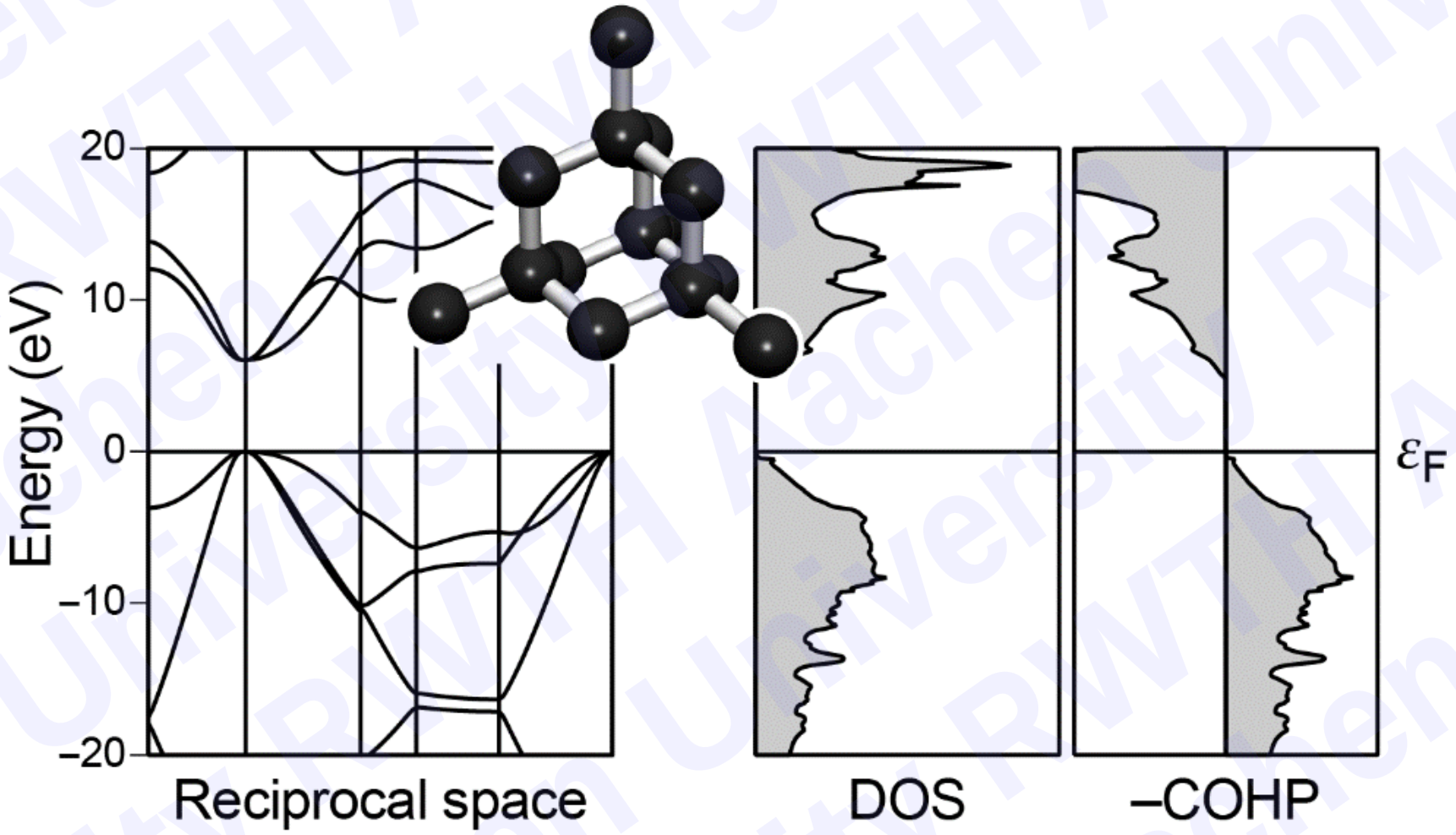


DFT: Crystal Orbital Hamilton Population, COHP

$$E = \underbrace{\int^{\varepsilon_F} \sum_A \sum_{\substack{\mu \\ \mu \in A}} P_{\mu\mu}(E) H_{\mu\mu}(E)\, dE}_{\text{net atomic energies}} + \underbrace{\int^{\varepsilon_F} 2 \sum_A \sum_{B>A} \sum_{\substack{\mu \\ \mu \in A}} \sum_{\substack{\nu \\ \nu \in B}} \mathrm{Re}[P_{\mu\nu}(E) H_{\mu\nu}(E)]\, dE}_{\text{bonding energies}}$$

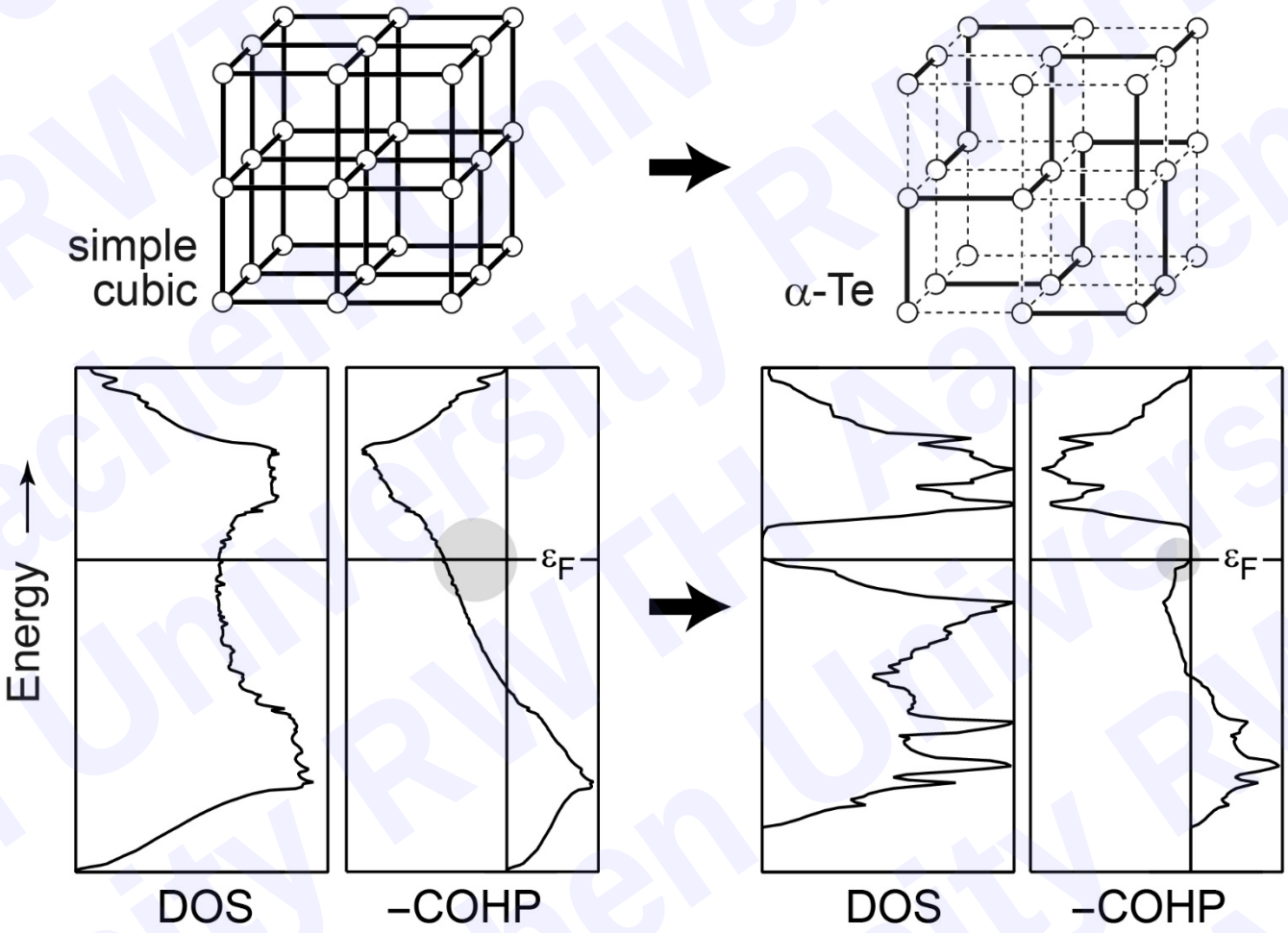
partitioning the energy, not the electrons, between the atoms and the bonds...

DFT: COHP for Diamond



R. Dronskowski, P. E. Blöchl,
J. Phys. Chem. **1993**, *97*, 8617

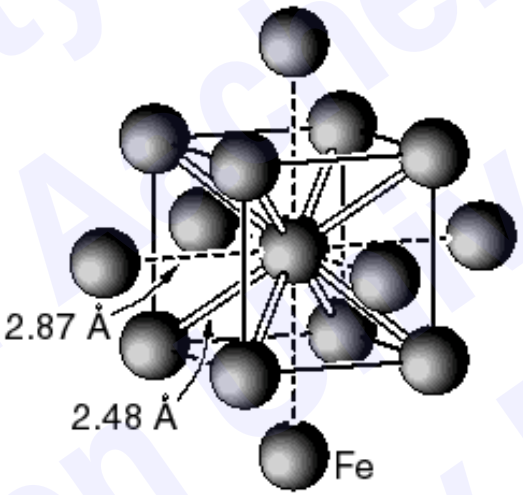
Example I: sc Tellurium is Peierls-unstable

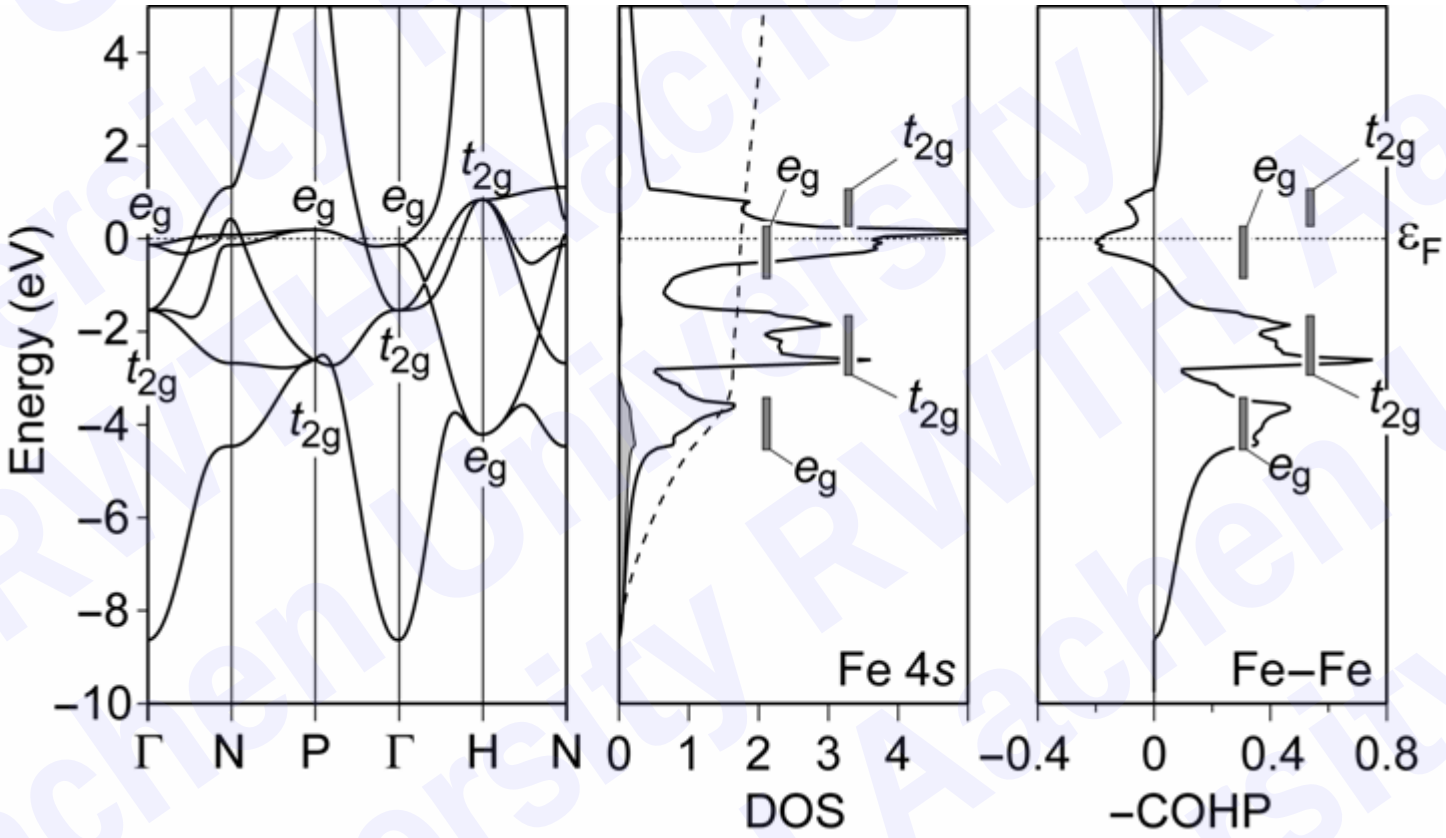


A. Decker, G. A. Landrum, R. Dronskowski,
Z. Anorg. Allg. Chem. **2002**, *628*, 295

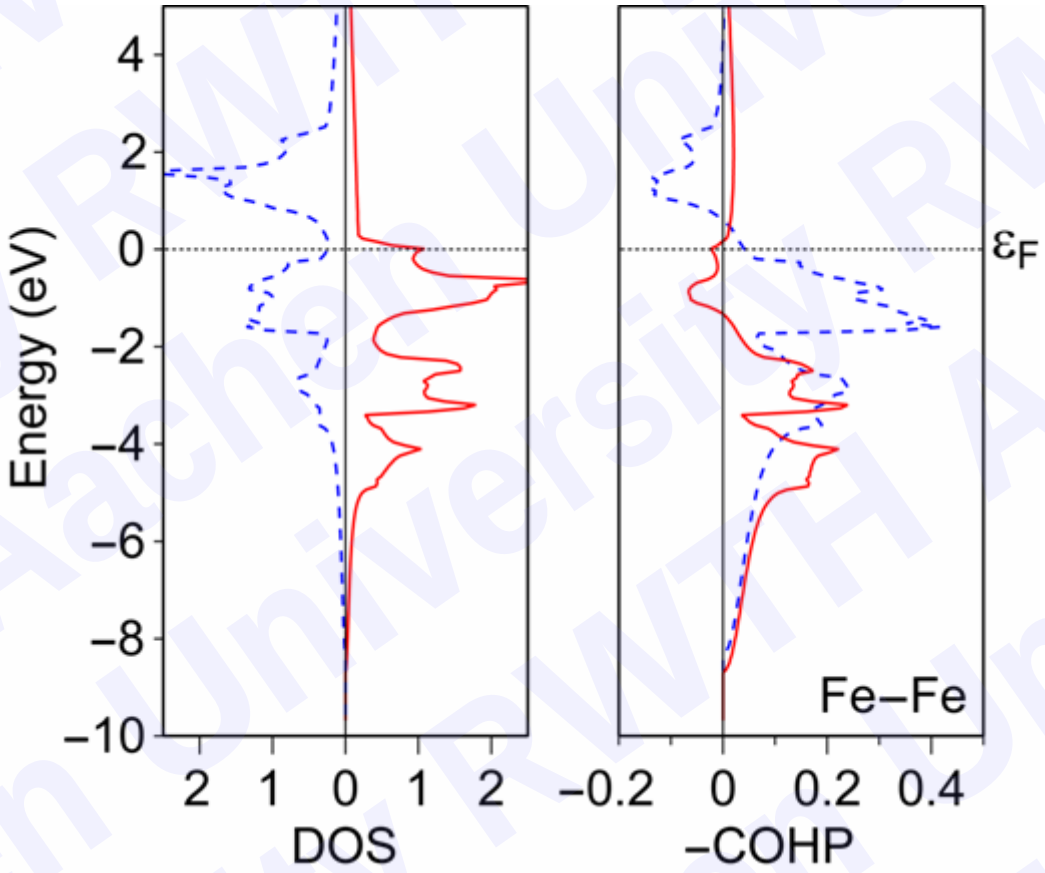
Example II: body-centered cubic Fe

and its corresponding non-realistic LDA band structure
without spin-polarization, on purpose:





Spin Polarization: Chemical Bonding



magnetic moment: 2.27 μ_B (exp.: 2.21 μ_B)

majority spin orbitals contract

minority spin orbitals expand

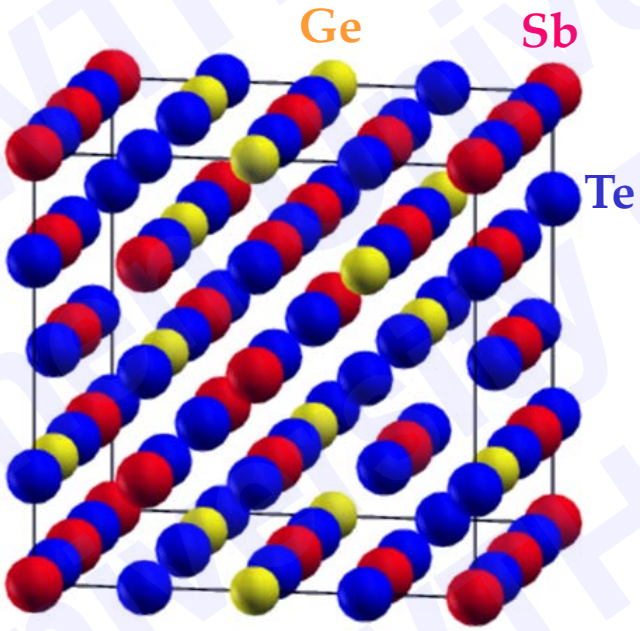
lowering of total energy by about 0.43 eV

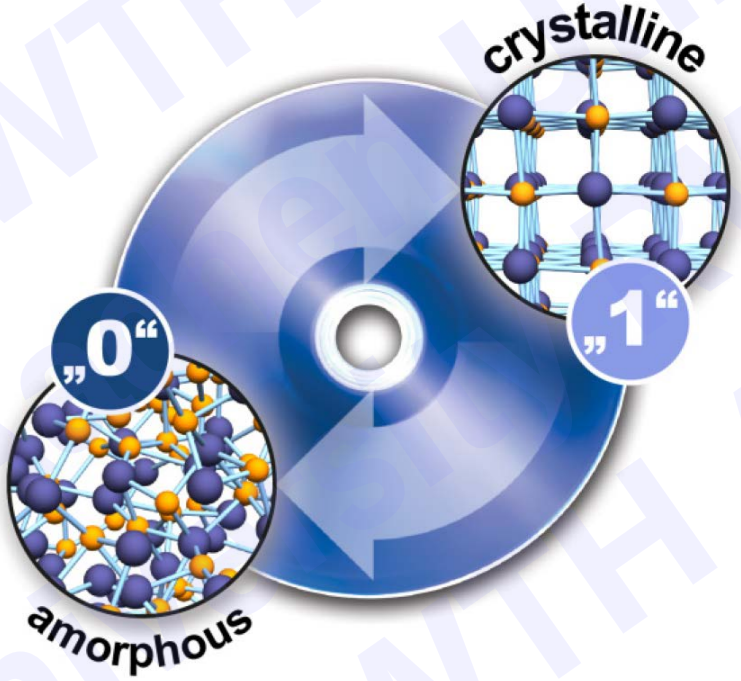
strengthening of iron–iron bonding by about 5%

minority spins roughly twice as strongly bonding as majority spins

G. A. Landrum, R. Dronskowski,
Angew. Chem. Int. Ed. **2000**, *39*, 1560

Example III: Ge–Sb–Te Phase-change Materials

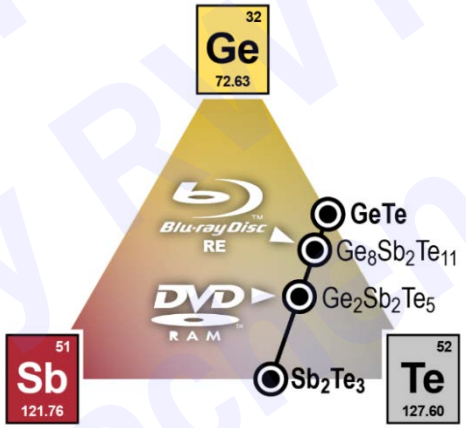


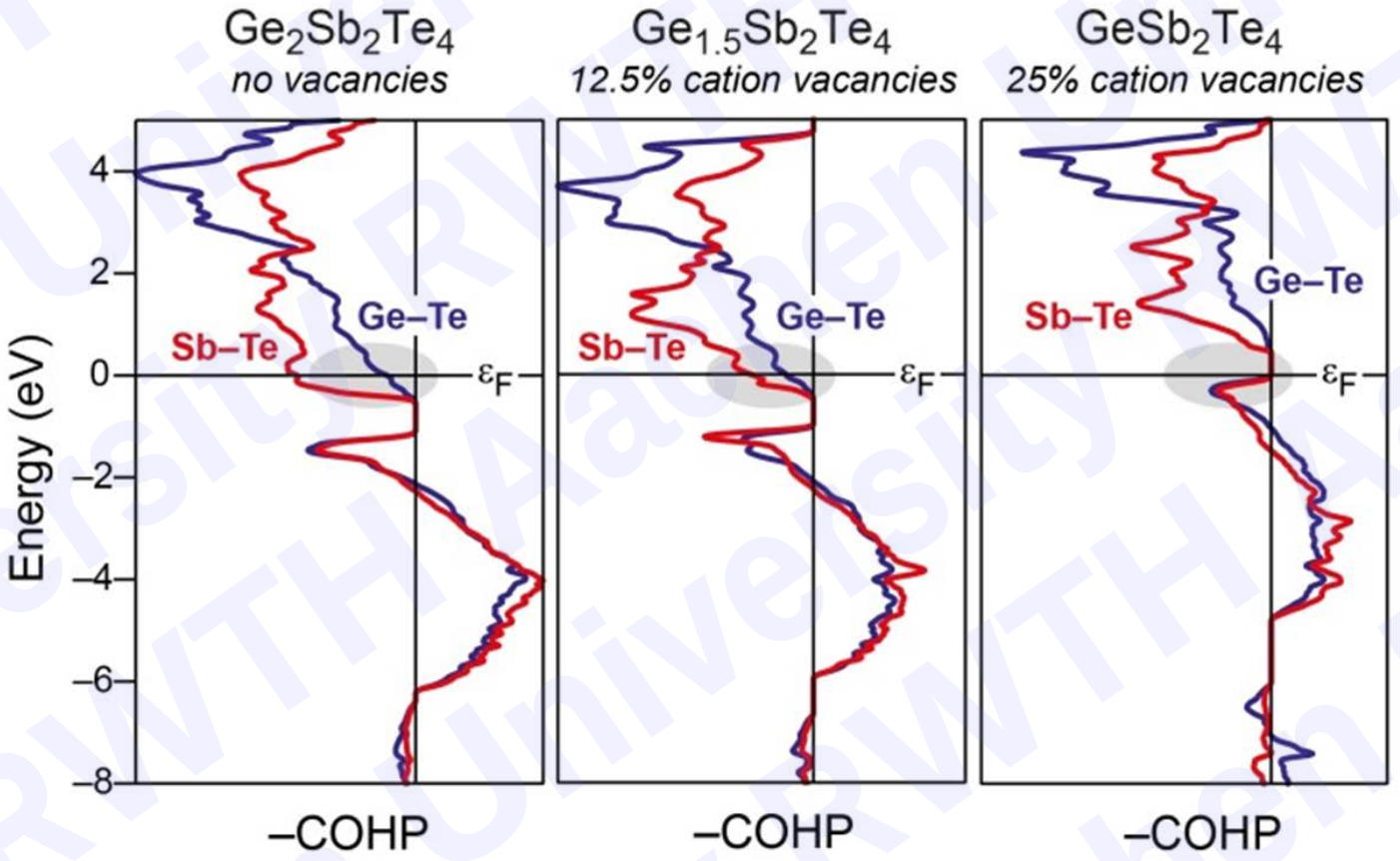


e.g., $Ge_2Sb_2Te_4$ with lots of Ge vacancies (≈ 20%) – **why?**

switching mechanism = *f*(vacancy nature)

Phase-change Materials: First COHP study

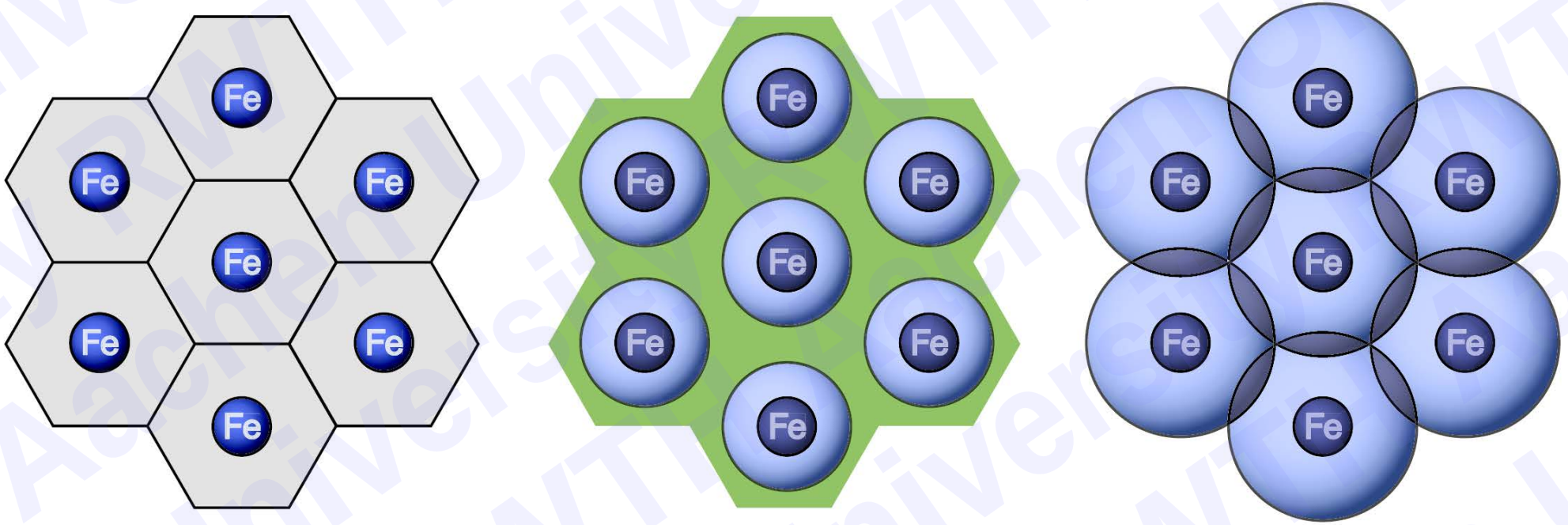




antibonding *Ge–Te and Sb–Te interactions in the highest bands; germanium vacancies annihilate antibonding states*

M. Wuttig, D. Lüsebrink, D. Wamwangi, W. Wełnic, M. Gilleßen, R. Dronskowski, *Nature Mater*. **2007**, *6*, 122

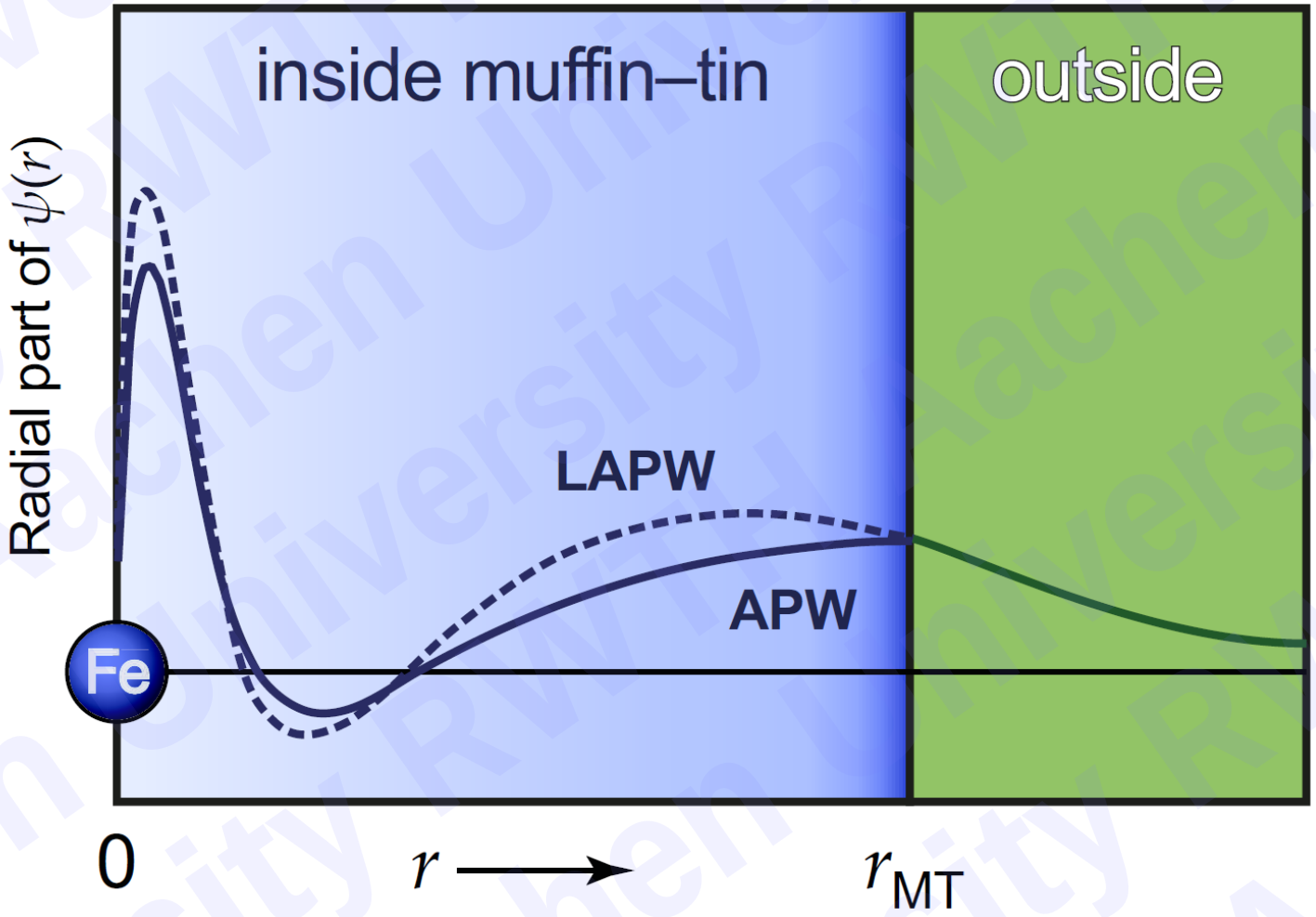
Wigner–Seitz, Muffin-Tin, Atomic-Spheres



Tight-Binding Linear-Muffin-Tin Orbitals
using the Atomic-Spheres-Approximation (ASA)

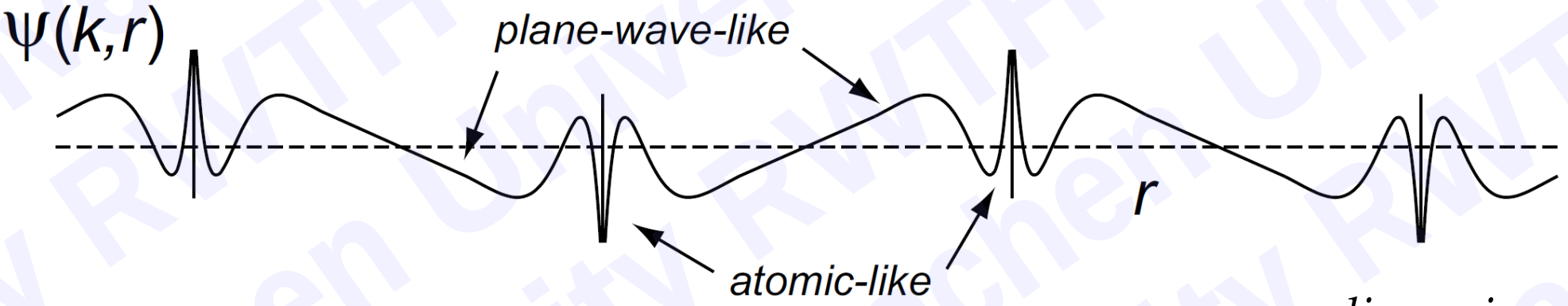
probably the most influential (among the chemists)
*periodic **orbital-based** electronic-structure method*

Machinery: "Linear Methods" LAPW and LMTO



O. K. Andersen,
Phys. Rev. B **1975**, *12*, 3060

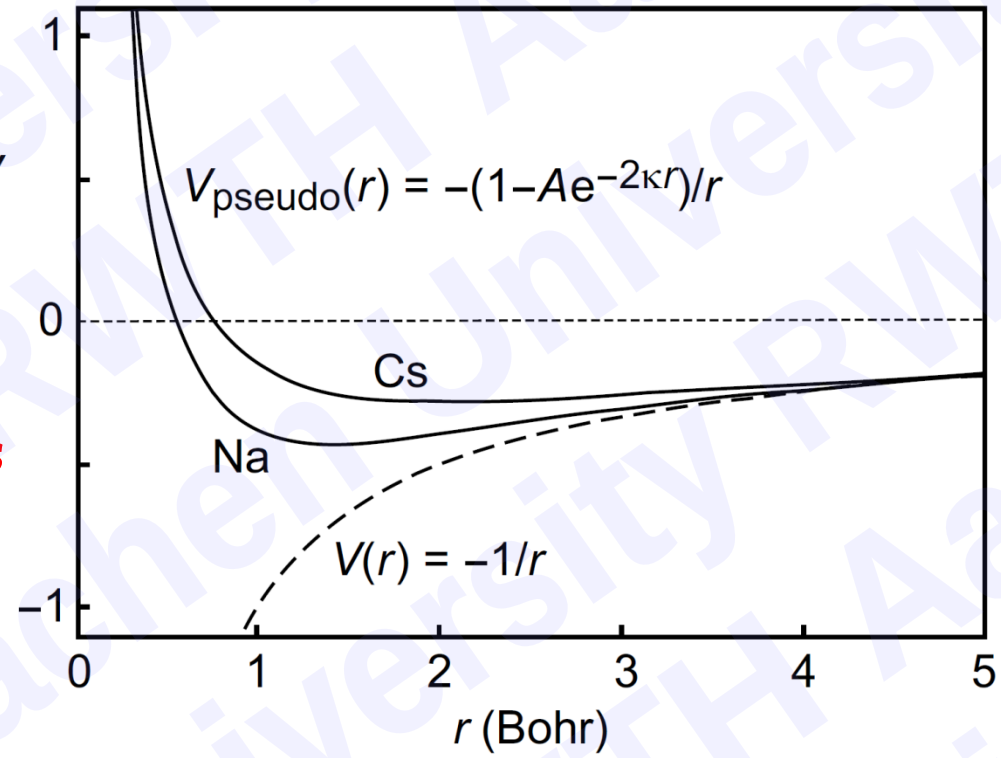
Hans Hellmann, *J. Chem. Phys.* 1935, 3, 61

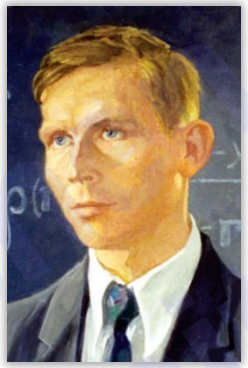


one-dimensional Na-3s Bloch function at **X**

the world's first pseudopotentials: Na and Cs

→ *plane waves, thus* ***reliable*** *forces!*

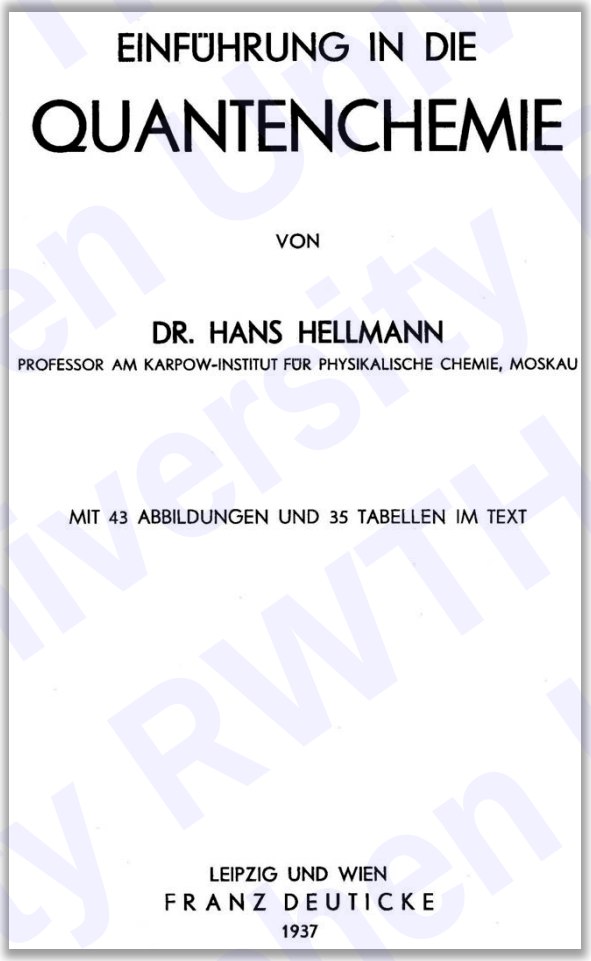


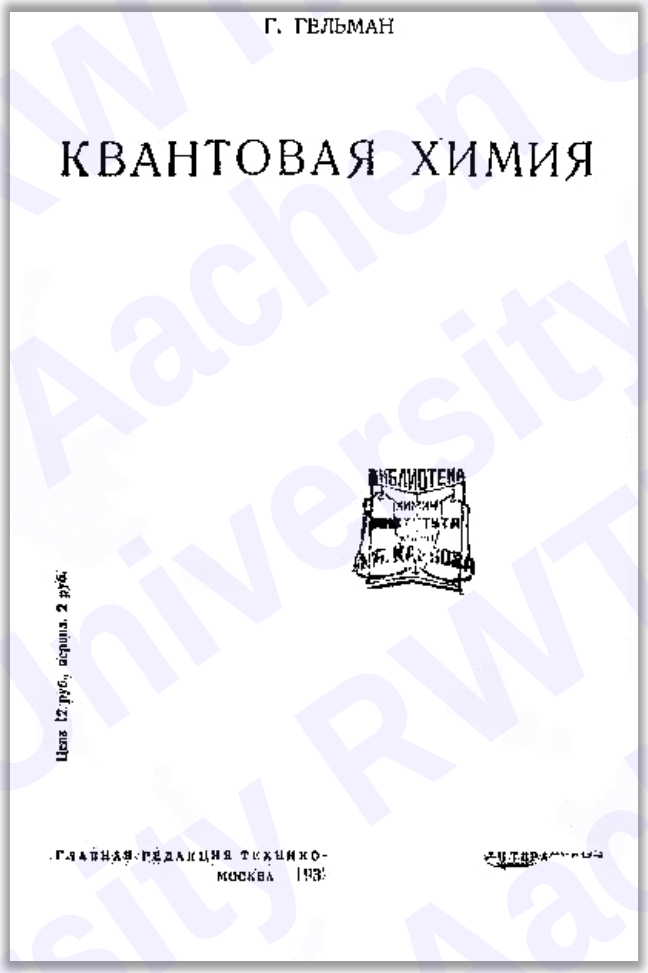


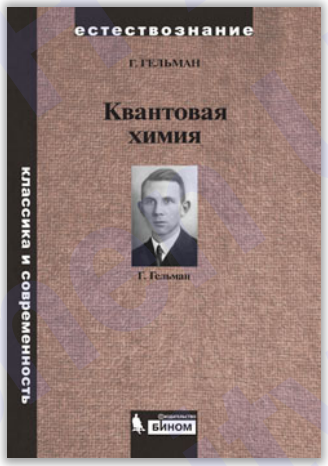
Emigration to the Soviet Union

Greta Hermine Hans

The World's First Quantum-Chemistry Textbooks

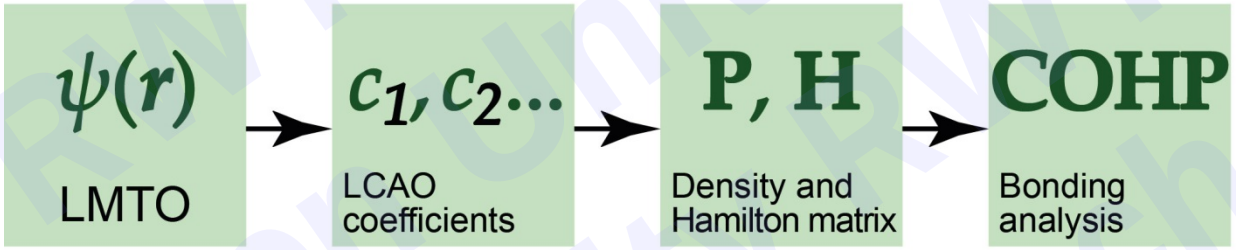




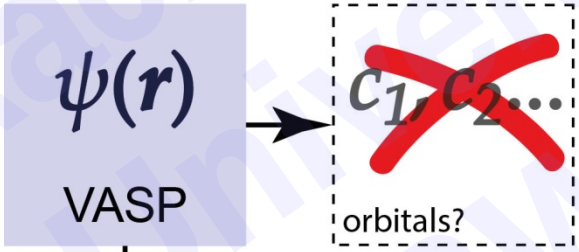


Retrieving the Chemistry

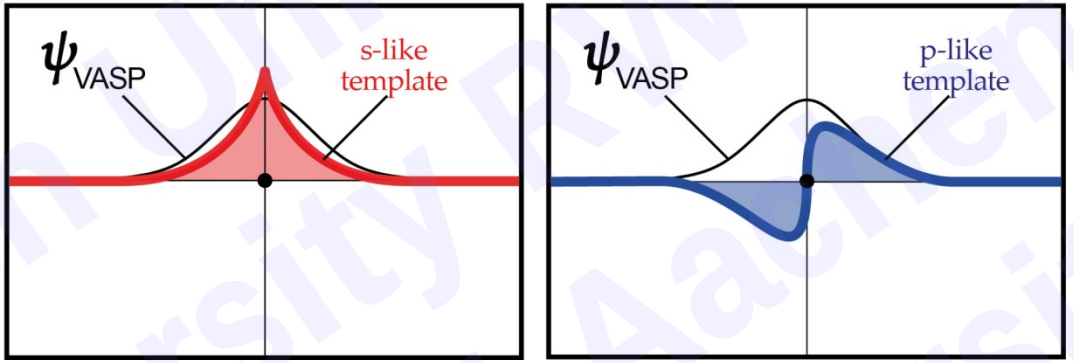
Traditionally: Tight-Binding LMTO-ASA (= densely packed atomic spheres)



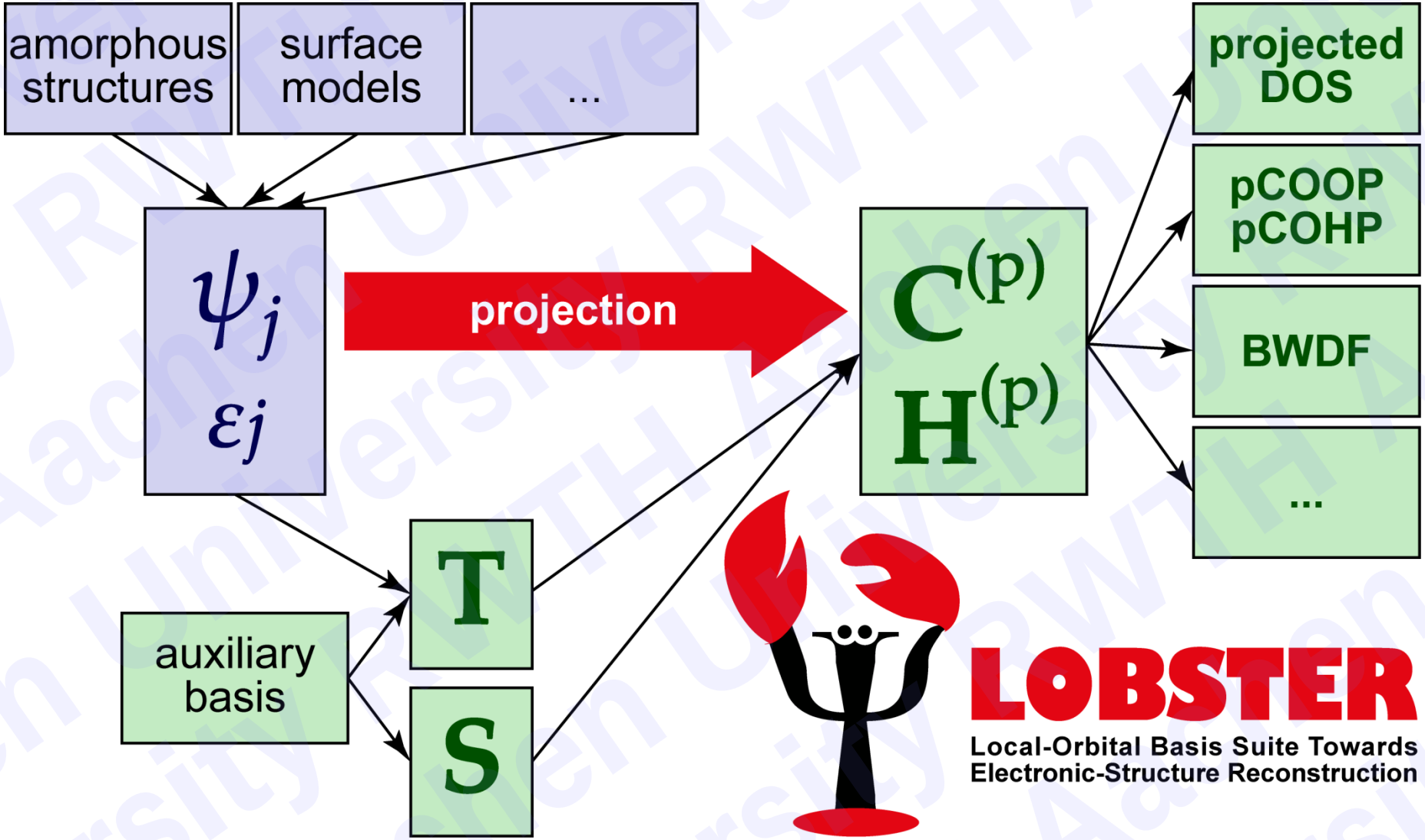
Modern: countless program packages with plane waves (e.g., VASP)



Idea: local auxiliary basis set as template



LOBSTER does it for you…



freely available at www.cohp.de

www.cohp.de

Journal of COMPUTATIONAL CHEMISTRY
WWW.C-CHEM.ORG
SOFTWARE NEWS AND UPDATES

LOBSTER: A Tool to Extract Chemical Bonding from Plane-Wave Based DFT

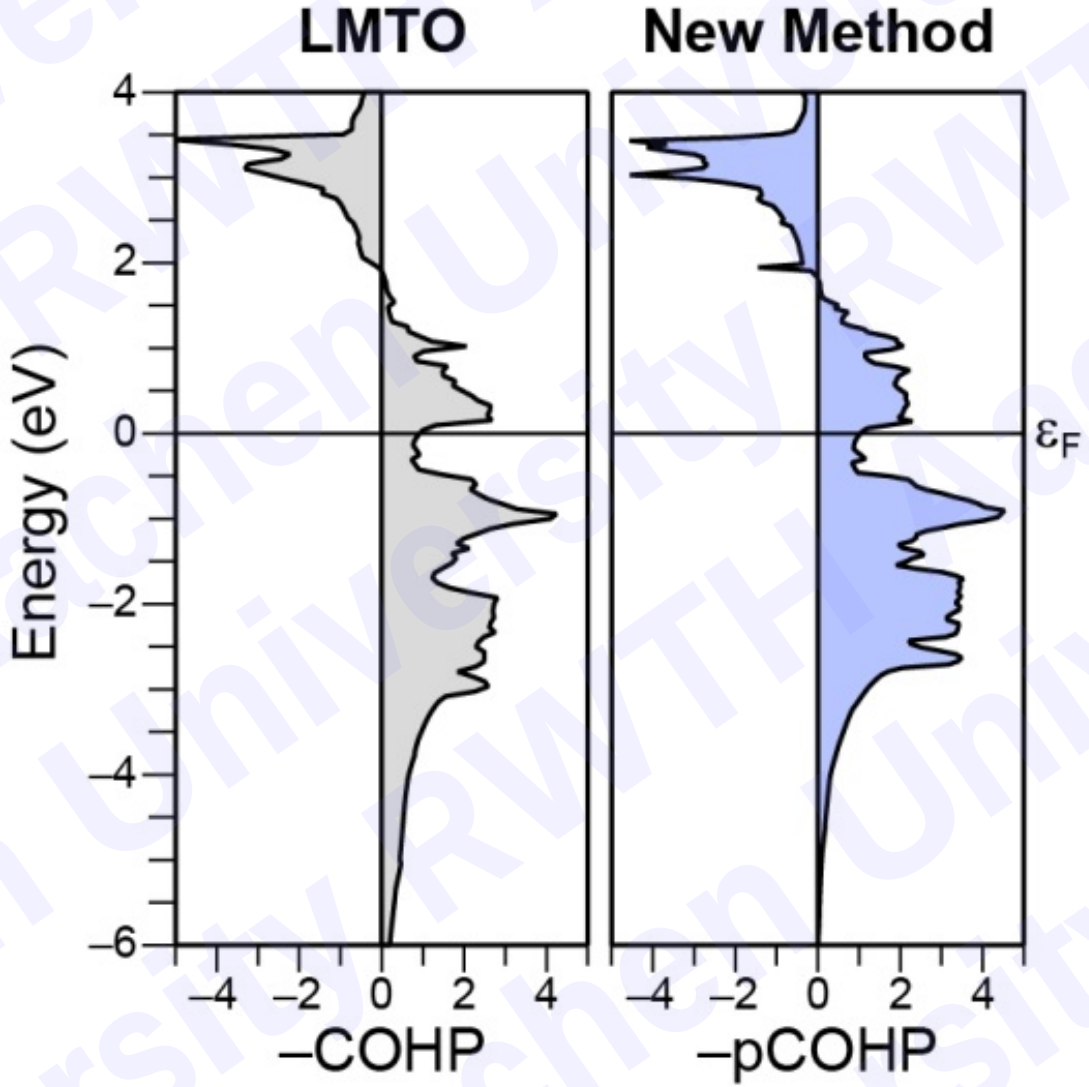
OPEN ACCESS

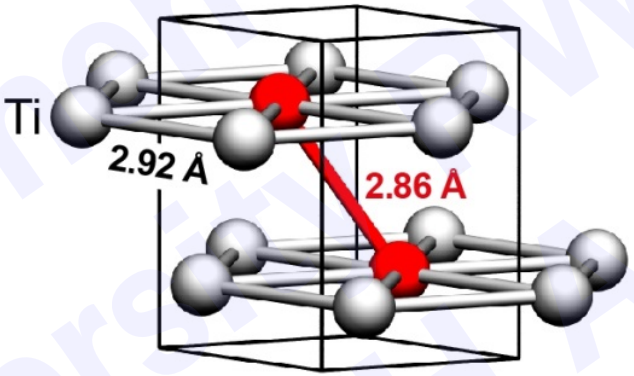
Stefan Maintz,[a] Volker L. Deringer,[a] Andrei L. Tchougréeff,[a,b,c] and Richard Dronskowski*[a,d]

Chair of Solid-State and Quantum Chemistry
RWTH AACHEN UNIVERSITY
Skoltech

First LOBSTER school in 2017 by CECAM

Titanium (hcp): Comparison with LMTO

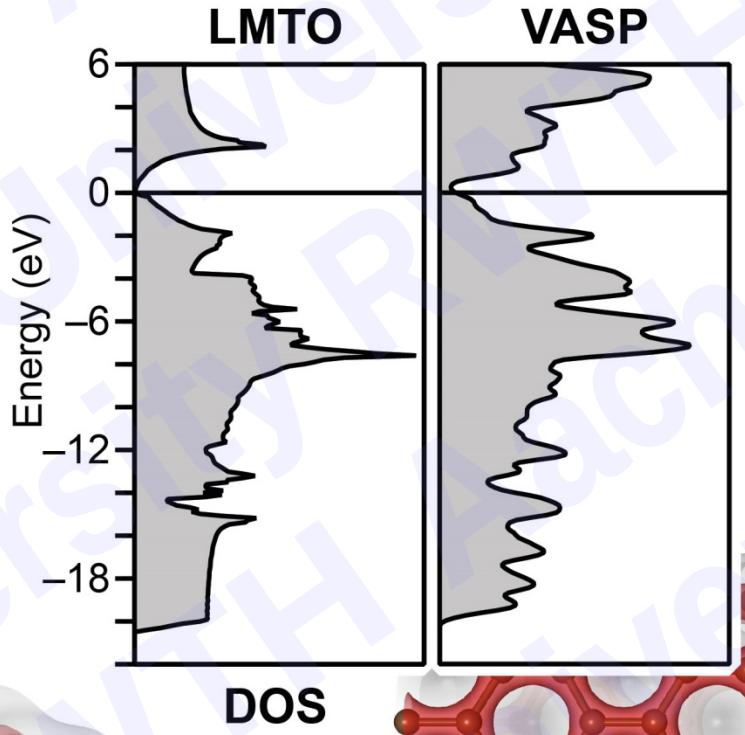




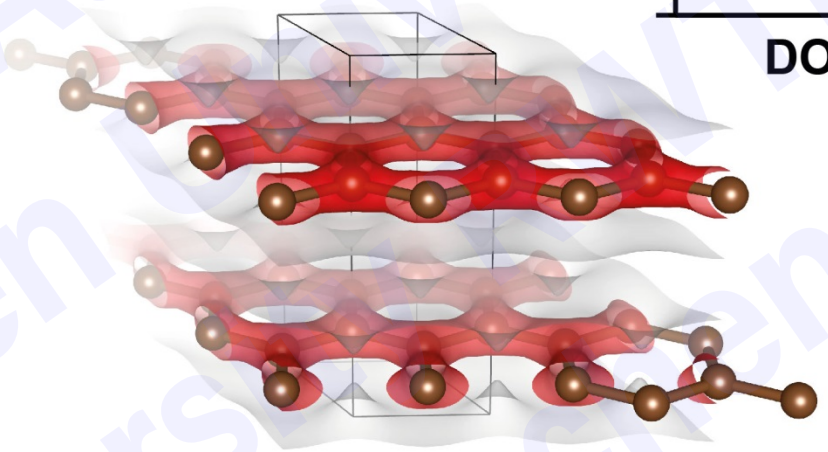
S. Maintz, V. L. Deringer,
A. L. Tchougréeff,
R. Dronskowski,
J. Comput. Chem. **2013**, *34*, 2557

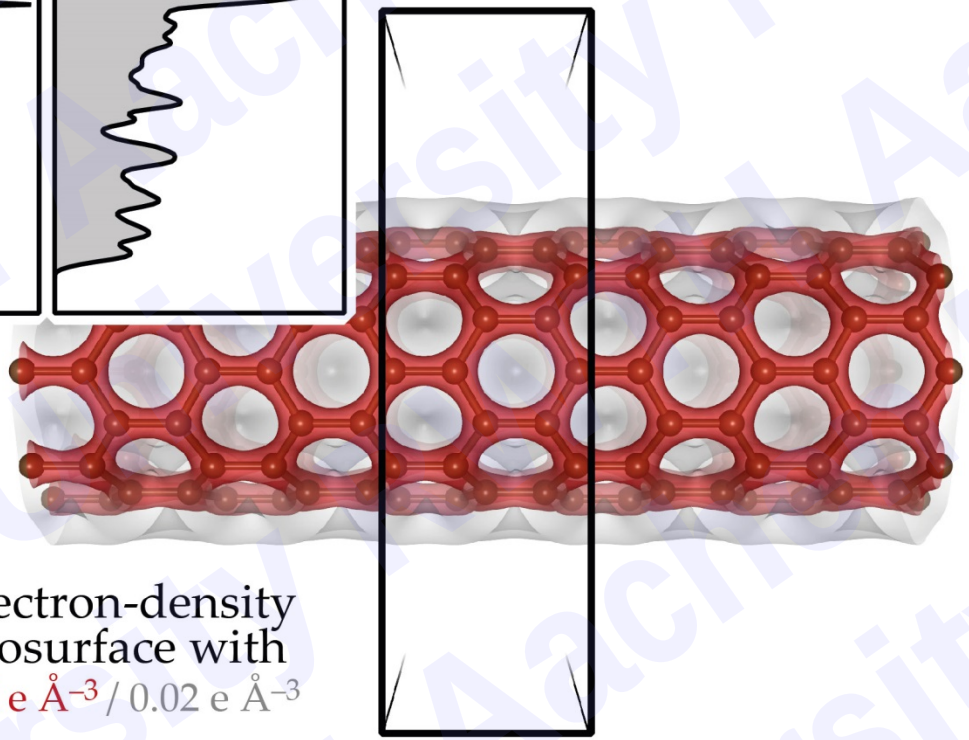
Graphite and Nanotube Density-of-States

closely packed graphite: easy job for LMTO and other local-orbital methods



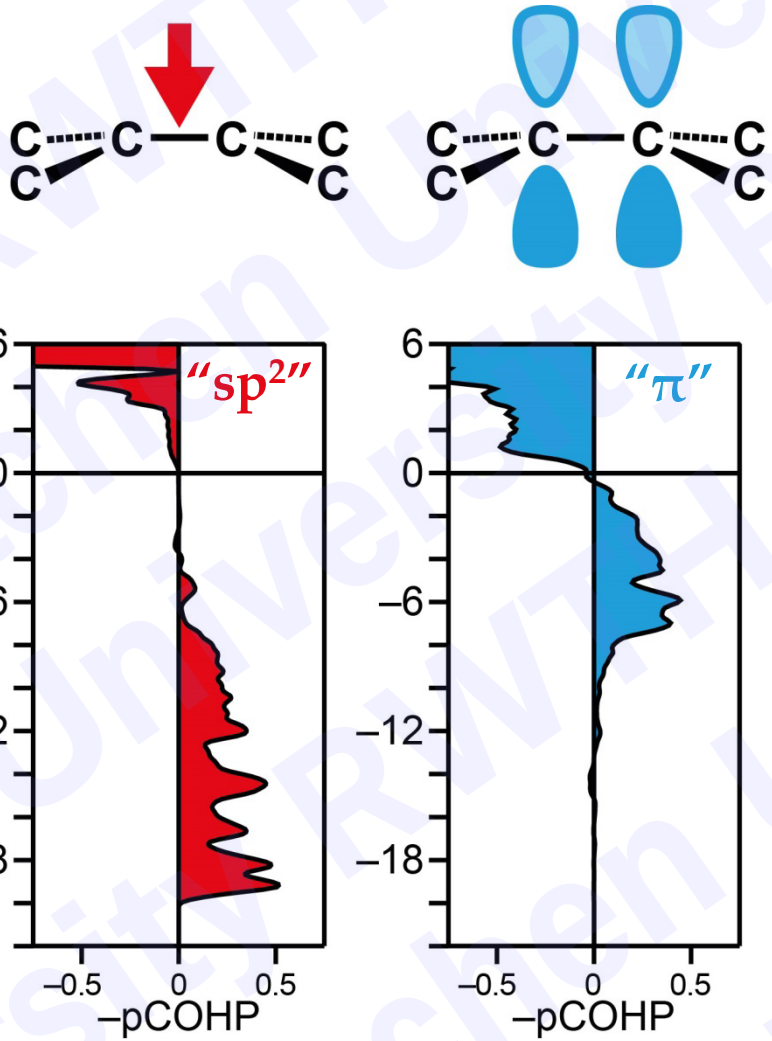
one-dimensional carbon nanotube in supercell: VASP is a reasonable choice

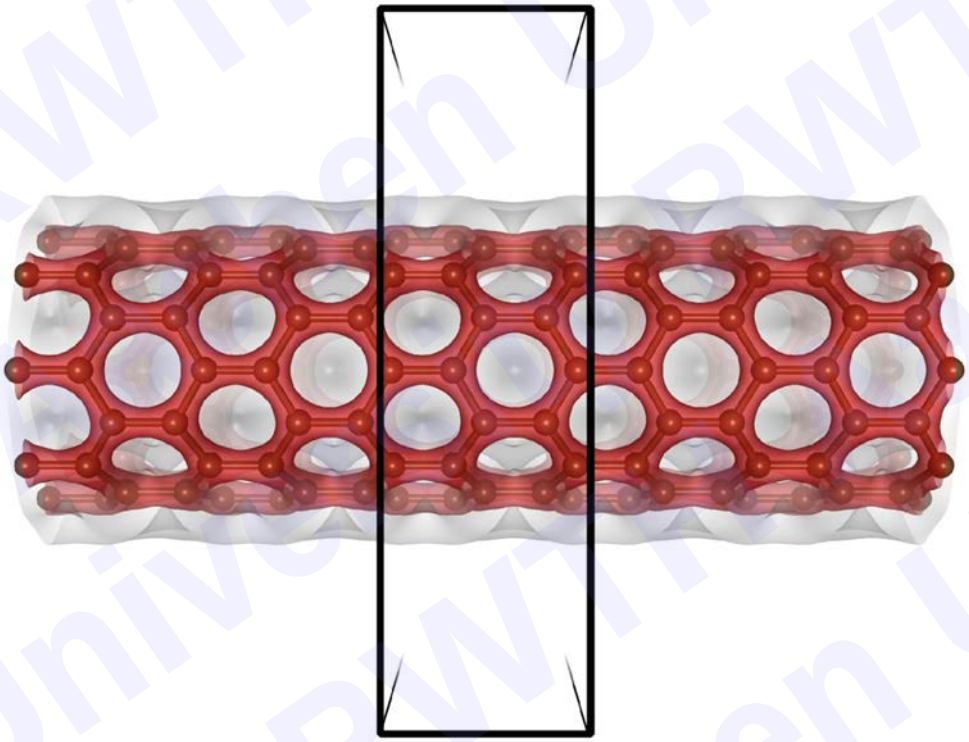




electron-density isosurface with
0.2 e Å^{-3} / 0.02 e Å^{-3}

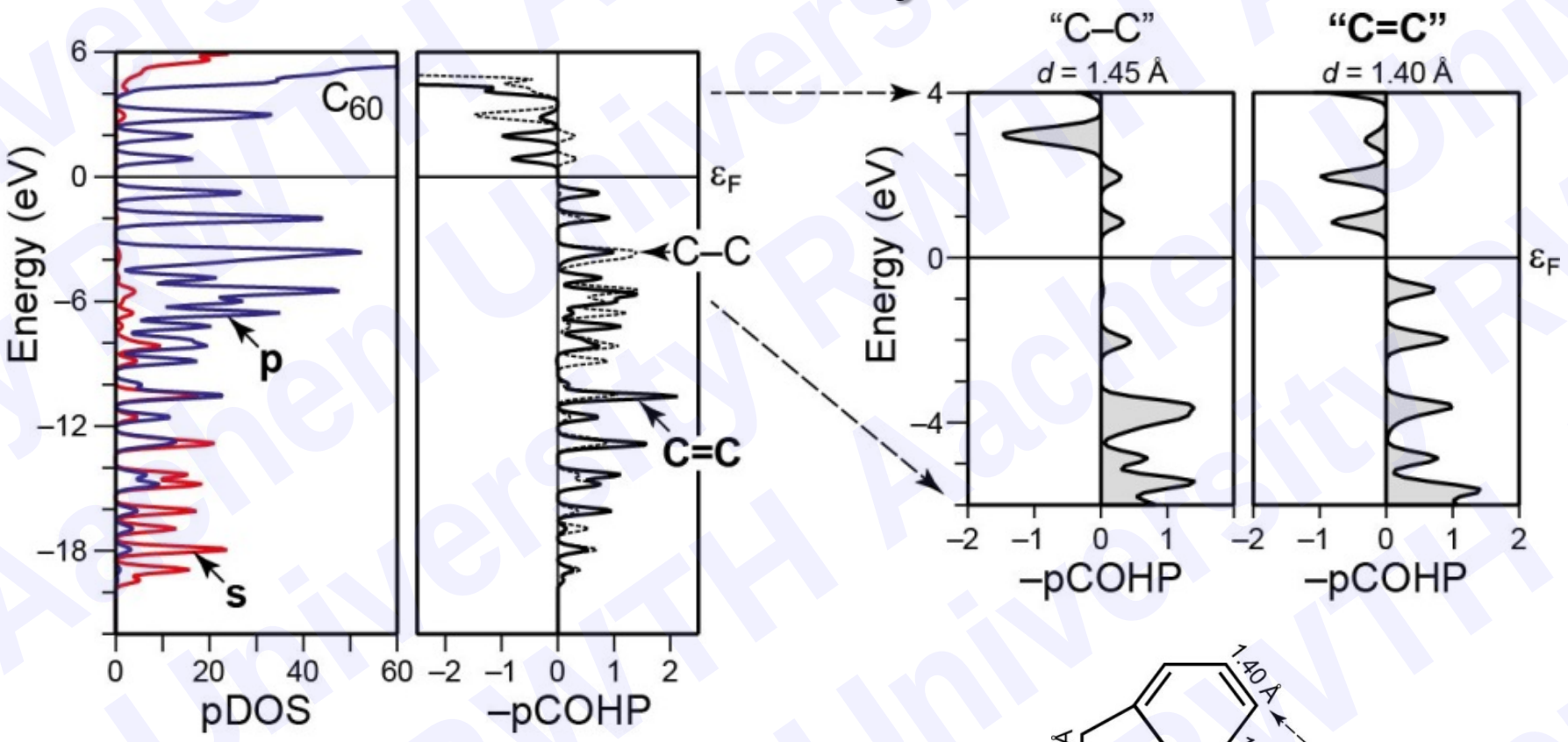
Chemical Bonding in the Carbon Nanotube

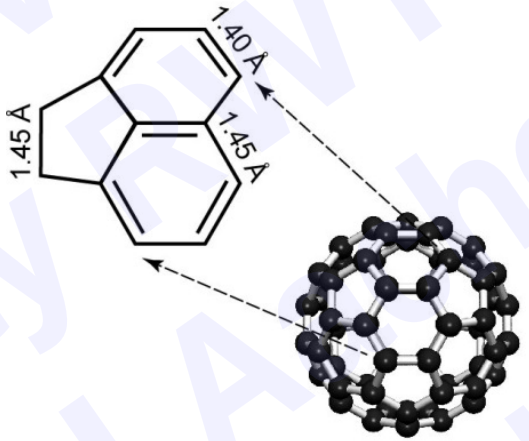




S. Maintz, V. L. Deringer,
A. L. Tchougréeff, R. Dronskowski,
J. Comput. Chem. **2016**, *37*, 1030

... and in the Carbon Buckyball



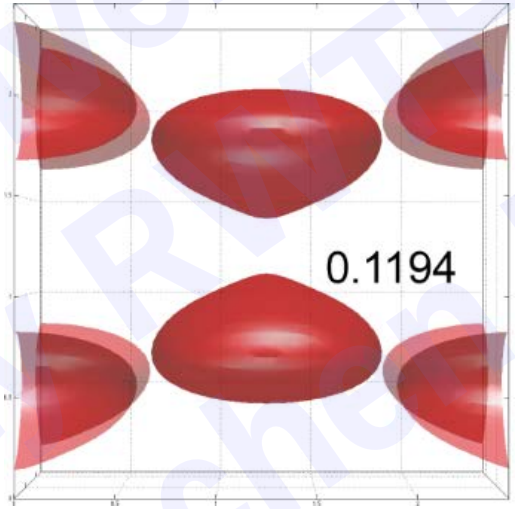


"double" bond: electronically optimized

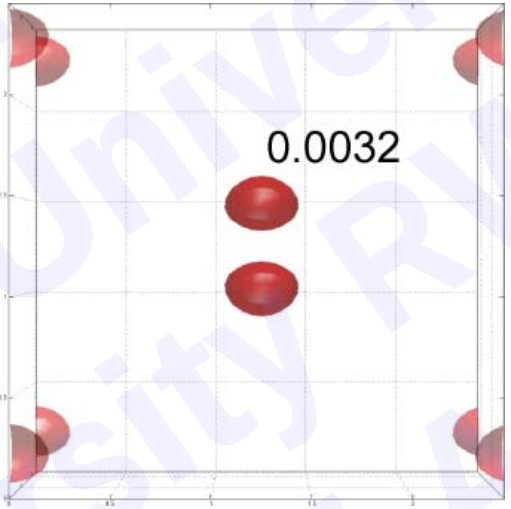
"single" bond: nonbonding contribution just below the HOMO and unoccupied bonding states right above

"double" bond ca. 9% stronger than the "single" bond

LOBSTER extended basis sets (e.g, for beryllium)



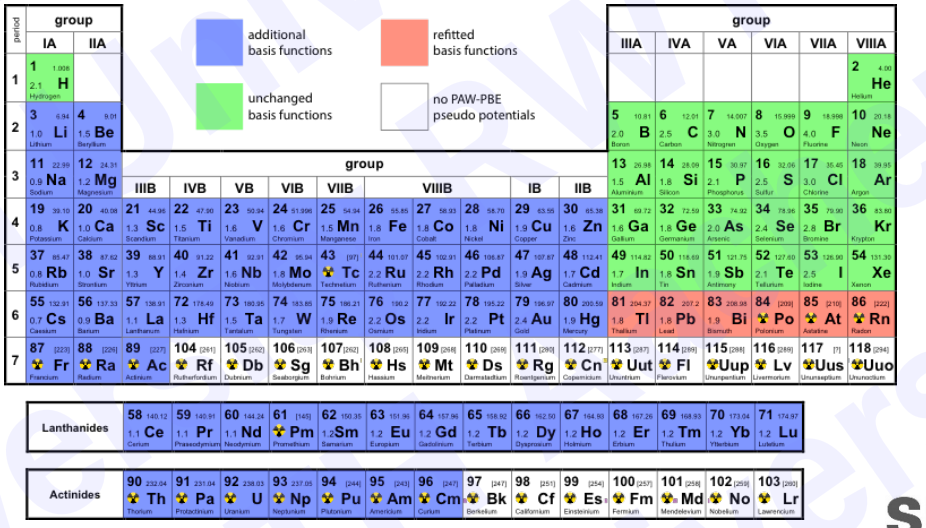
1s, 2s



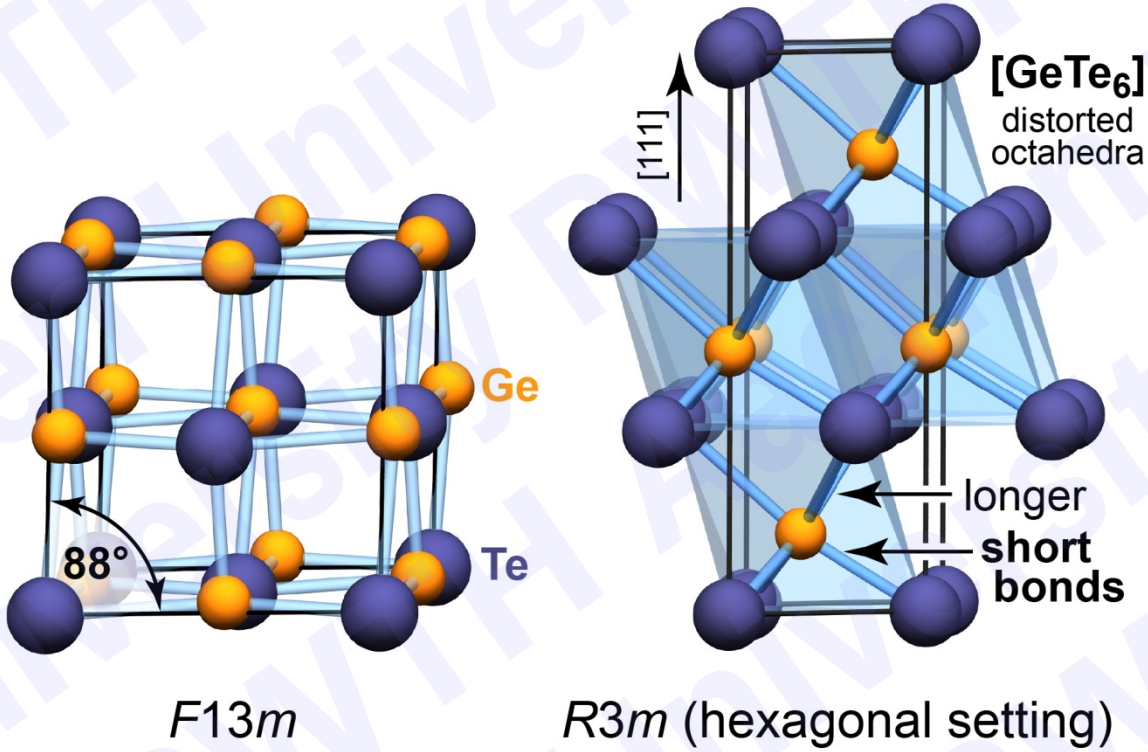
1s, 2s, 2p

Isosurfaces (in Å^{-3}) at 65% of the differences between the ABINIT*-based PAW densities and the* LOBSTER*-projected densities for the fourth band of β-Be at* **Γ**

available since LOBSTER *2.1.0*



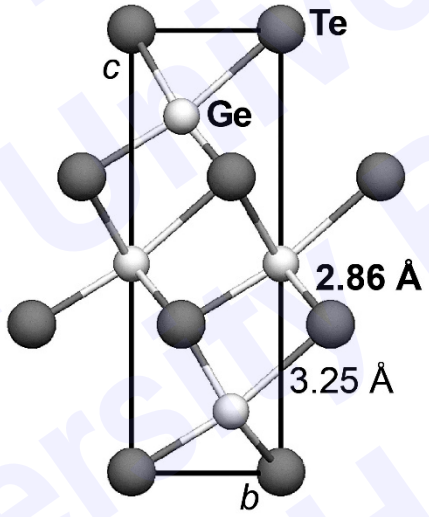
GeTe, a Phase-change Prototype

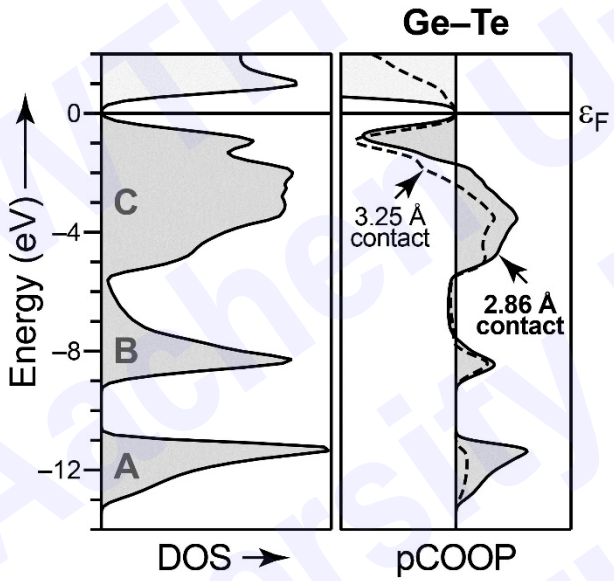


Synthesis: W. Klemm, G. Frischmuth, *Z. Anorg. Allg. Chem.* **1934**, *218*, 249
Structure: K. Schubert, H. Fricke, *Z. Naturforsch.* **1951**, *6a*, 781; J. Goldak, C. S. Barrett, D. Innes, W. Youdelis, *J. Chem. Phys.* **1966**, *44*, 3323; T. Chattopadhyay, J. X. Boucherle, H. G. von Schnering, *J. Phys. C: Solid State Phys.* **1987**, *20*, 1431

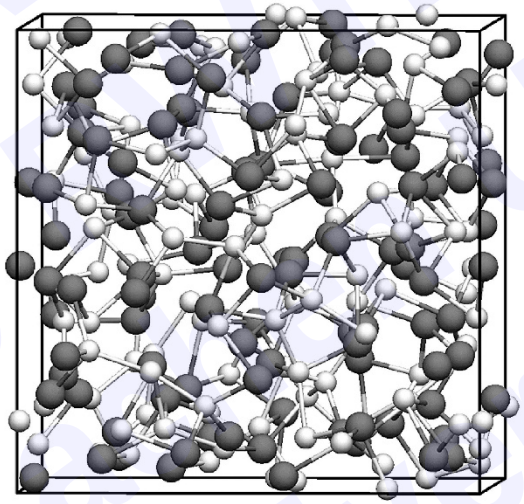
GeTe: crystalline and amorphous states

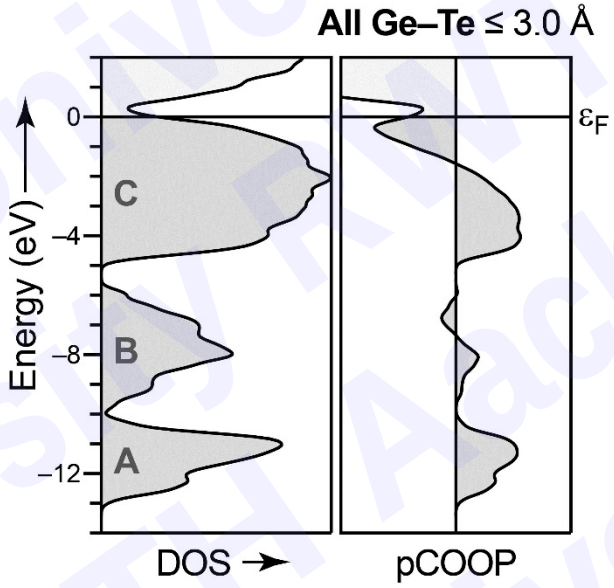
Crystalline GeTe



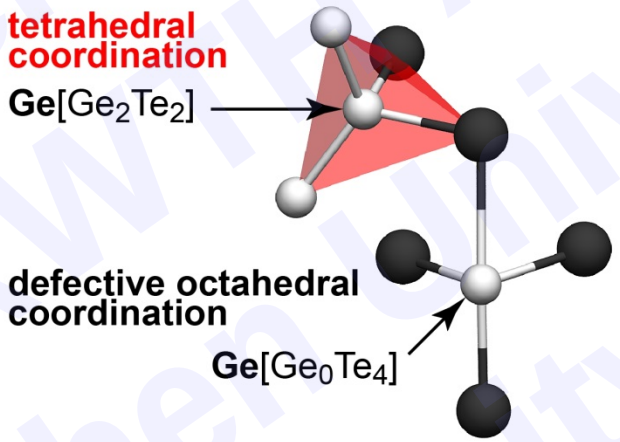


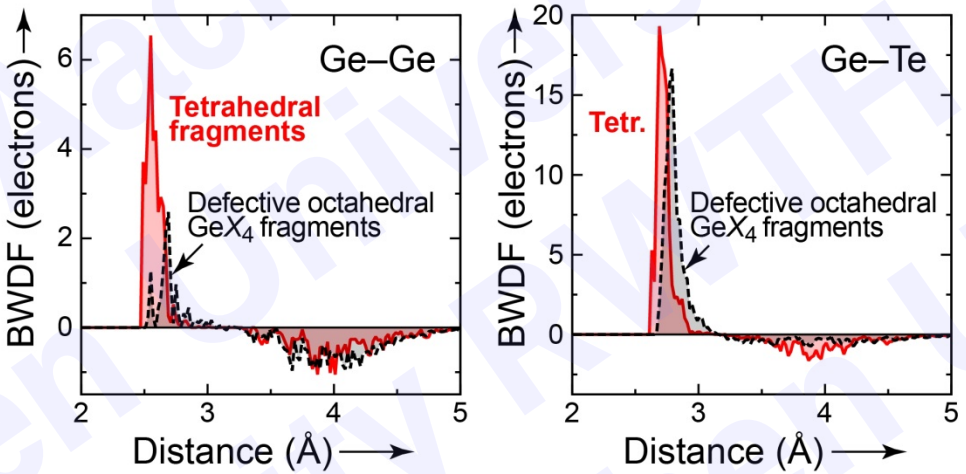
Amorphous GeTe

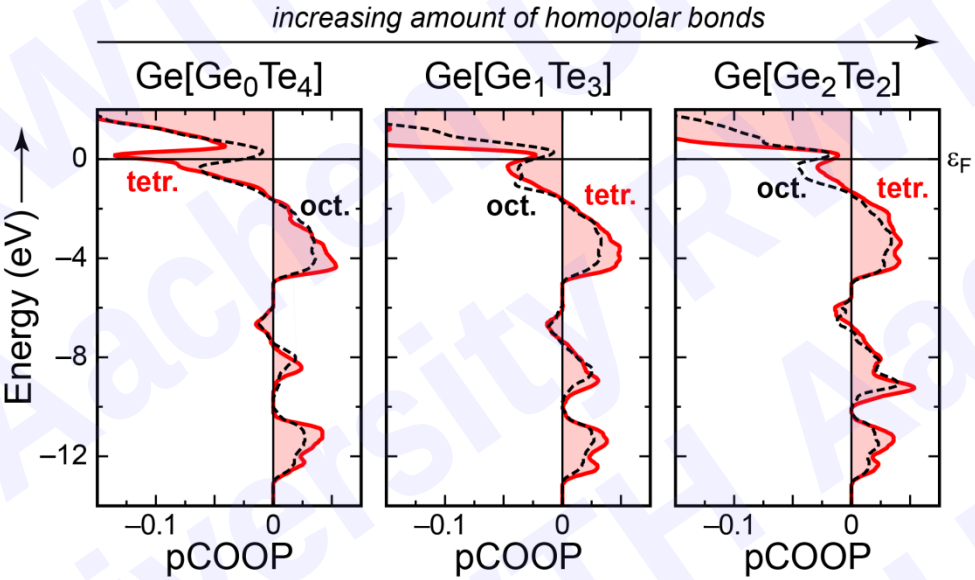




Why are there homopolar Ge–Ge Bonds?

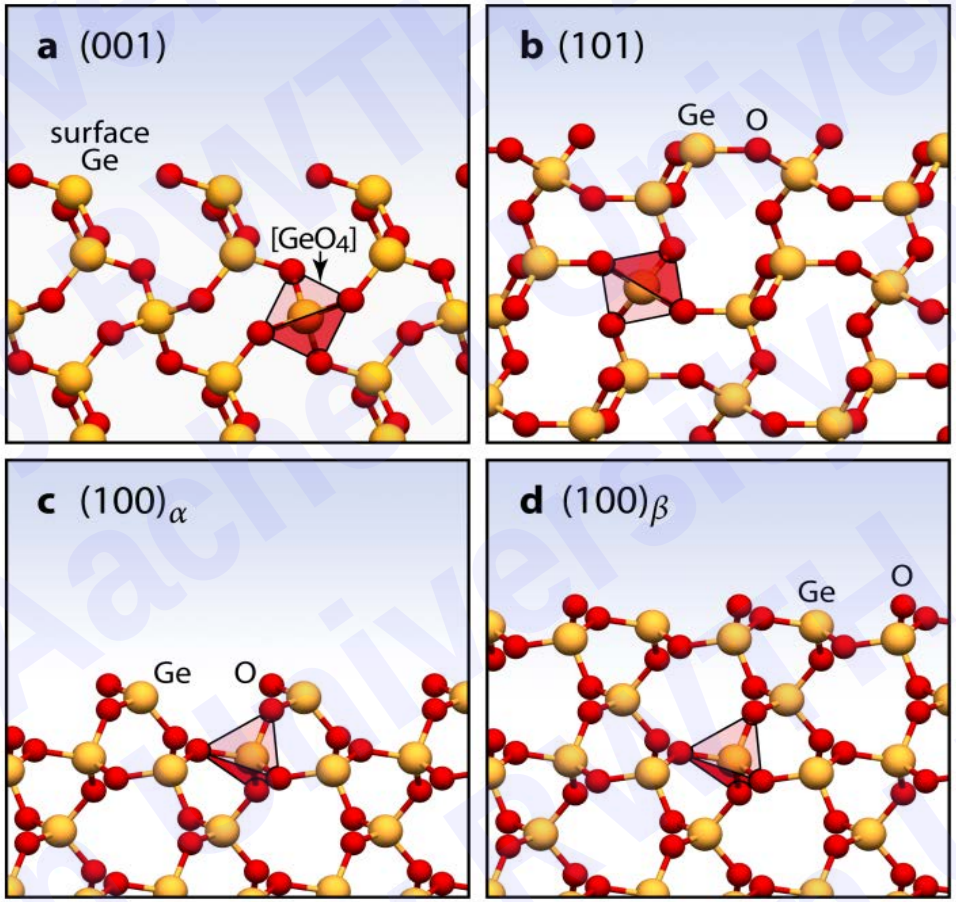






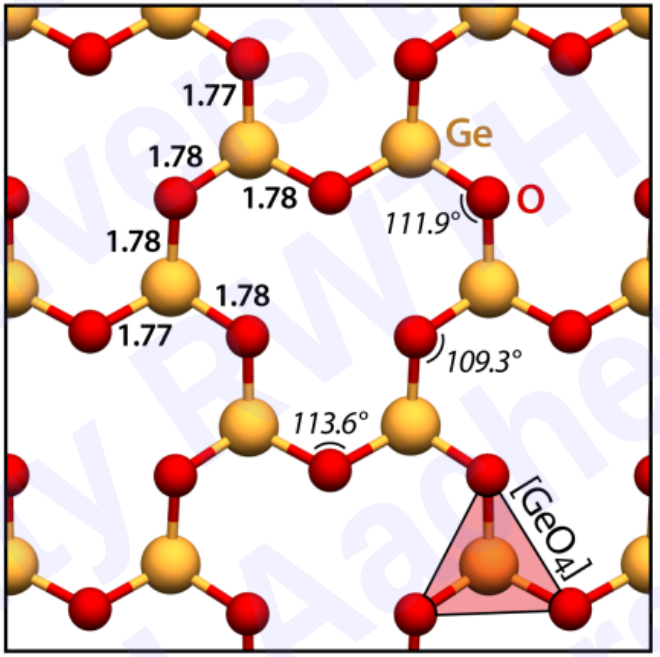
V. L. Deringer, W. Zhang, M. Lumeij, S. Maintz,
M. Wuttig, R. Mazzarello, R. Dronskowski,
Angew. Chem. Int. Ed. **2014**, *53*, 10817

GeO_2 Surface Structures



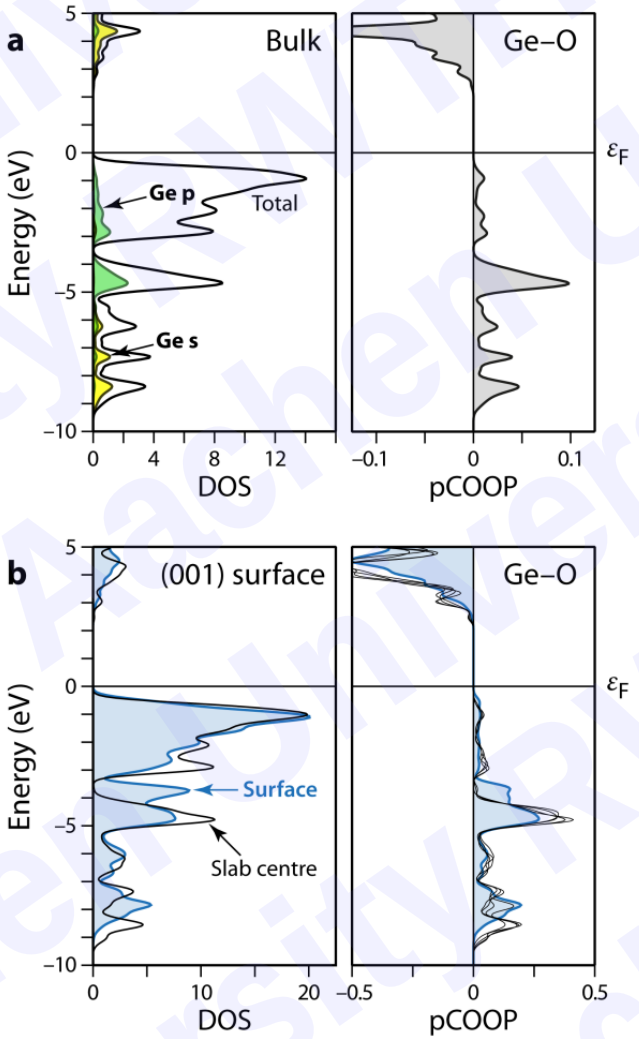
Surface Energies (meV Å^{-2})

	Cleaved	*Reconstructed*
(001)	138	31
$(100)_\alpha$	114	26
$(100)_\beta$	135	74
(101)	110	42

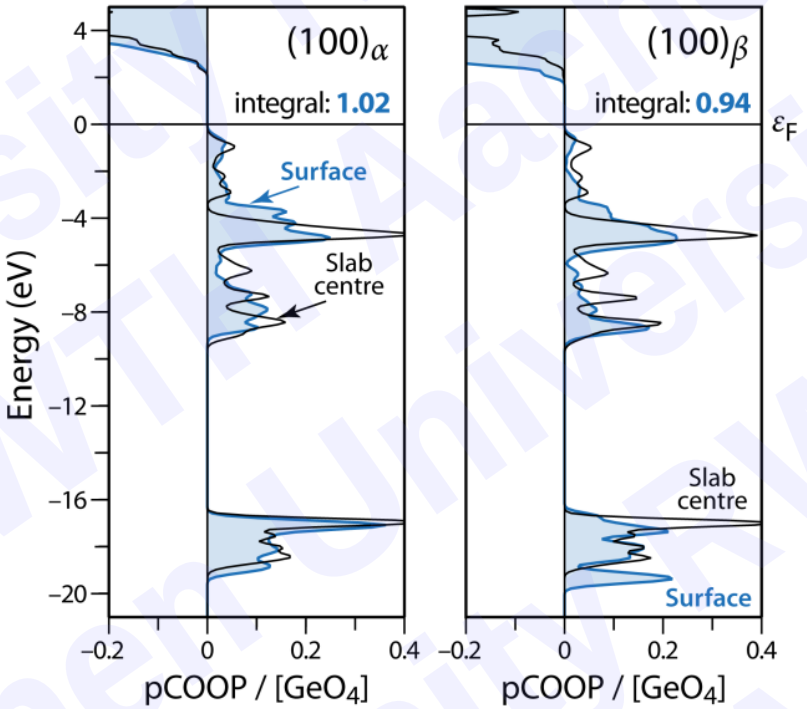


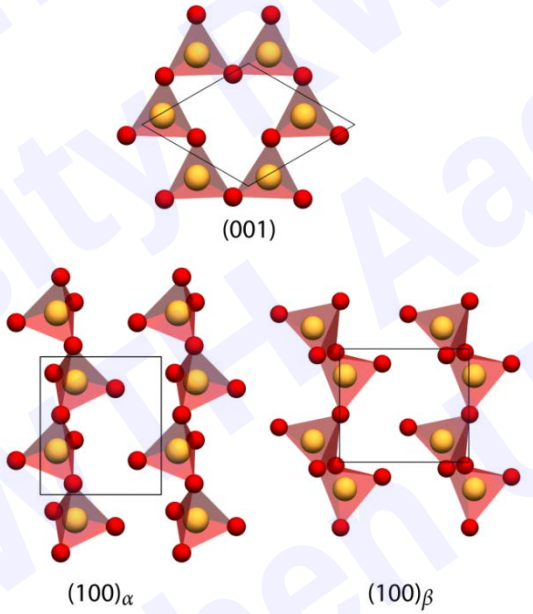
(001)

GeO_2 Surface Energies = *f* (Chemical Bonding)



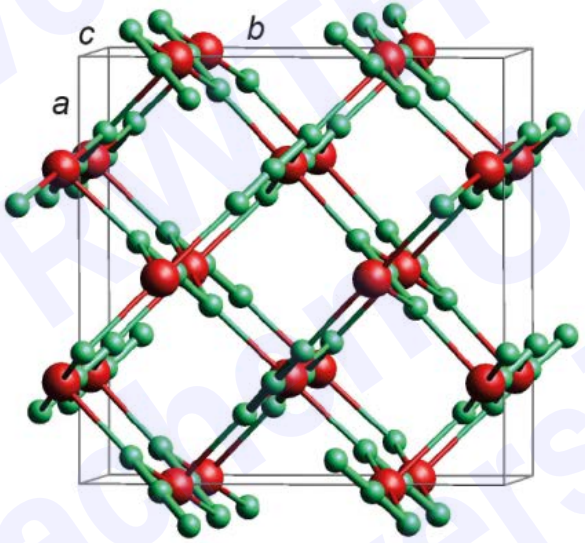
surface energies scale with the number of shared edges: Pauling's 3rd rule, but beyond the bulk

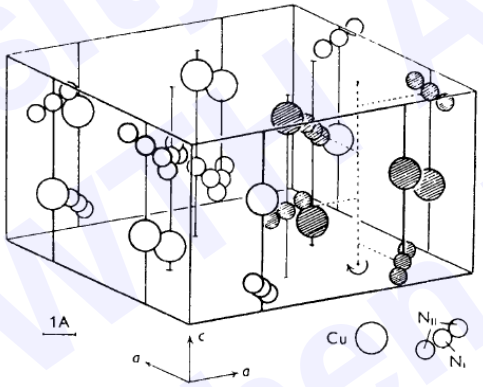




V. L. Deringer, R. Dronskowski,
Chemical Science **2014**, *5*, 894

Explosive copper azide



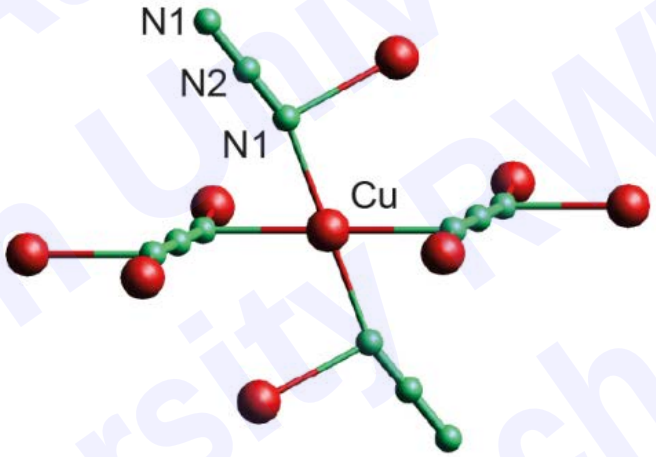


Acta Cryst. (1948). **1**, 115

Die Kristallstruktur des einwertigen Kupferazids, CuN_3

Von Heinz Wilsdorf

Institut für allgemeine Metallkunde, Göttingen, Deutschland



Solved and refined using estimated (!) X-ray intensities of the powder...

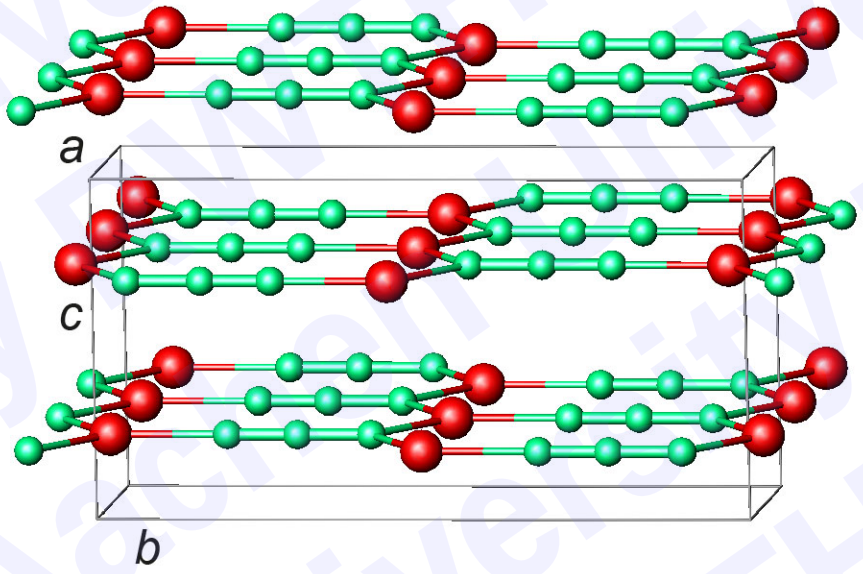
$I4_1/a$, a = 8.653(1), c = 5.594(1) Å

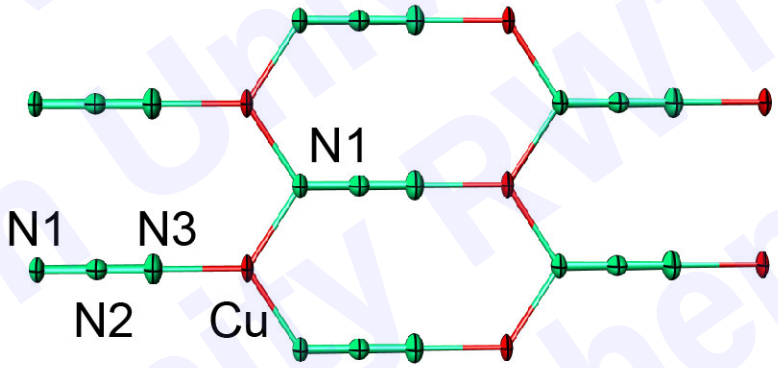
Cu–N = 2 × 2.23(1) & 2 × 2.30(1) Å

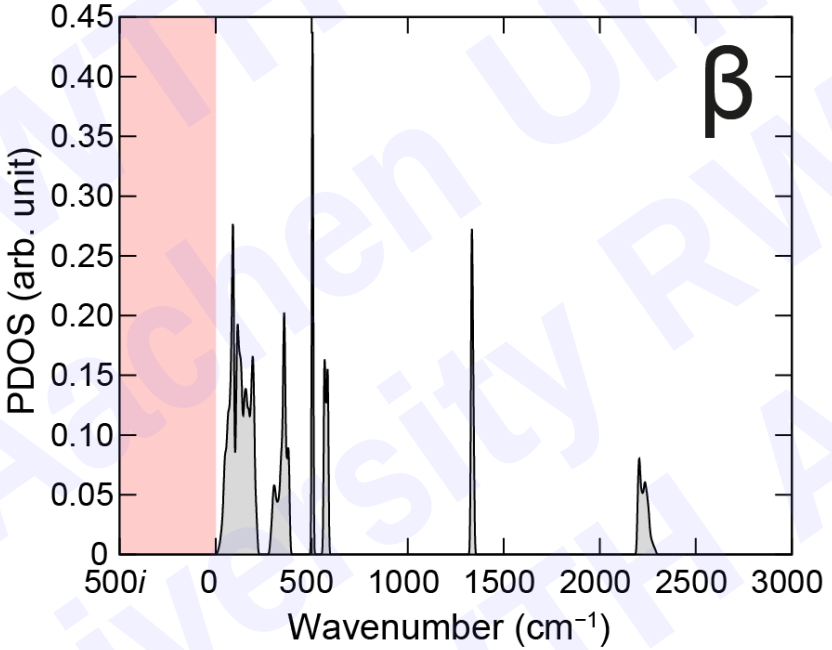
N–N = 1.17(1) Å with $D_{\infty h}$ shape

BOS(Cu) = 0.68

A new explosive copper azide (β), graphene-like



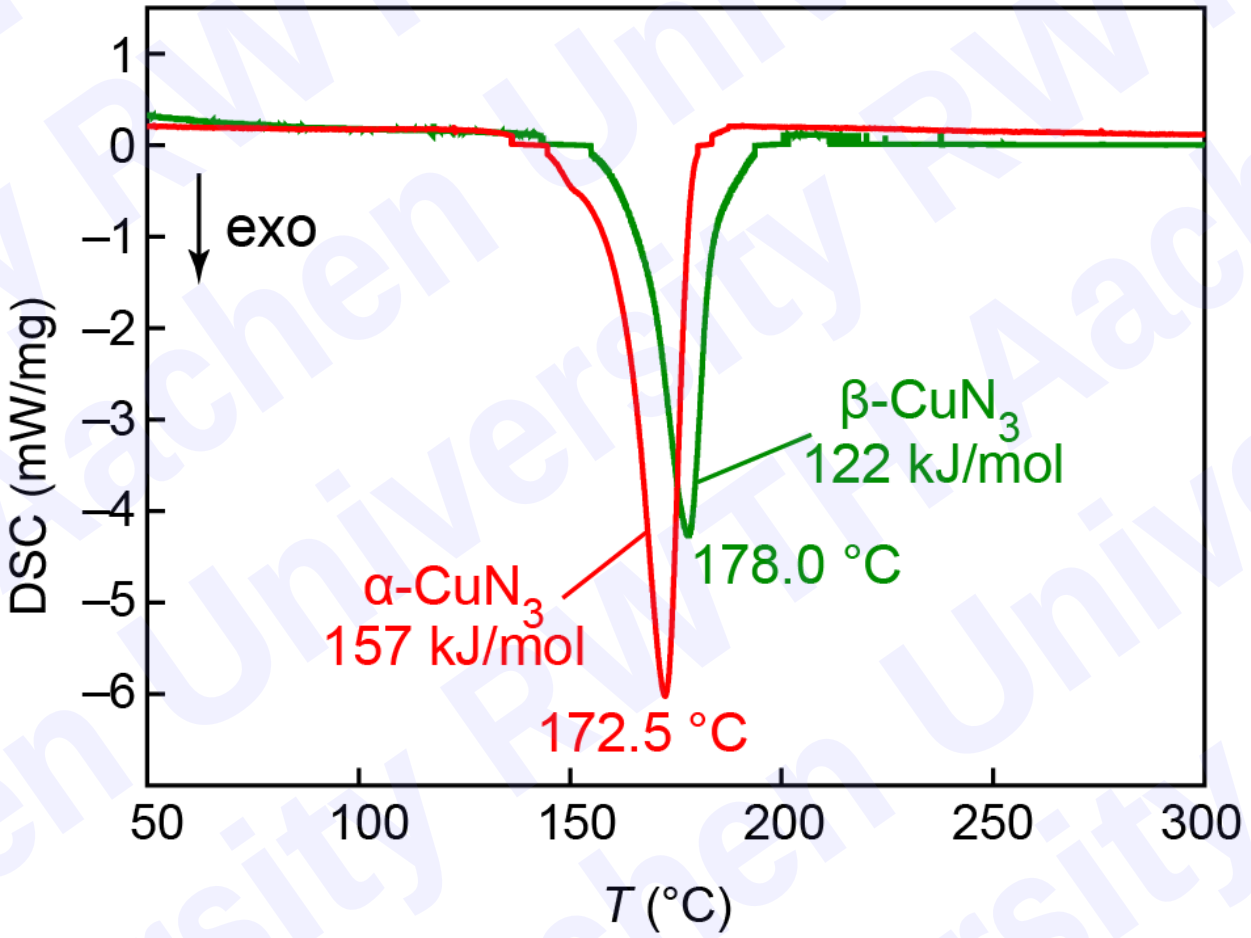


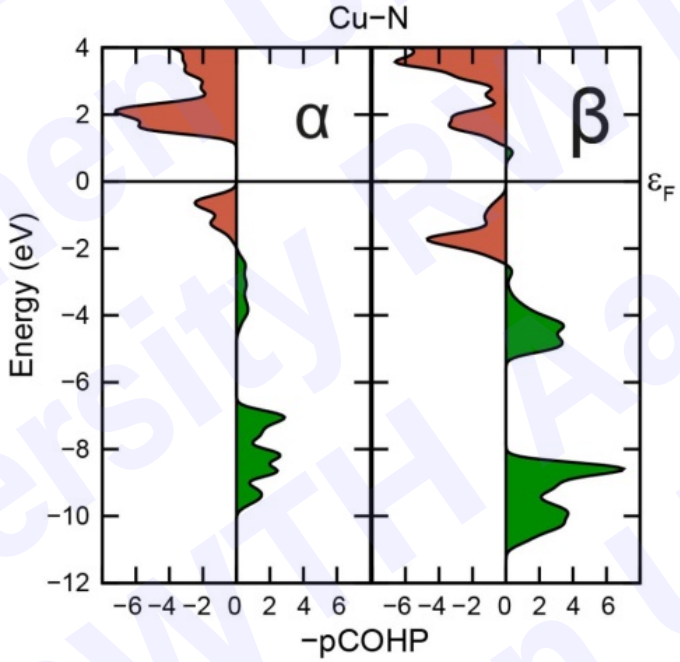


Cmcm, a = 3.3635(7), b = 10.669(2),
c = 5.5547(11) Å , $R_1(I)$ = 0.025
Cu–N = 2 × 1.999(2) & 1.910(4) Å
N–N = 1.140(6) & 1.203(6) Å, $C_{\infty v}$

BOS(Cu) = 1.14

Calorimetry with a *very* small sample ☺





X. Liu, J. George, S. Maintz, R. Dronskowski,
Angew. Chem. Int. Ed. **2015**, *54*, 1954

ε-TiO, a never-seen-before Polymorph

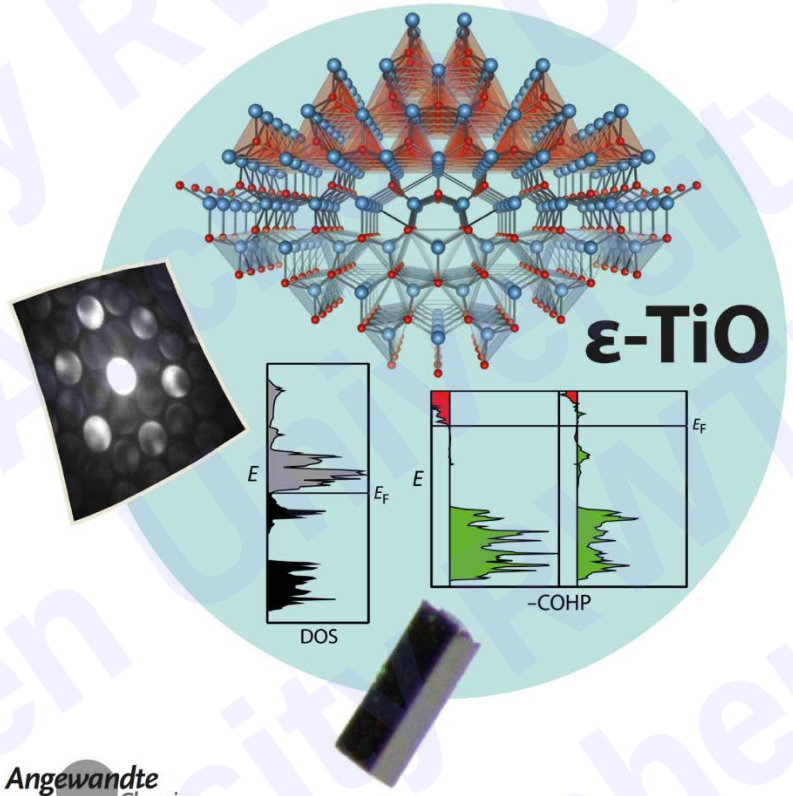
GDCh Communications Angewandte International Edition Chemie

Polymorphism Hot Paper

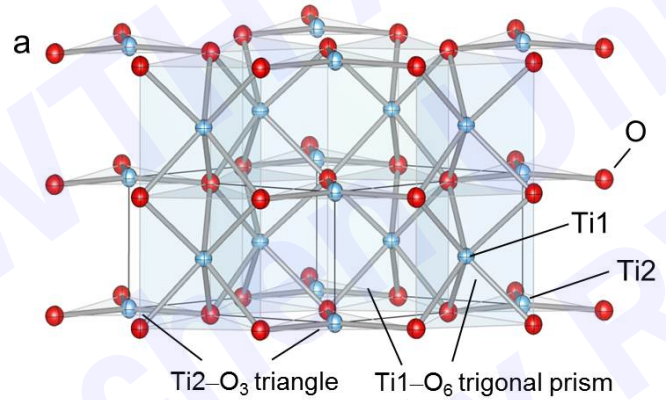
International Edition: DOI: 10.1002/anie.201510479
German Edition: DOI: 10.1002/ange.201510479

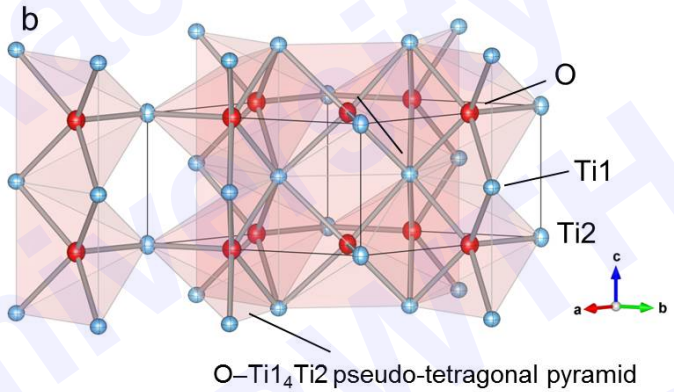
ε-TiO, a Novel Stable Polymorph of Titanium Monoxide

Shinsaku Amano, Dimitri Bogdanovski, Hisanori Yamane, Masami Terauchi, and Richard Dronskowski**



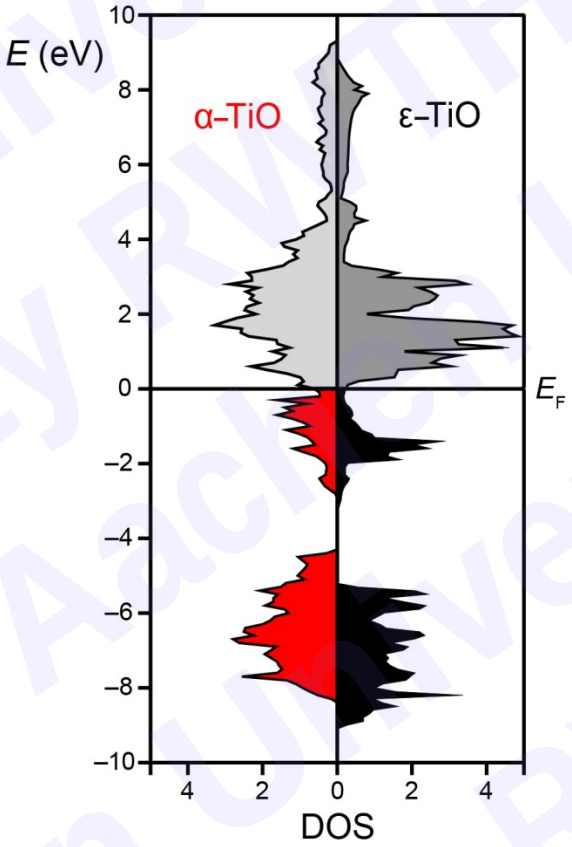
Angewandte International Edition Chemie

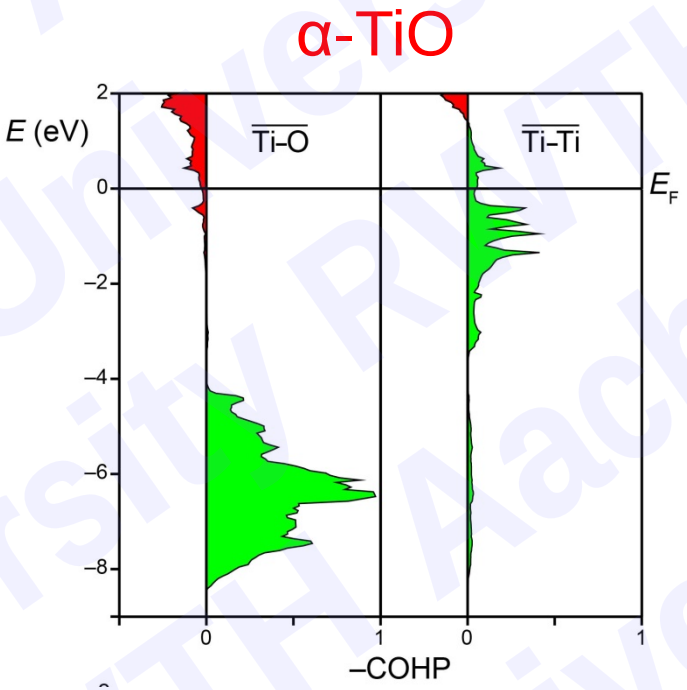


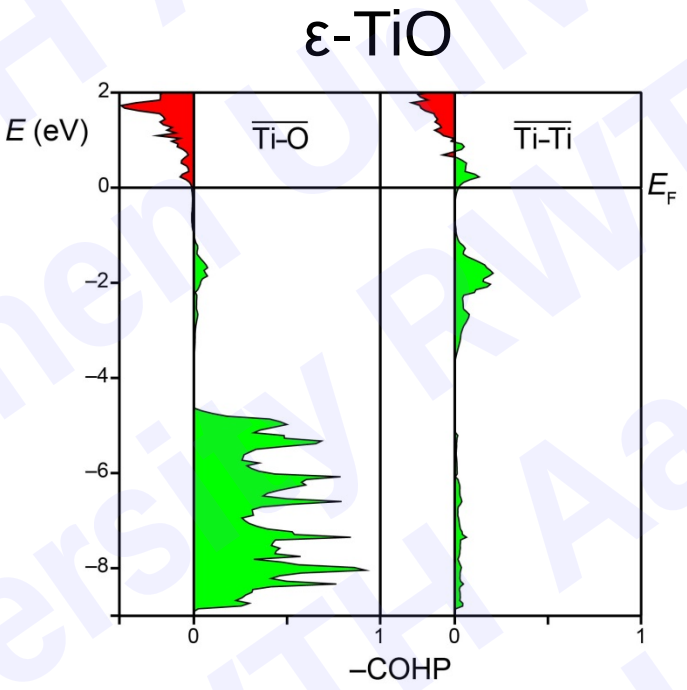


α-TiO (monoclinic, defect rocksalt type) considered as ground state since mid 1960s;
ε-TiO (hexagonal, ca. 4% more dense) grown from Bi melt

ε-TiO: DOS, total energy, and COHP





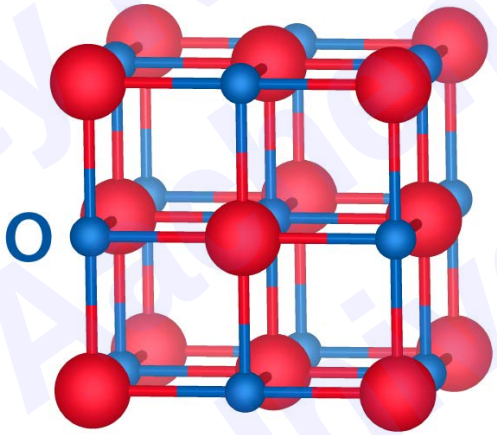


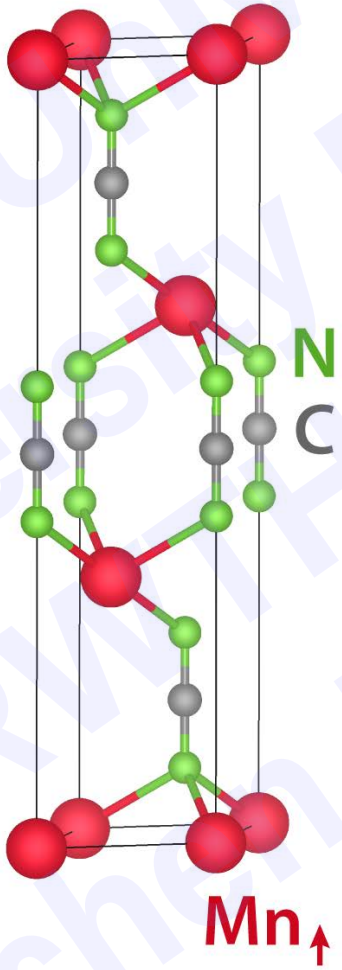
ε-TiO shows smaller DOS at Fermi level but no imaginary frequencies, favored by $\Delta H = 8$ kJ mol^{-1} vs. α-TiO; ε-TiO has ***no*** *antibonding Ti–O levels, hence stronger Ti–O but weaker Ti–Ti bonds:*

ε-TiO = more salt-like, more stable oxide

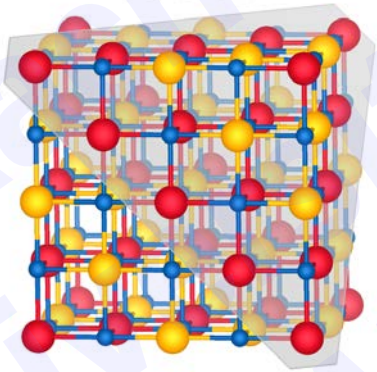
S. Amano, D. Bogdanovski, H. Yamane, M. Terauchi, R. Dronskowski, *Angew. Chem. Int. Ed.* **2016**, *55*, 1652

Correlated Stuff: MnO and MnNCN



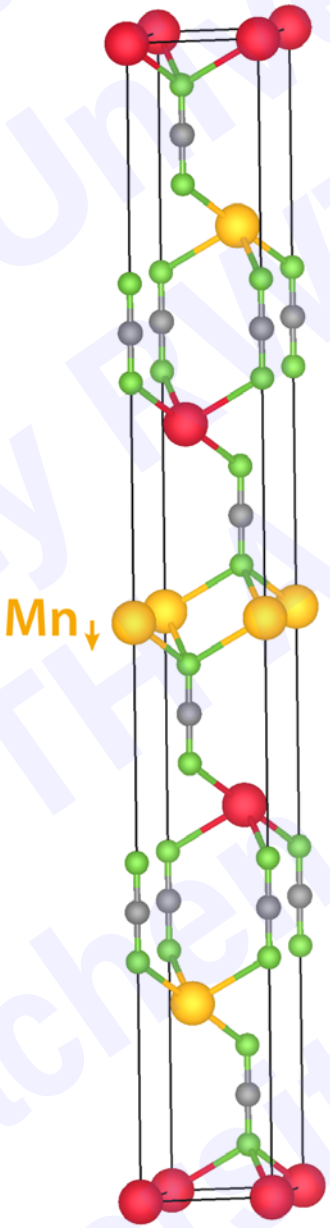


AFM2

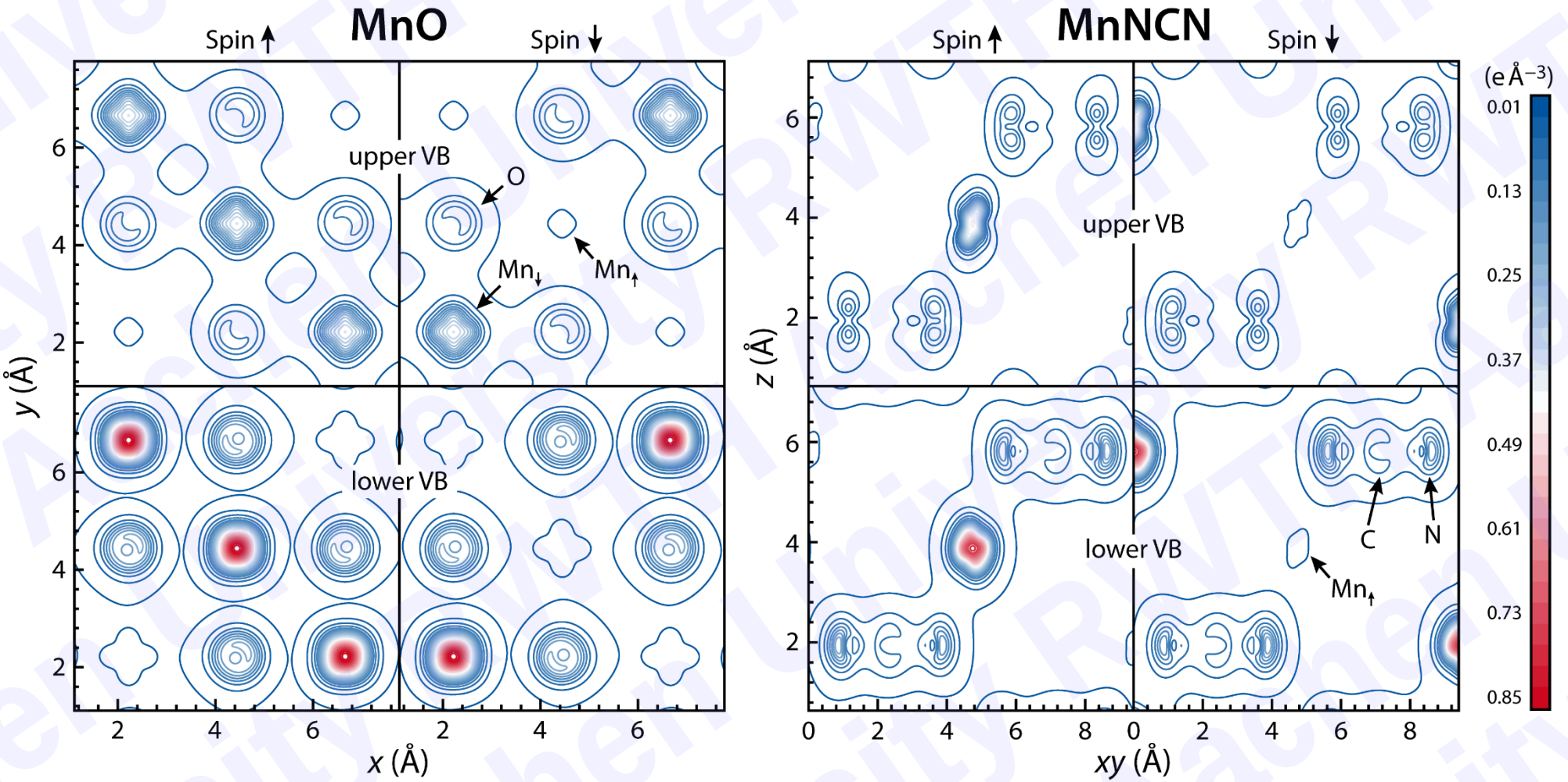


W. L. Roth,
Phys. Rev.
1958, *110*, 1333

AFM

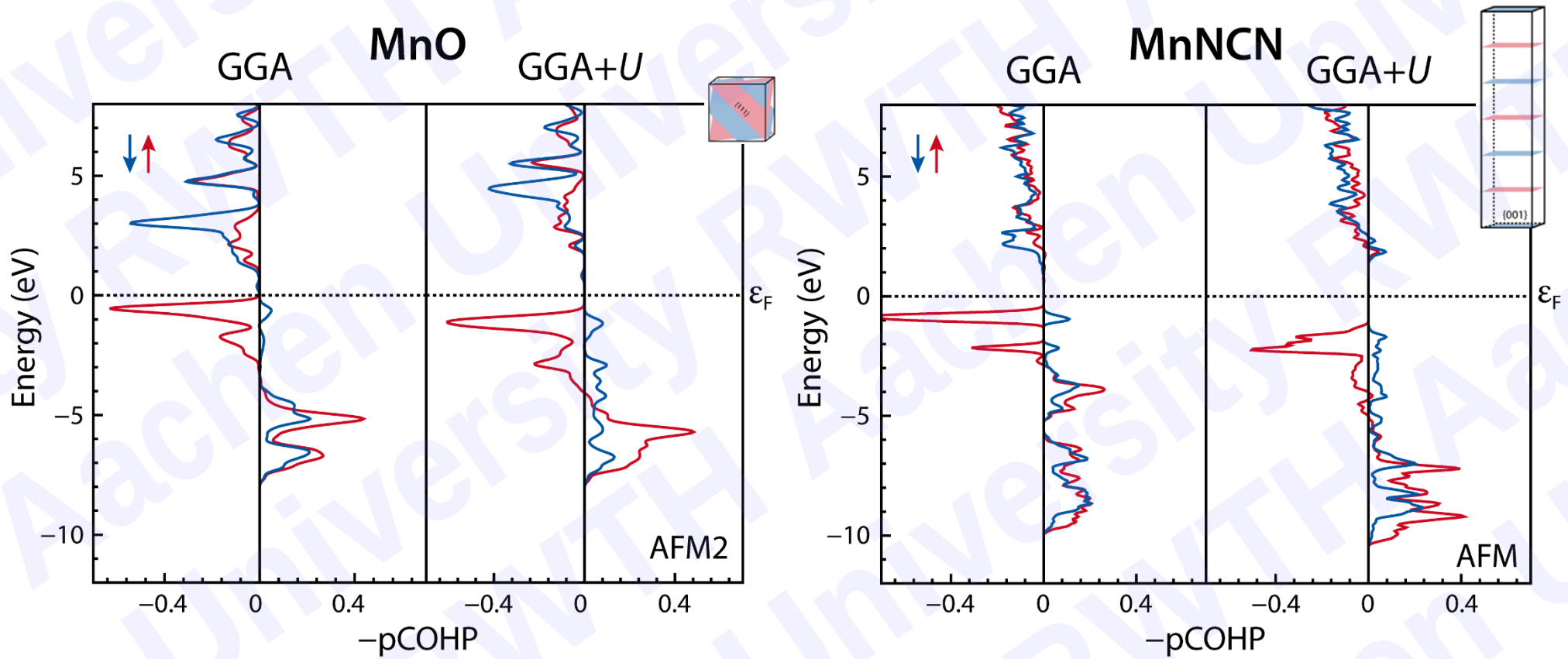


AFM charge densities based on GGA+*U*



obvious differences in "spheridicity" mirror chemistry

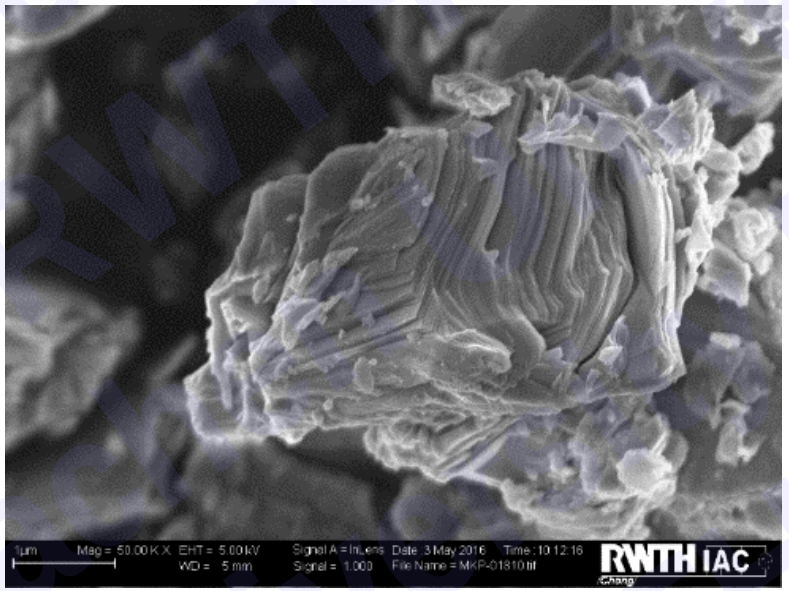
Mn–O versus Mn–N bonding: AFM case

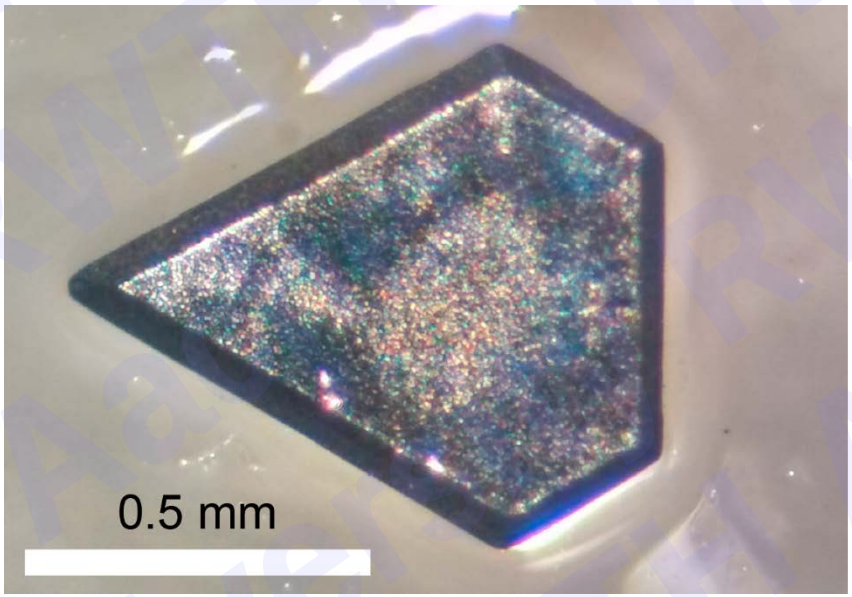


contracted ***majority spin orbitals bond less strongly*** *than the diffuse minority spin orbitals;* ***carbodiimide more covalent*** *by ca. 23% (band width);* ***integrated COHP correctly indicates the true magnetic state***

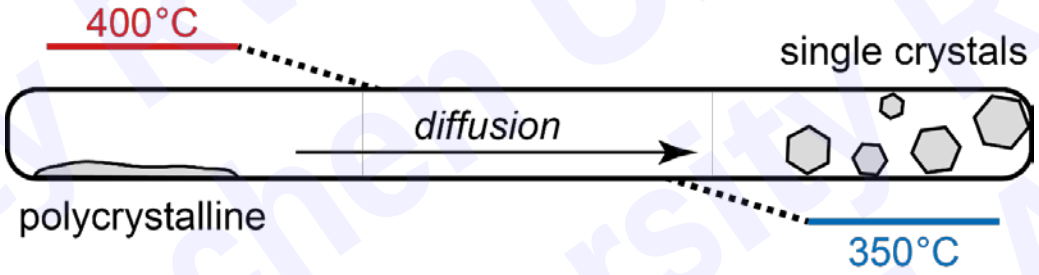
R. Nelson, P. M. Konze, R. Dronskowski,
J. Phys. Chem. A **2017**, *121*, 7778

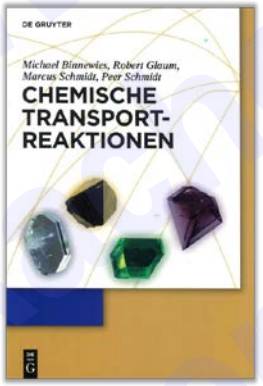
$GeSe_{1-x}Te_x$: Transport with GeI_4 at 400 °C



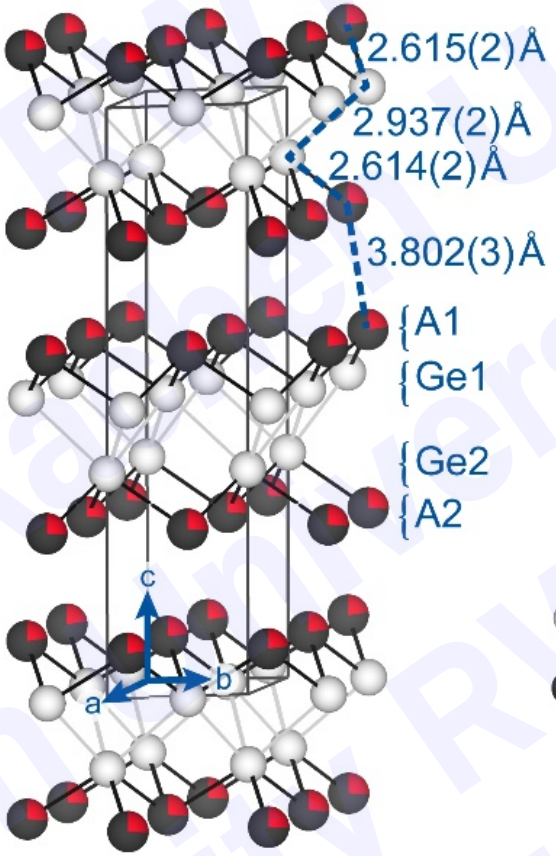


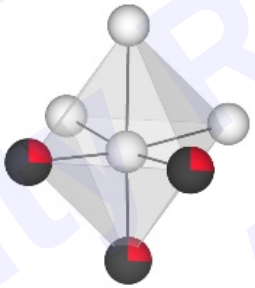
J. A. Muir, R. J. Cashman,
Bull. Am. Phys. Soc. **1966**, *8*, 34

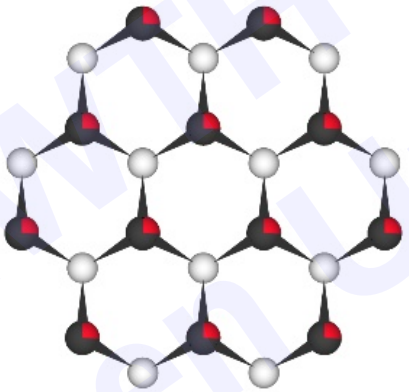


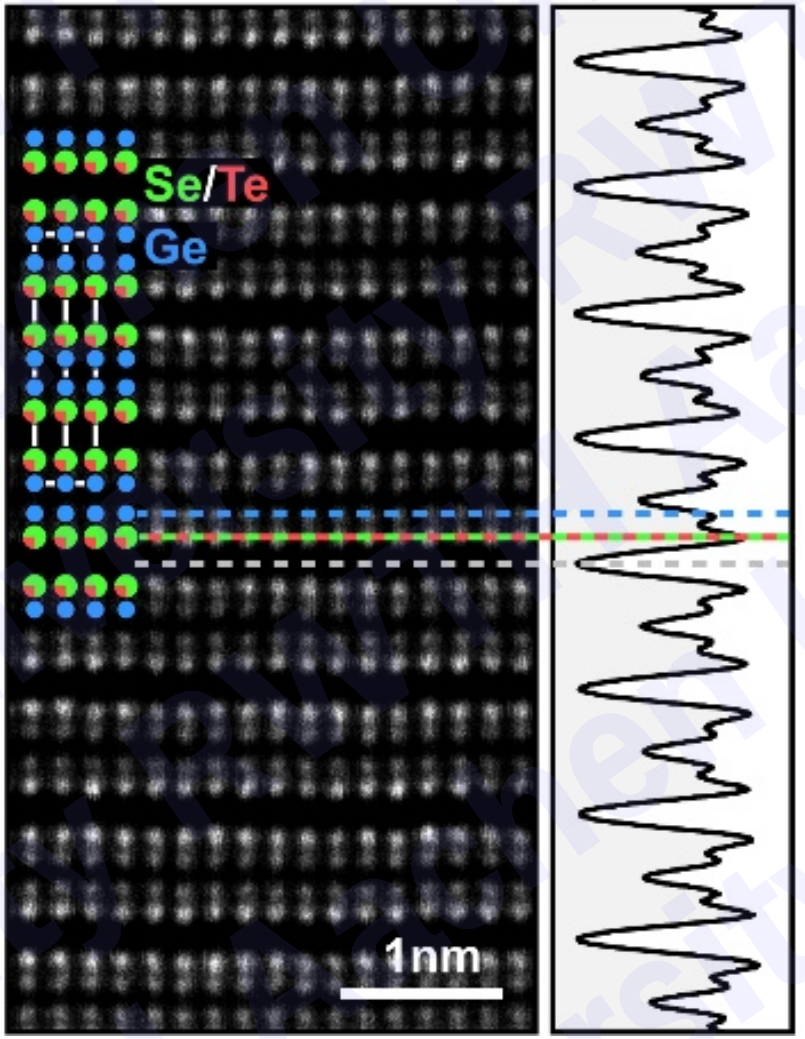


Ge_4Se_3Te, Structure & TEM: Ge–Ge = 2.94 Å

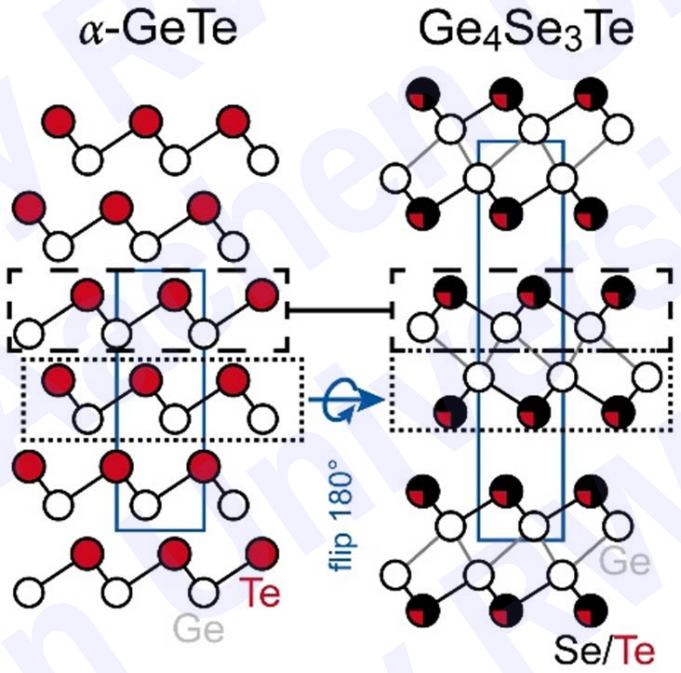


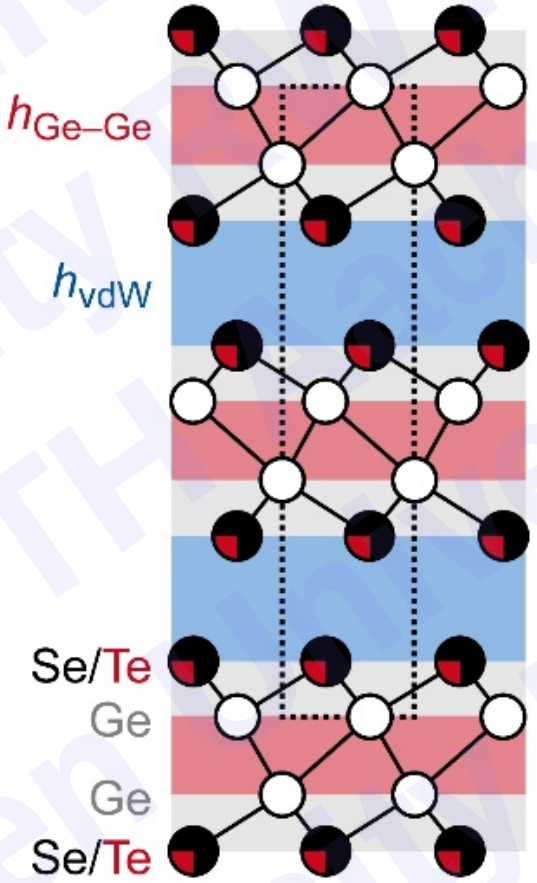


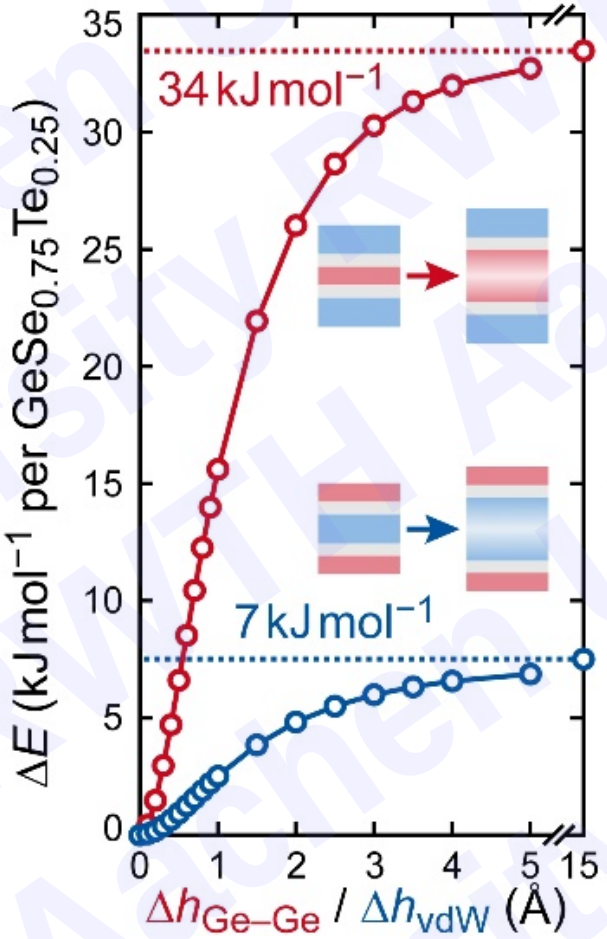




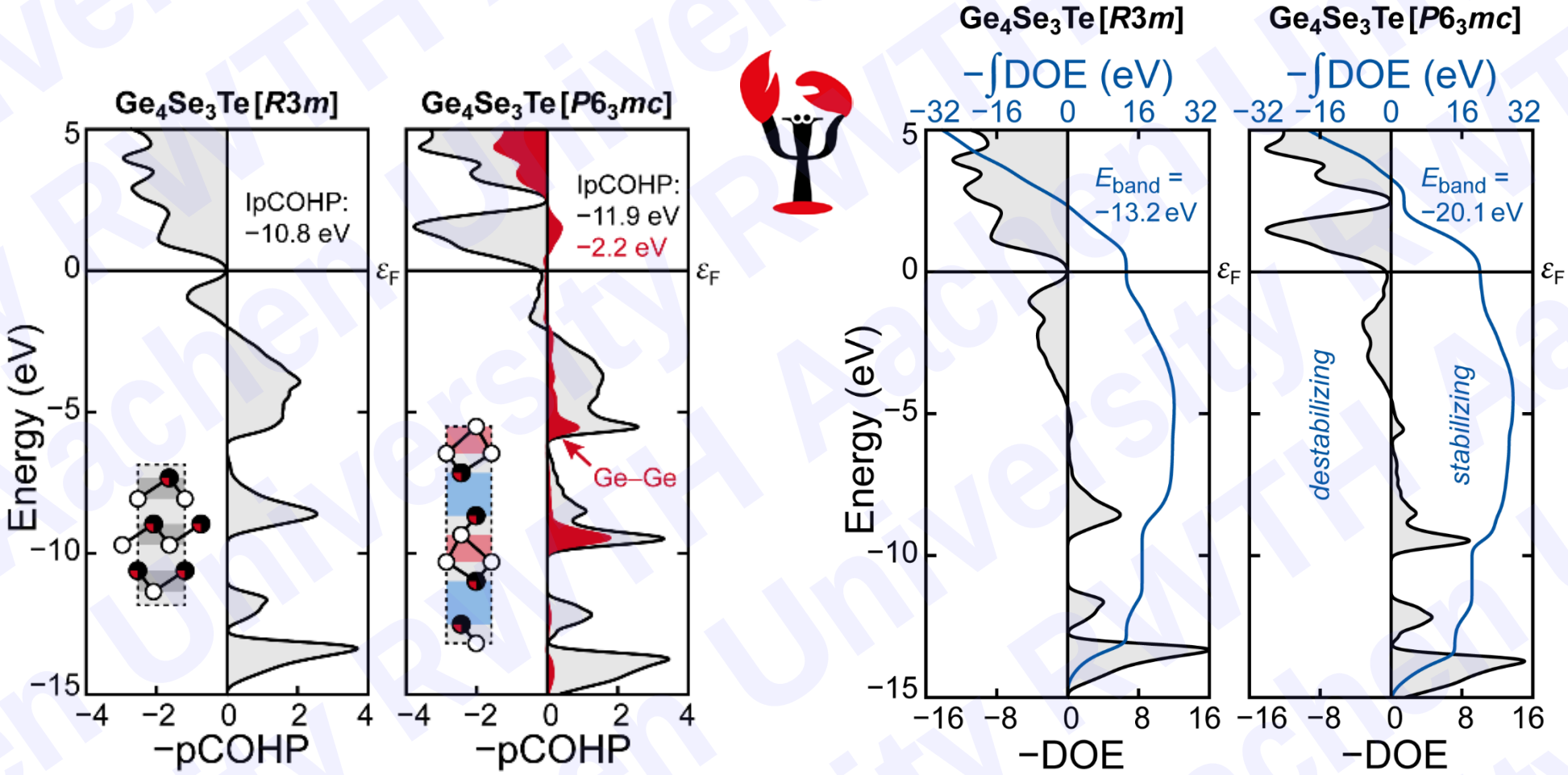
Ge_4Se_3Te: layers & forces (DFT+dispersion)





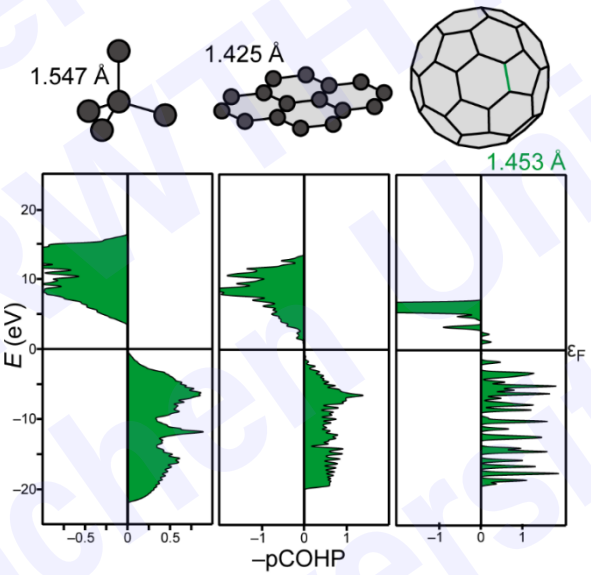


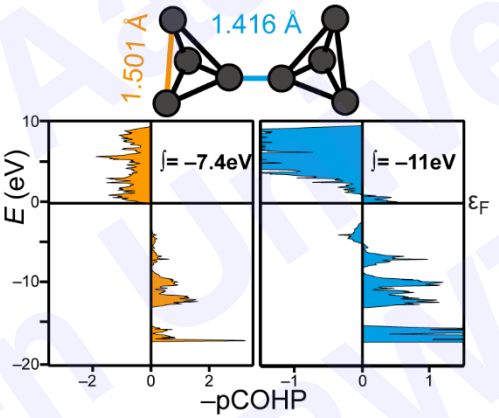
Ge_4Se_3Te: pCOHP & DOE



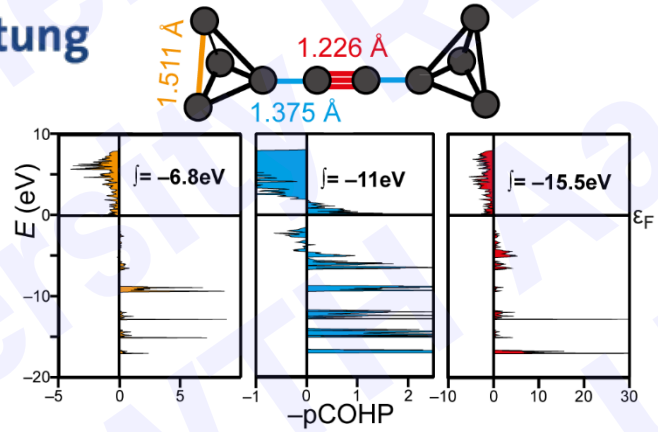
M. Küpers, P. M. Konze, S. Maintz, S. Steinberg, A. M. Mio, O. Cojocaru-Mirédin, M. Zhu, M. Müller, M. Luysberg, J. Mayer, M. Wuttig, R. Dronskowski, *Angew. Chem. Int. Ed.* **2017**, *56*, 10204

Bonding in Carbon Allotropes

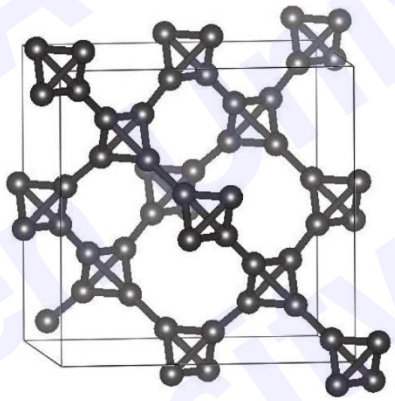




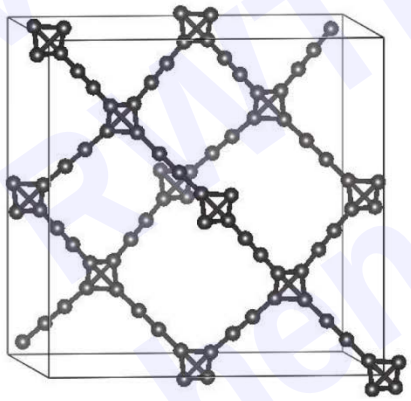
VolkswagenStiftung



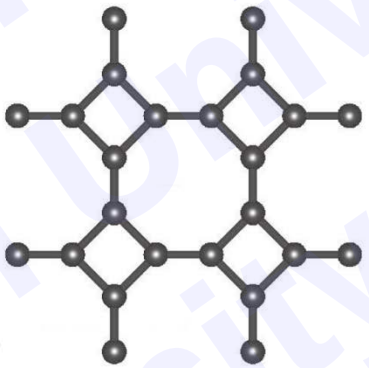
T-carbon

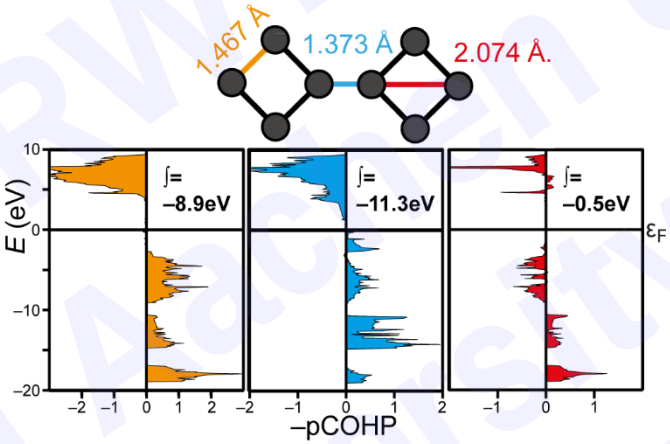


TY-carbon



T-graphene

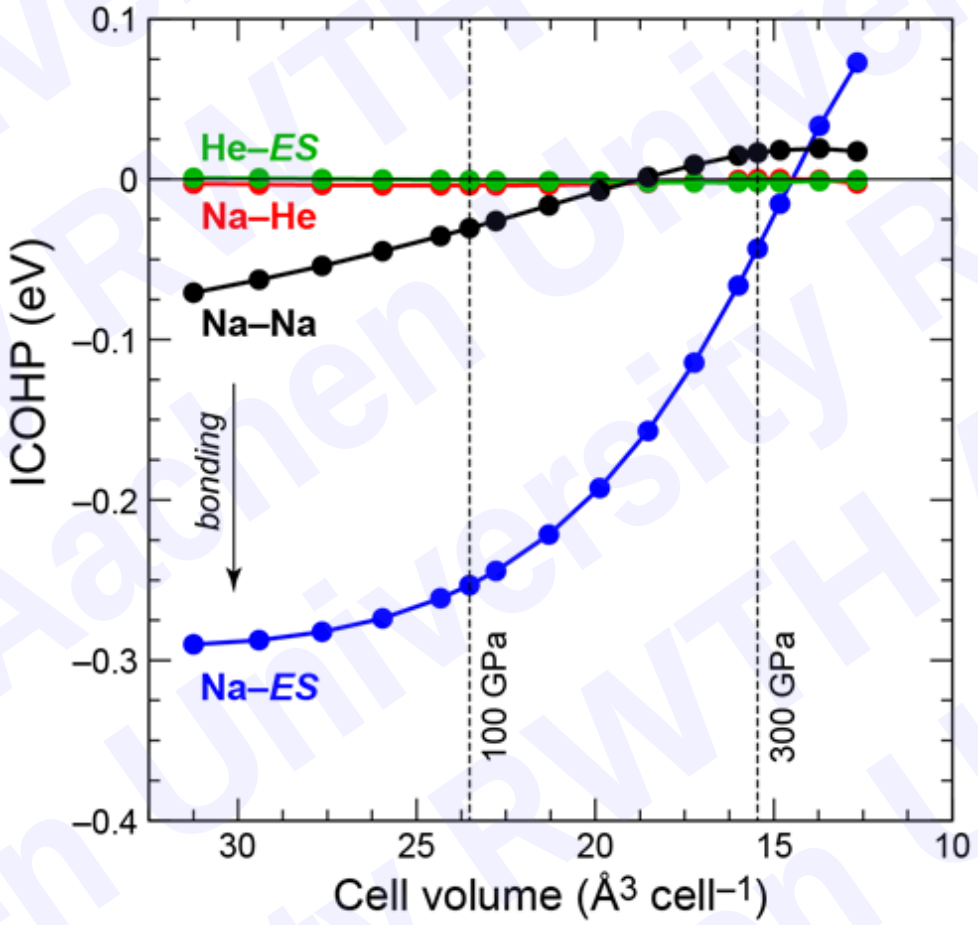


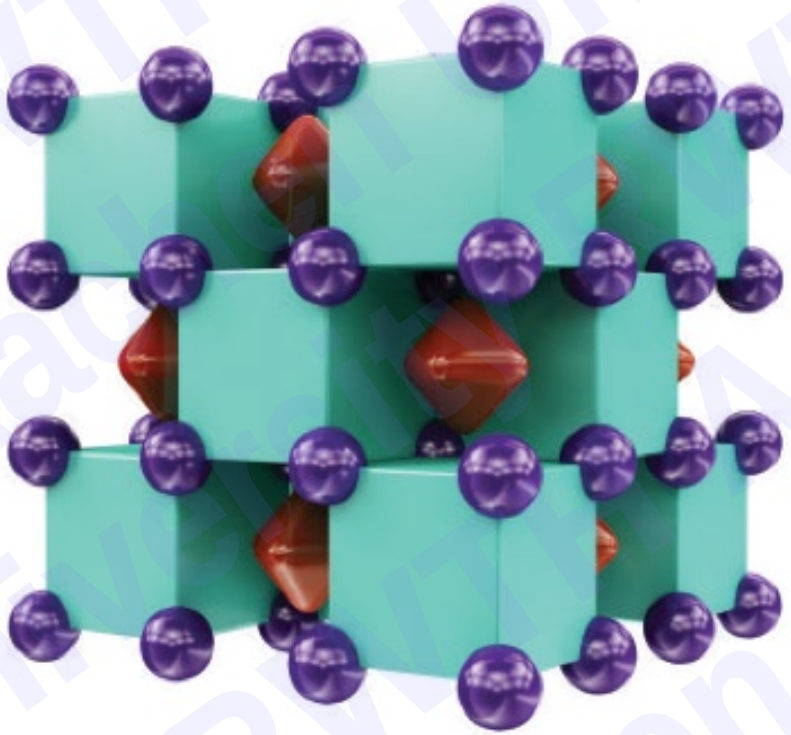


M. Esser, A. A. Esser, D. M. Proserpio, R. Dronskowski, *Carbon* **2017**, *121*, 154

Chair of Solid-State and Quantum Chemistry
RWTH AACHEN UNIVERSITY
Skoltech

$p > 100$ GPa: $Na_2He = (Na^+)_2He(e^-)_2$





X. Dong, A. R. Oganov, A. F. Goncharov, E. Stavrou, S. Lobanov, G. Saleh, G.-R. Qian, Q. Zhu, C. Gatti, V. L. Deringer, R. Dronskowski, X.-F. Zhou, V. Prakapenka, Z. Konôpková, I. Popov, A. I. Boldyrev, H.-T. Wang, *Nature Chem.* **2017**, *9*, 440

Summary

Population analysis: crystal-orbital overlap populations (COOP) & crystal-orbital Hamilton populations (COHP) well established

a) Crystal structure of Te is bonding-driven, a 3D Peierls distortion – b) Itinerant magnets in "nonmagnetic" view: antibonding states yield ferromagnets; nonbonding states yield antiferromagnets – c) Bonding of phase-change materials determines their stoichiometry

Chemical-bonding information can eventually be projected from plane-wave calculations using an exact analytic algorithm, programmed into LOBSTER

Crystal defects, surfaces, molecular crystals, nanomaterials etc. can all be quantum-chemically studied, including C & Nanotube & Ti & amorphous GeTe & GeO_2 surfaces & H bonding & CuN_3 & TiO & MnNCN/MnO & Ge_4Se_3Te & carbons & Na_2He and so forth

(Inorganic) Solid State Chemistry

I. *Materials and Structure of Solids*

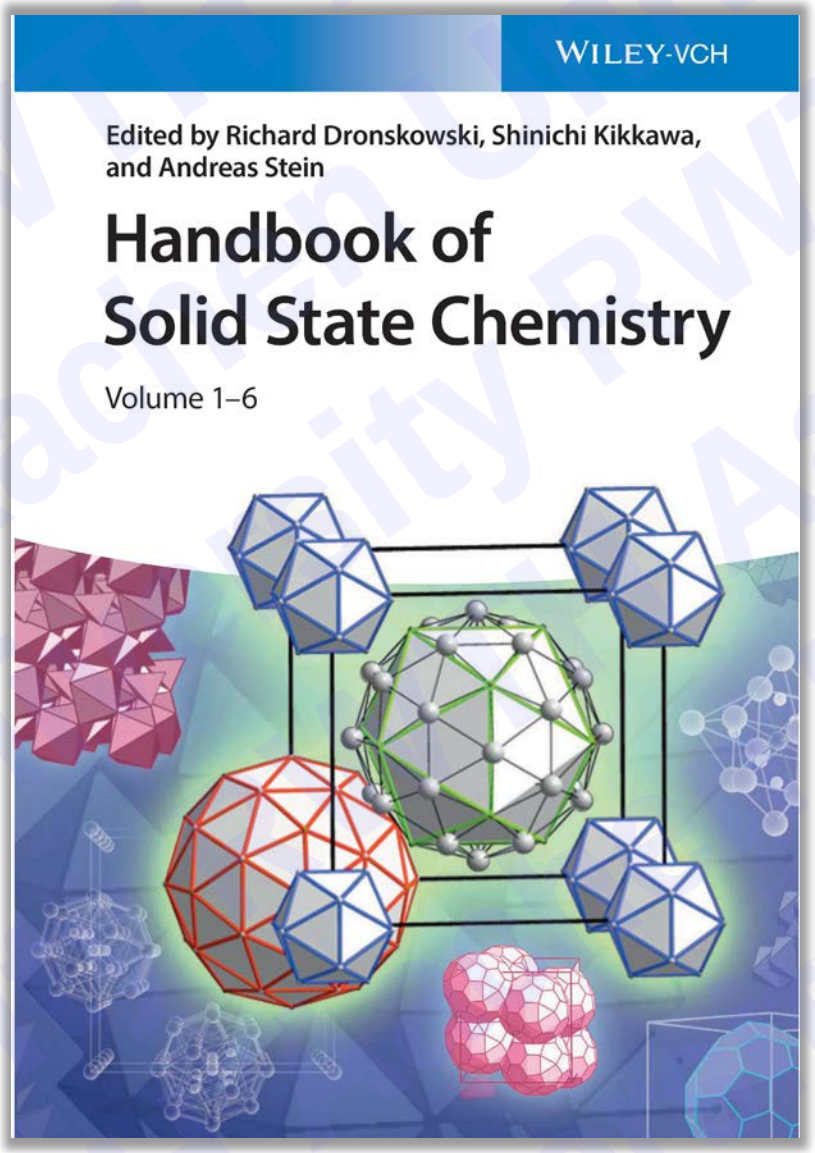
II. *Synthesis*

III. *Characterization*

IV. *Nano and Hybrid Materials*

V. *Theoretical Description*

VI. *Functional Materials*



Happy Theorists & Experimentalists

Emperor Karl and the Aachen Cathedral

Karl der Große
747–814 AD