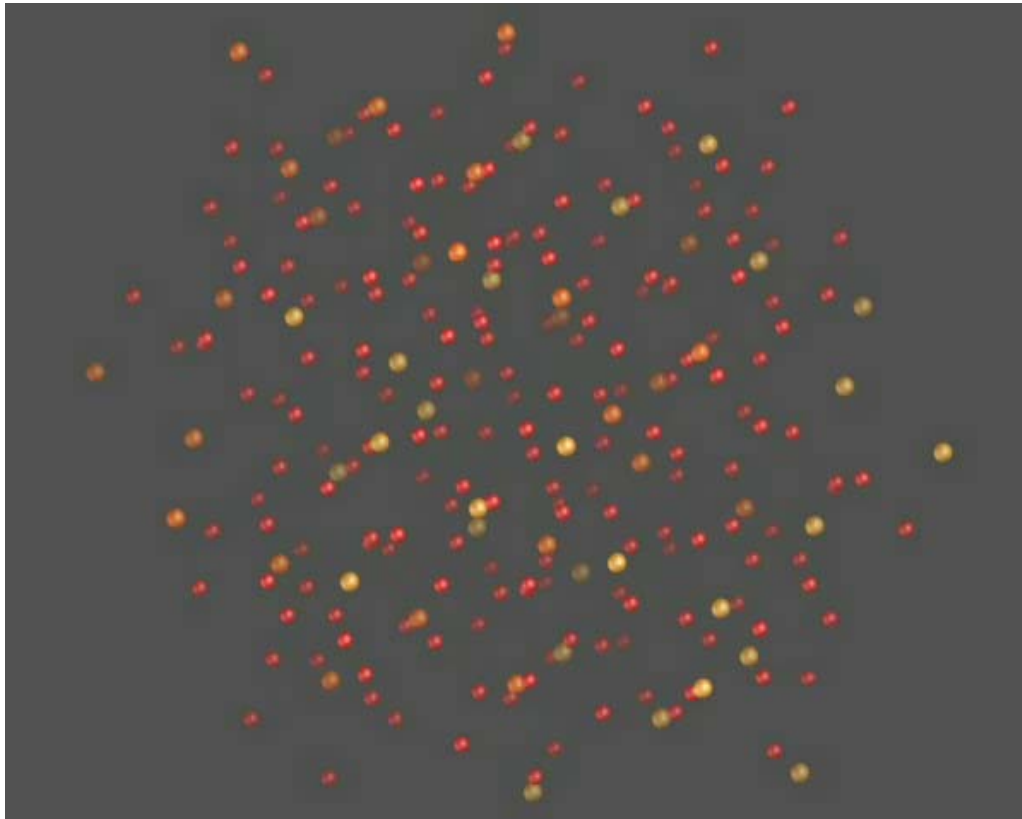




Chemical Bonding in Crystalline Compounds



Das ich erkenne, was die Welt
Im Innersten zusammenhält,
Schau alle Wirkenskraft und Samen
Und tu nicht mehr in Worten kramen

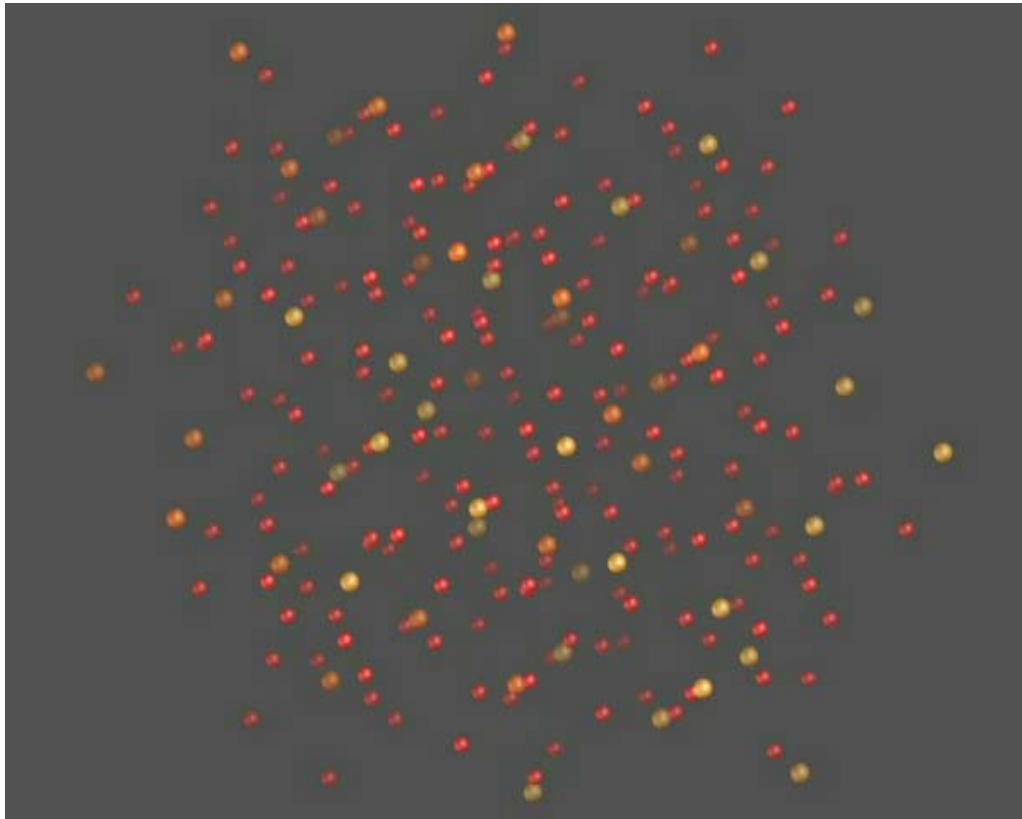
Johann Wolfgang von Goethe
Faust I



Chemical Bonding in Crystalline Compounds



Why are metal atoms in a crystal arranged in a certain manner ?



RhBi₄:

Ia3d

a=14.928 Å

120 atoms / cell

A description:

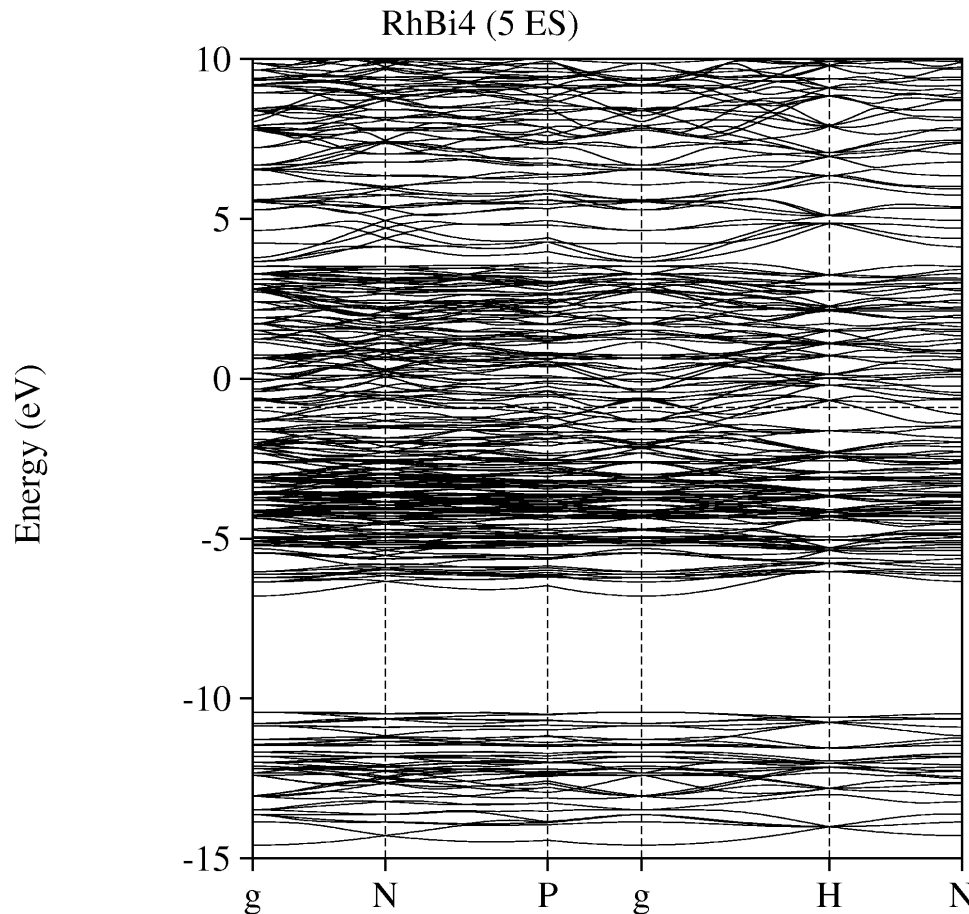
Balls flying concerted in space



Chemical Bonding in Crystalline Compounds



Why are metal atoms in a crystal arranged in a certain manner ?



RhBi₄:

Ia3d

$a=14.928 \text{ \AA}$

120 atoms / cell

Another description:

Dispersion of
Kohn-Sham eigenvalues
in the Brillouin zone



Chemical Bonding – prior to Quantum Mechanics



The ideas of **Walther Kossel** and **Gilbert N. Lewis**

1916.

№ 3.

ANNALEN DER PHYSIK. VIERTE FOLGE. BAND 49.

1. *Über Molekülbildung als Frage des Atombaues;
von W. Kossel.*

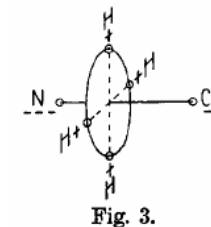
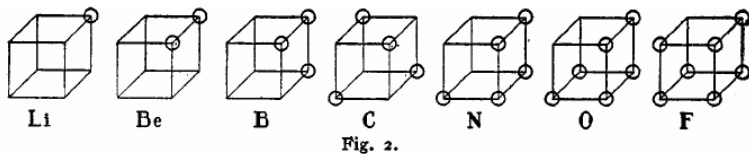
pages 229 - 362

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

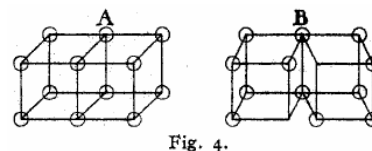
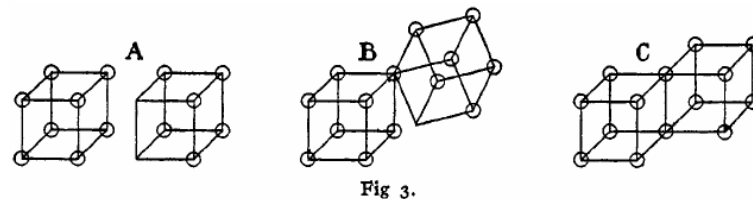
THE ATOM AND THE MOLECULE.

By GILBERT N. LEWIS.
Received January 26, 1916.

J. Am. Chem. Soc. **38** (1916), 762 - 784



geladene Stickstoff auf das ihm gleichnamig geladene Chlor ausübt — bestimmen. Das Chlorion erhält so naturgemäß eine ausgezeichnete Lage, wie sie ihm zukommen muß, da es als Produkt der elektrolytischen Dissoziation auftritt. Um eine unverbindliche Andeutung zu geben, wie danach etwa das Molekül des Ammoniumchlorids gebaut sein mag, gibt Fig. 3 ein Schema der Lagerung der Schwerpunkte, wie es danach etwa zu denken ist.



I₂

the two forms of ethylene¹ as $\text{H}:\overset{\cdot\cdot}{\text{C}}:\overset{\cdot\cdot}{\text{C}}:\text{H}$ and $\text{H}:\overset{\cdot\cdot}{\text{C}}:\overset{\cdot\cdot}{\text{C}}:\text{H}$.

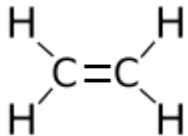


Chemical Bonding – prior to Quantum Mechanics



The consequences:

- pairing of electrons
- atoms attempt to achieve a noble gas shell (→octet rule)
- atoms may share electron pairs
- there is a relation between valency and the octet rule



→ Lewis structures have become an **order principle in chemistry**

covalent bond → sharing of electron pairs (Lewis)

ionic bond → transfer of electrons (Kossel)

Besides Kossel and Lewis:

van der Waals bond

metallic bond



Quantum Mechanics



A many-body system of n **atomic nuclei** and n **indistinguishable electrons** is described by a wavefunction

$$\Psi(\{\mathbf{r}\}, \{\boldsymbol{\sigma}\}, \{\mathbf{R}\}, t)$$

The probability to find at a given time N nuclei in N very small volume elements ΔT_λ and n electrons in n very small volume elements $\Delta \tau_n$ is

$$\Delta W = \Psi^* \cdot \Psi \Delta \tau_1 \cdots \Delta \tau_n \Delta T_1 \cdots \Delta T_N$$

$$0 \leq \Delta W \leq 1$$

The sum (integral) of all probabilities is equal to the probability of finding all particles in whole space is 1 (the wavefunction is normalized)

$$\int \cdots \int \Psi^* \cdot \Psi d\tau_1 \cdots d\tau_n dT_1 \cdots dT_N = 1$$

The content of this page is a **postulate** of quantum mechanics



Electron Density



The probability to find a single electron in volume element $\Delta\tau_n$ is

$$\Delta W(1) = \left[\int \cdots \int \Psi^* \cdot \Psi d\tau_2 \cdots d\tau_n dT_1 \cdots dT_N \right] \Delta\tau_1$$

thus the probability density for one electron is $\frac{\Delta W(1)}{\Delta\tau_1}$

as the electrons are indistinguishable, the electron density is

$$\rho = n \cdot \frac{\Delta W(1)}{\Delta\tau_1}$$

due to normalization is $\int dW(1) d\tau_1 = 1$ and $\int \rho d\tau_1 = n$



Bonding Concepts and Quantum Mechanics



Chemical concepts of bonding,
local covalent bonding, charge transfer, etc.
are not strictly defined in the quantum mechanical formalism



quantum mechanics:

ab initio calculations

ensemble of nuclei and indistinguishable electrons



no formal bridge

chemical concepts:

interpretation of certain quantities

local bonds, charge transfer,
(still dominated by Kossel and Lewis)



quantum mechanics:

ab initio calculations

Hartree-Fock (+ MP2, + local ansatz, + incr. method)
DFT
(LDA + U)
(LDA + DMFT)

no formal bridge

chemical concepts:

interpretation of certain quantities

local bonds, charge transfer,
(still dominated by Kossel and Lewis)



quantum mechanics:

ab initio calculations

Hartree-Fock (+ MP2, + local ansatz, + incr. method)
DFT
(LDA + U)
(LDA + DMFT)

no formal bridge

chemical concepts:

interpretation of certain quantities

molecular orbitals
local basis functions
electron density
properties being related to the pair density

local orbital
PDOS, COOP, COHP
'Atoms In Molecules'
 $\nabla^2\rho(\mathbf{r})$, ELF, LOL, ELI

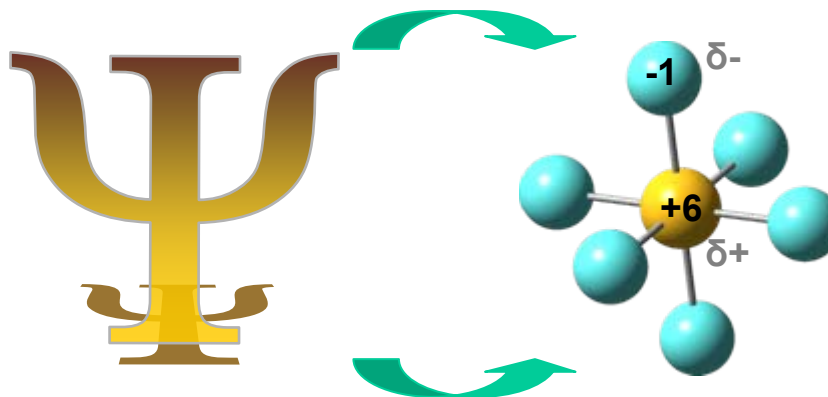


Charge Concepts

DOI: 10.1002/anie.200803605

A Piece of the Picture—Misunderstanding of Chemical Concepts

Martin Jansen and Ulrich Wedig**



oxidation state:

heuristic concept, category of classification criteria

effective charge:

many ways to derive charges from wavefunctions
- occupancy of atomic orbitals
- partitioning of position space



Examples



Metal atoms in a negative oxidation state

A. Karpov, J. Nuss, R. Dinnebier,
M. Jansen, M. Konuma

Platinides

Homo-cubane cluster

V. Saltykov, J. Nuss, M. Jansen



Electrons in voids

C. Schmidt, R. Dinnebier,
M. Jansen

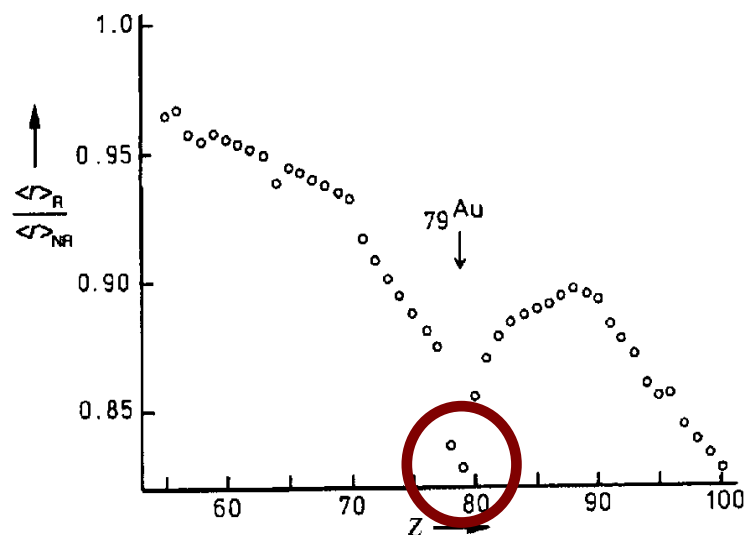




Metal Atoms in a Negative Oxidation State



The ratio of relativistic and nonrelativistic 6s shell radii



From
P. Pyykkö, J. P. Desclaux
Acc. Chem. Res. **12** (1979), 276

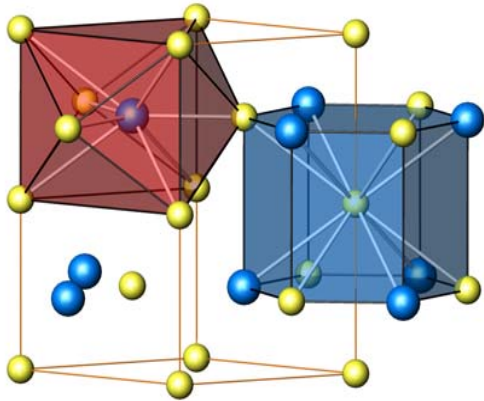
Electron Affinities

recommended values (eV) from
Andersen, Haugen, Hotop
J. Phys. Chem. Ref. Data 28 (1999), 1511

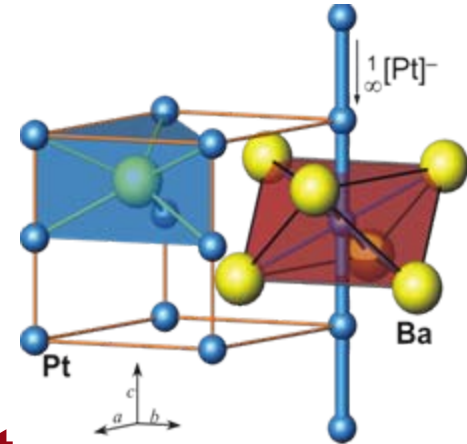
Au	2.31	Br	3.36
Pt	2.13	I	3.06
Ir	1.56	S	2.08
Ag	1.30	Se	2.02
Rh	1.14		
Pd	0.56		



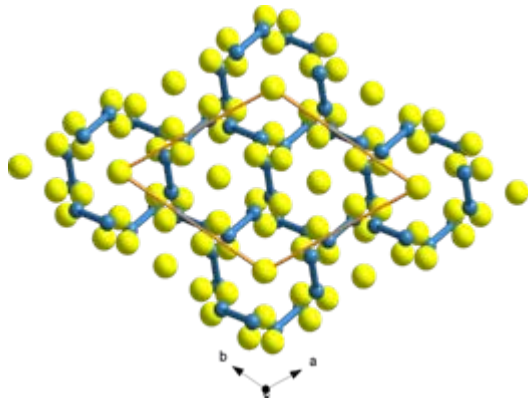
Platinides



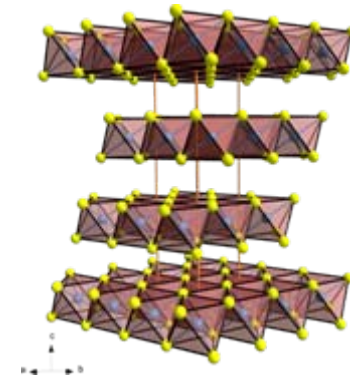
Cs₂Pt



BaPt



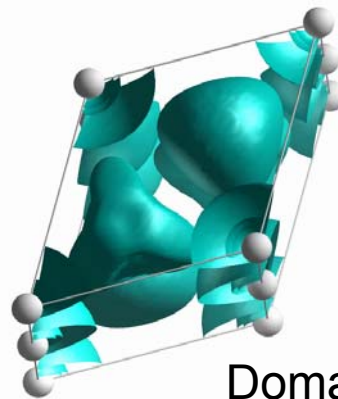
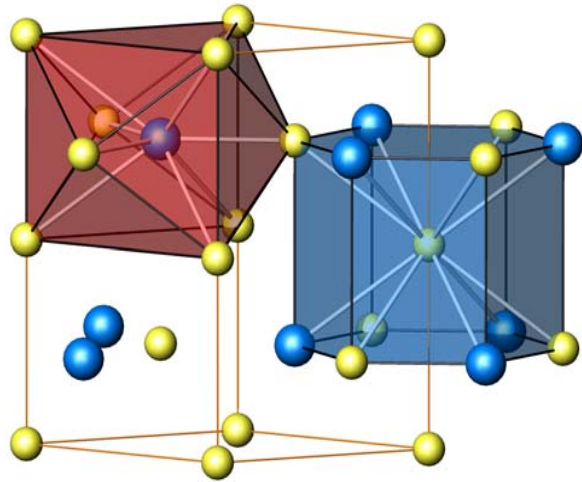
Ba₃Pt₂



Ba₂Pt

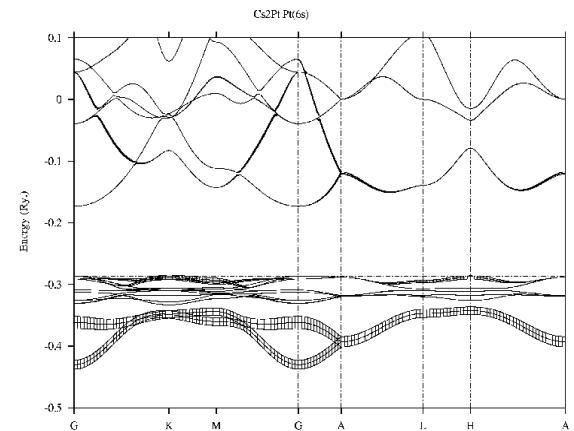


Cs₂Pt



Domains of the ELF (0.35)

TB-LMTO-ASA Pt 6s fatbands



- Ionic insulator
- Ni₂In structure type
- Affiliation to the alkali-metal monochalcogenides
- AIM charge of Pt: -1.6 e⁻





The Cs₂Pt Molecule



Large errors with the optimized lattice constants:

LDA (vBH): a: -3%; c: -22%
GGA (BLYP): a: +5%; c: -9%

Cause of the errors:

Dispersion interactions between filled shells

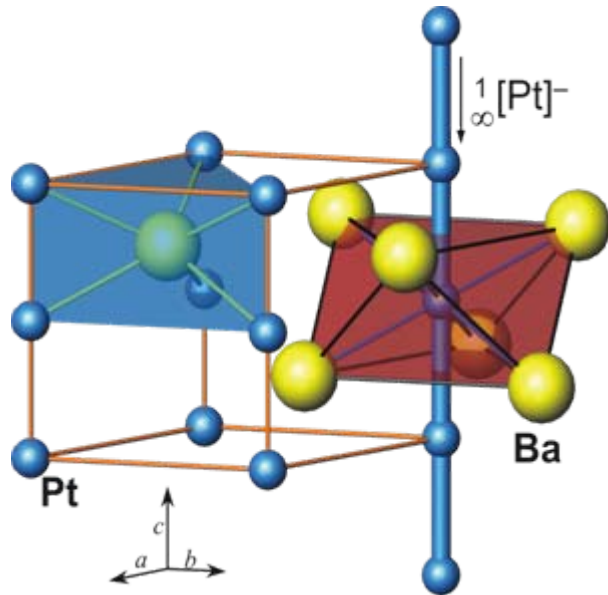
The Cs₂Pt molecule: bond length (lÅ) and bond angle (l°)

HF	not	HF	3.32	HF	3.17
Cs semi-core (5s5p) frozen	bound	no polarisation functions	117	+ 1 tight d function on Cs	129
HF	3.12	CCSD(T)	3.13	CCSD(T)	2.97 (3.11)
+ further polarisation functions	1.30	semi-core (5s5p) not correlated (FC)	1.38	semi-core valence correlation	133 (121)

(non relativistic)



BaPt

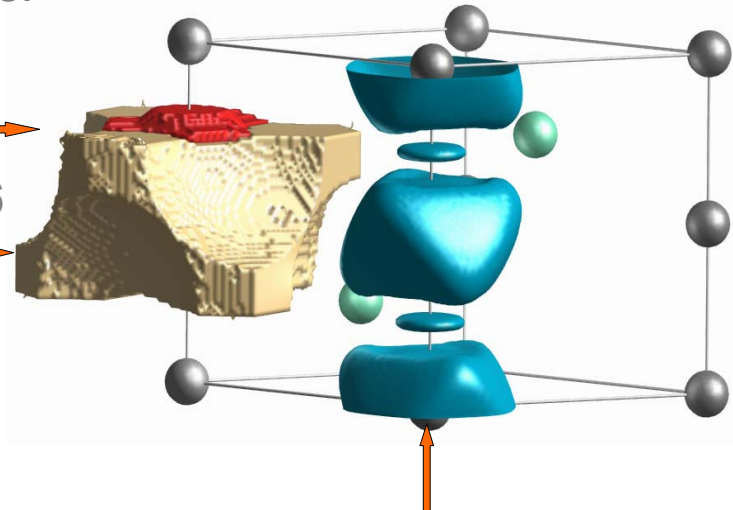


- NiAs structure type
- Extreme low c/a ratio: 1.07
- 2D metallic conductivity ?

Basin sets:

$$n_e = 0.5$$

$$n_e = 10.6$$



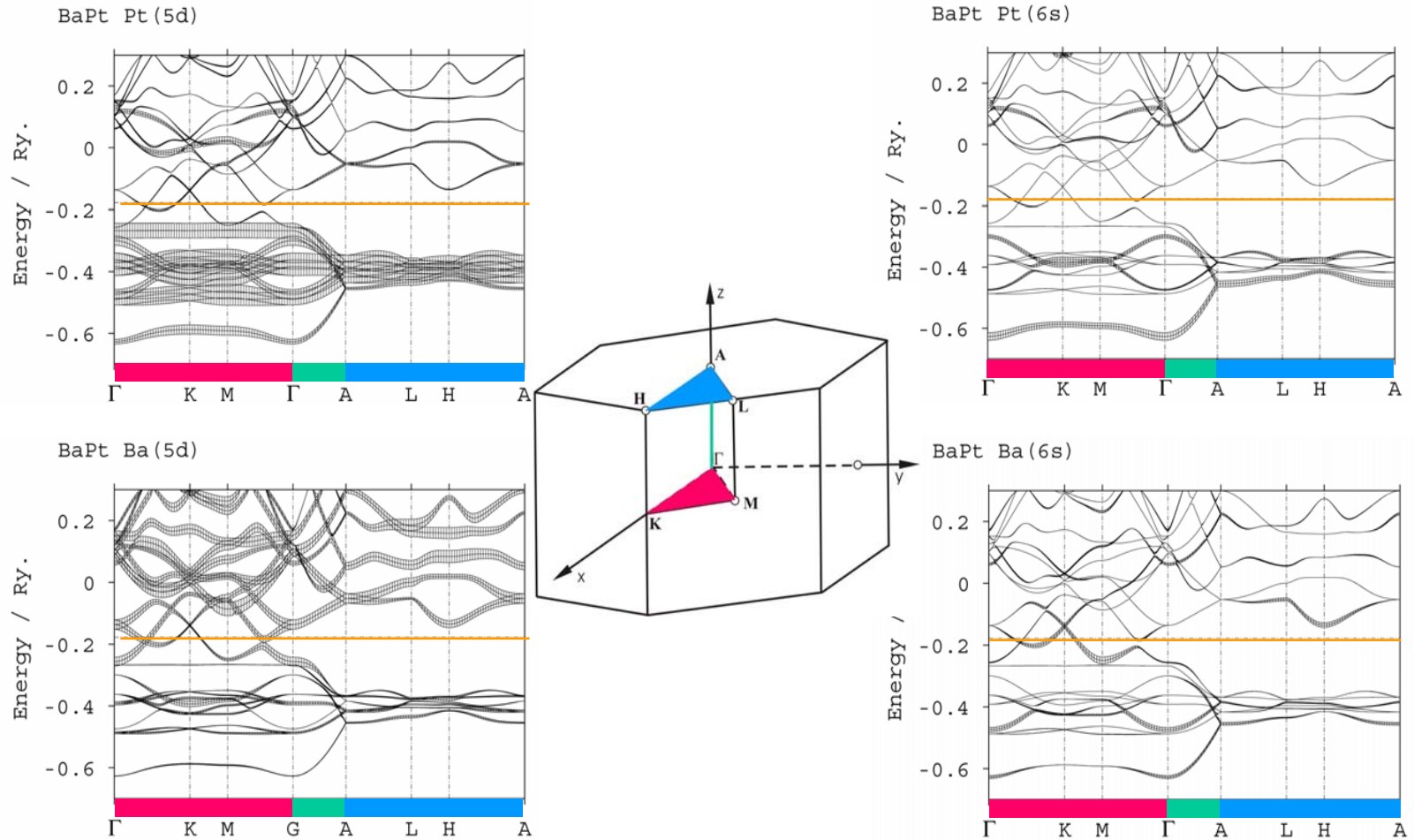
ELF-domains: $\eta = 0.32$

Pt-basin of the electron density: $n_e = 10.9$



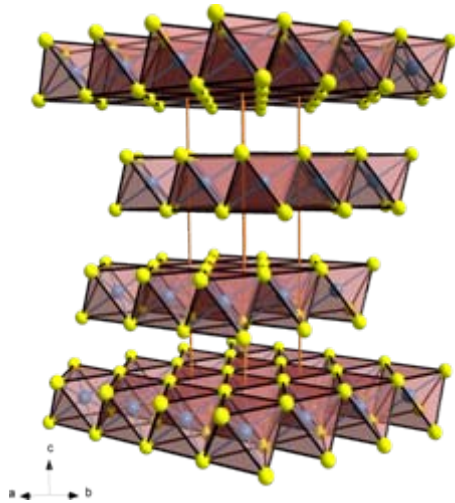


BaPt Band Structure

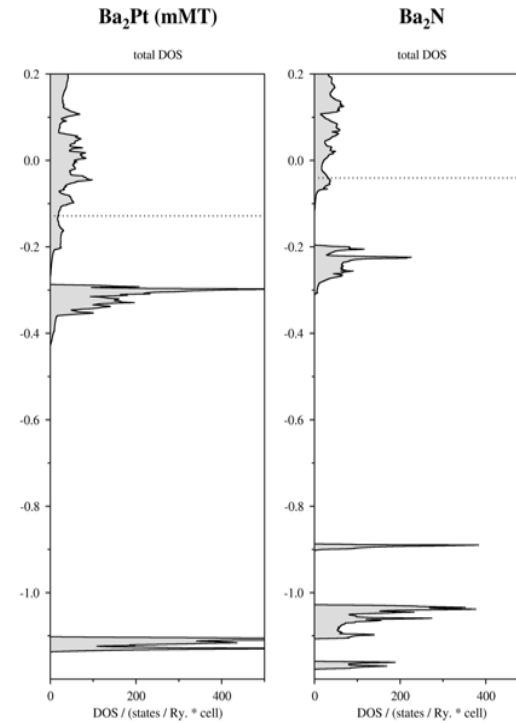




Ba₂Pt

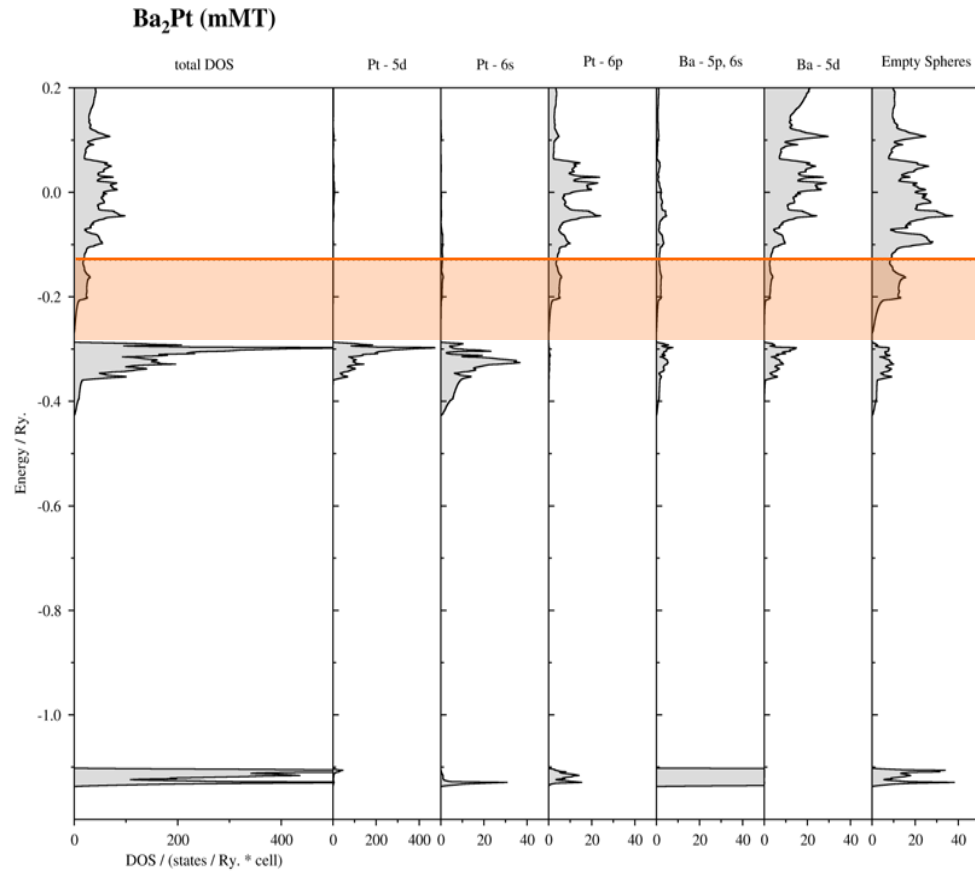


- CdCl₂ structure type
- Layered structure
- Similarities to the subnitride Ba₂N

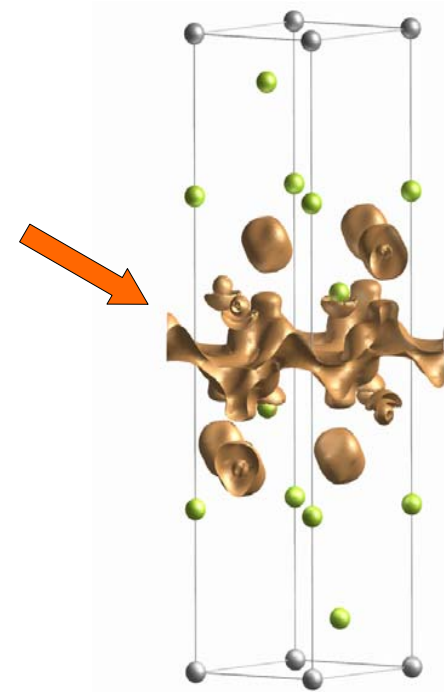




Ba₂Pt



Total and partial densities of states



Electron density of the upper valence bands
 $\rho = 0.003 \text{ e}^- / \text{Bohr}^3$

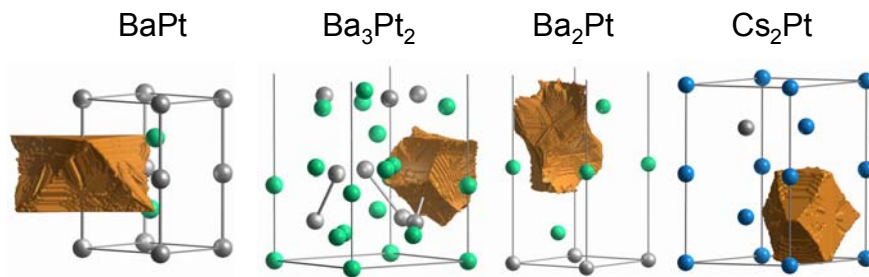


Partial Charges, oxidation states and related properties

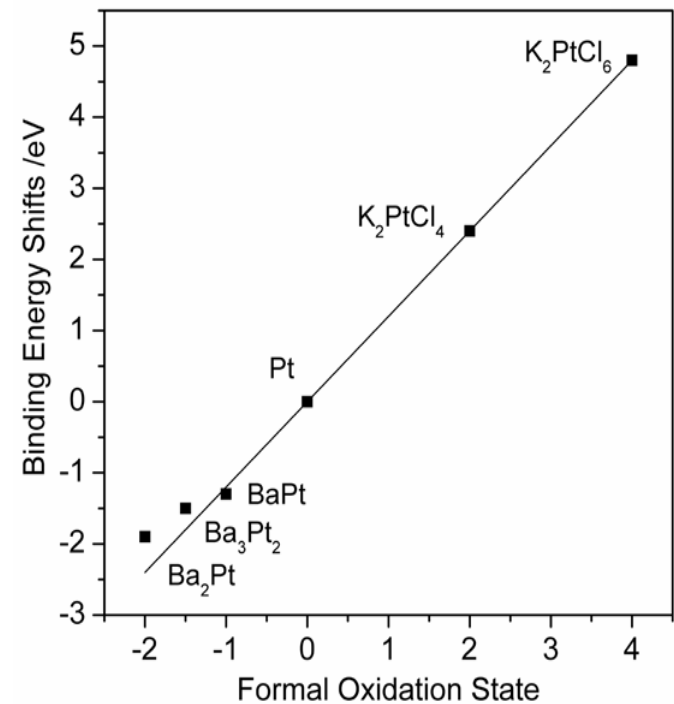


Formal description q(QTAIMAC)

Cs ₂ Pt	(Cs⁺)₂(Pt²⁻)	-1.6
BaPt	(Ba²⁺)₁[Pt⁻]	-0.9
Ba ₃ Pt ₂	(Ba²⁺)_{1.5}(Pt^{1.5-})	-1.2
Ba ₂ Pt	(Ba²⁺)₂(Pt²⁻)	-1.8



ESCA
Pt 4f_{7/2} binding energy shifts





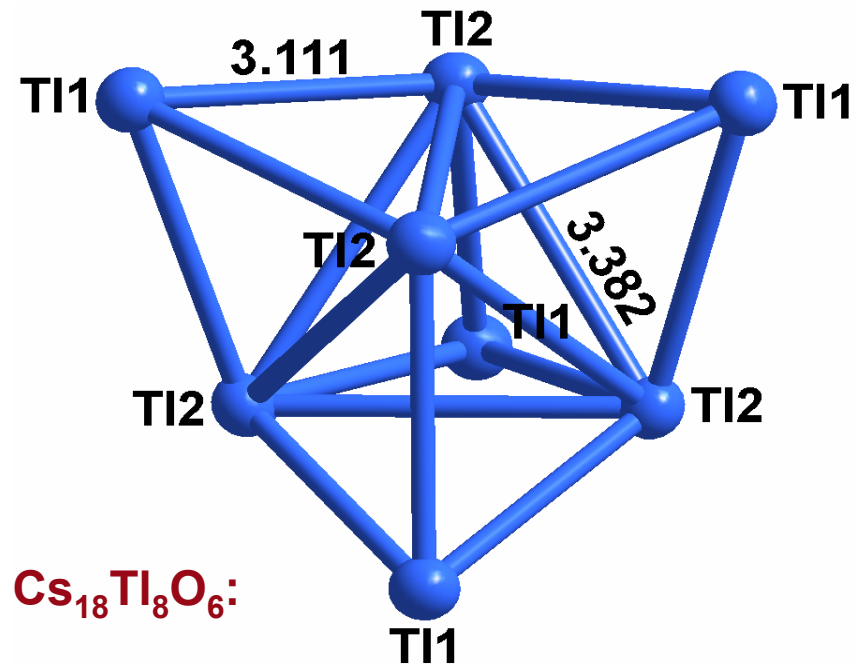
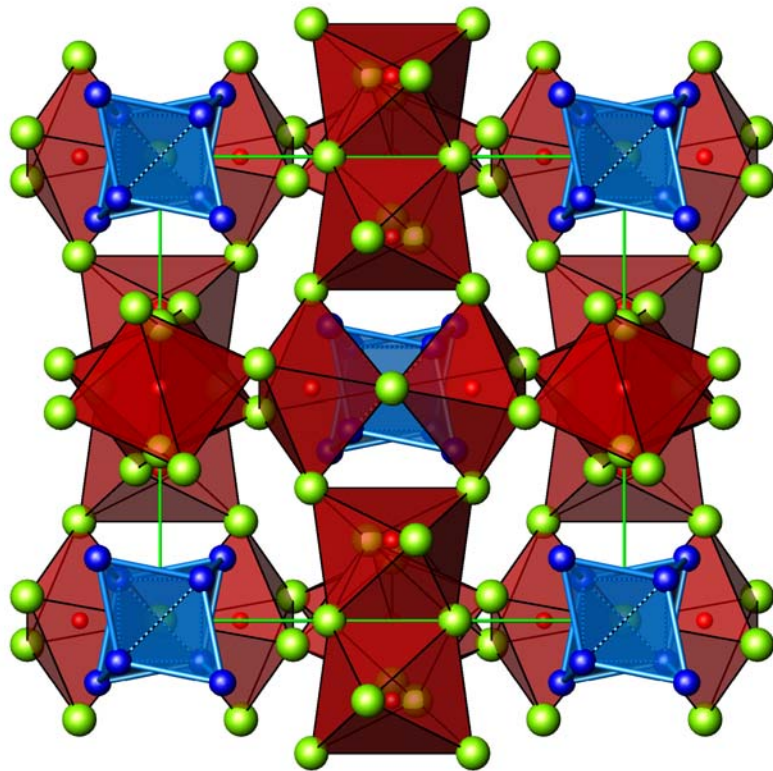
Platinides - Conclusions



- **The Platinides are intermetallic compounds.**
- **In all cases, platinum unambiguously has a negative oxidation state.**
- **A part of the valence electrons form covalent or ionic substructures.**
- **In the extreme case (Cs_2Pt), no valence electrons are left for metallic conductivity.**
- **There are parallels to compounds containing main group anions.**
- **The relativistic contraction of the 6s-shell determines the chemical behaviour of Pt.**
- **The polarization of the outer core shell of the cations must be considered.**
- **Electron correlation has a non negligible influence.**



$\text{Cs}_{18}\text{Tl}_8\text{O}_6$ – the First Homo-Cubane Cluster



$\text{Cs}_{18}\text{Tl}_8\text{O}_6$:

space group I23

Z=4

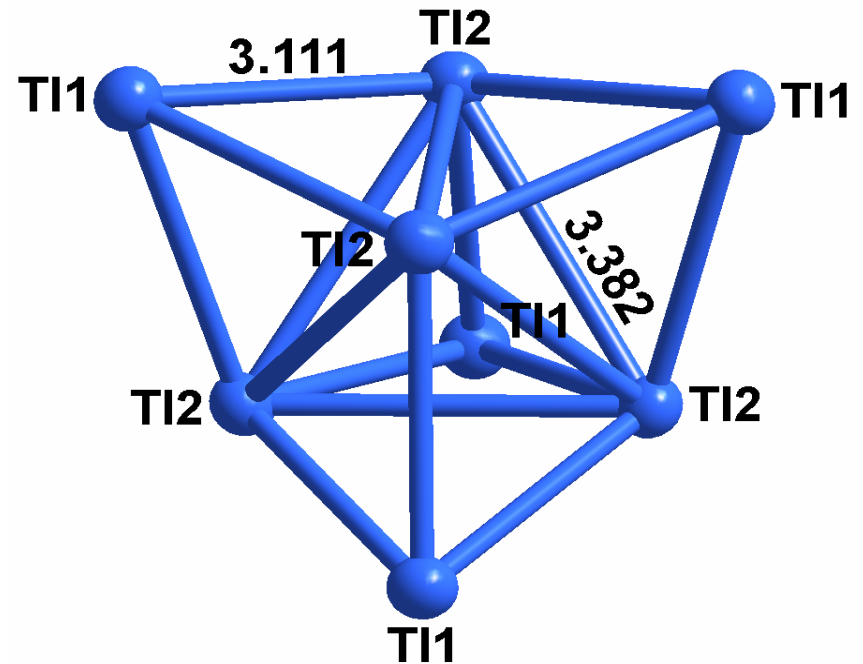
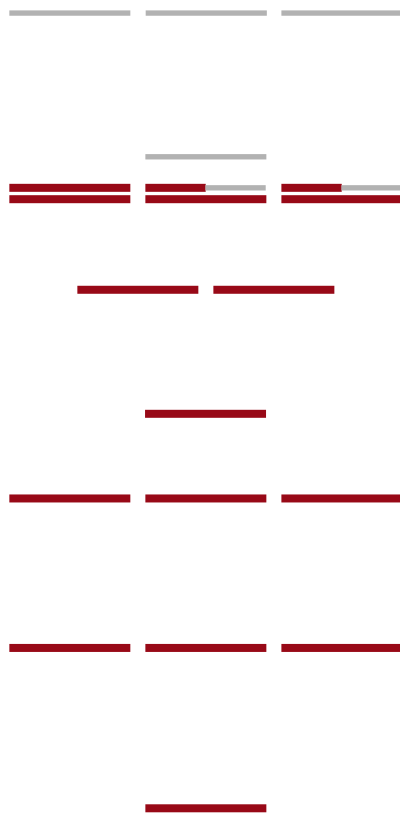
a=13.372 Å



The $[\text{Tl}_8]^{6-}$ tetrahedral star



Extended Hückel MO picture:



EHT: open shell, degenerate HOMO
expt.: diamagnetic, no Jahn-Teller distortion

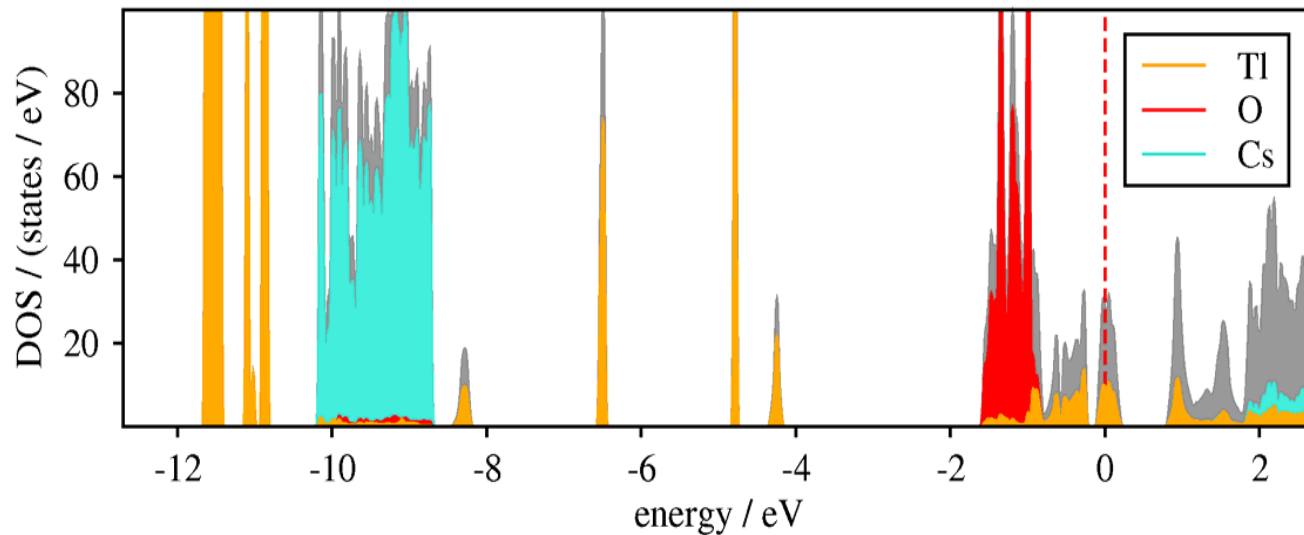


$\text{Cs}_{18}\text{Ti}_8\text{O}_6$ – Density of States



Calculation: FPLAPW with WIEN2k, PBE functional (GGA)

non-spinpolarized - without spin-orbit coupling



EHT, Cluster

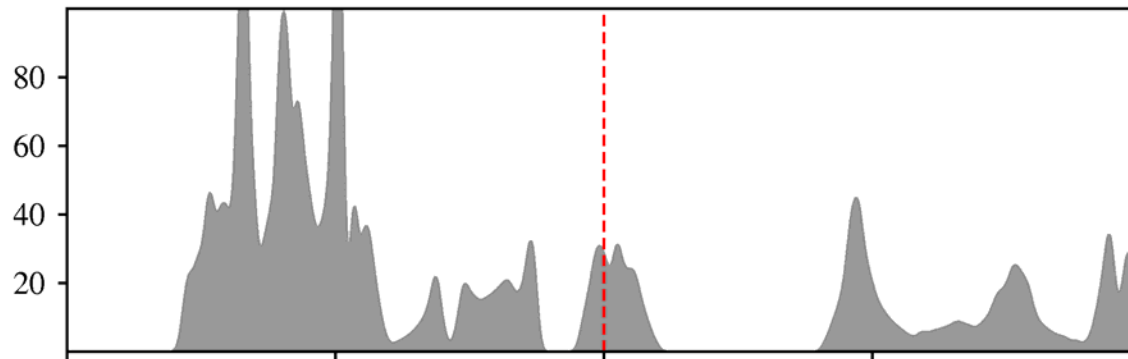




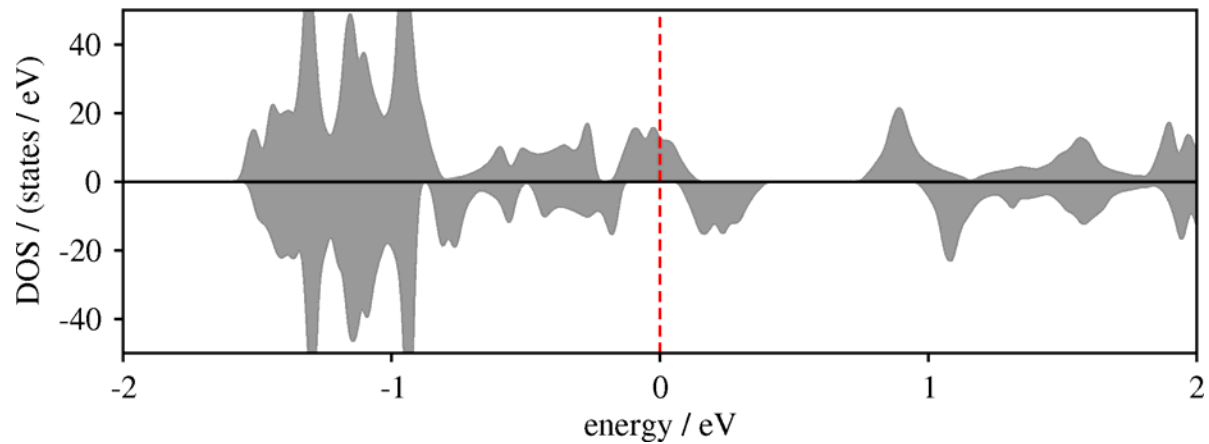
$\text{Cs}_{18}\text{Tl}_8\text{O}_6$ – Density of States



non-spinpolarized - without spin-orbit coupling



spinpolarized - without spin-orbit coupling

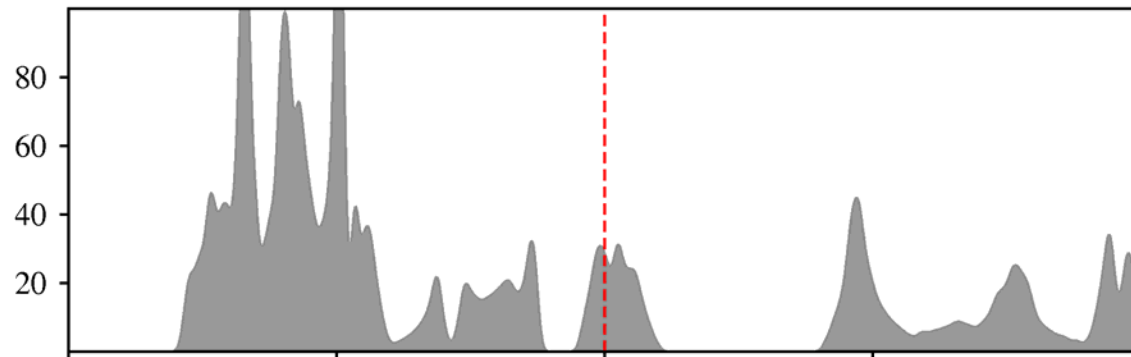




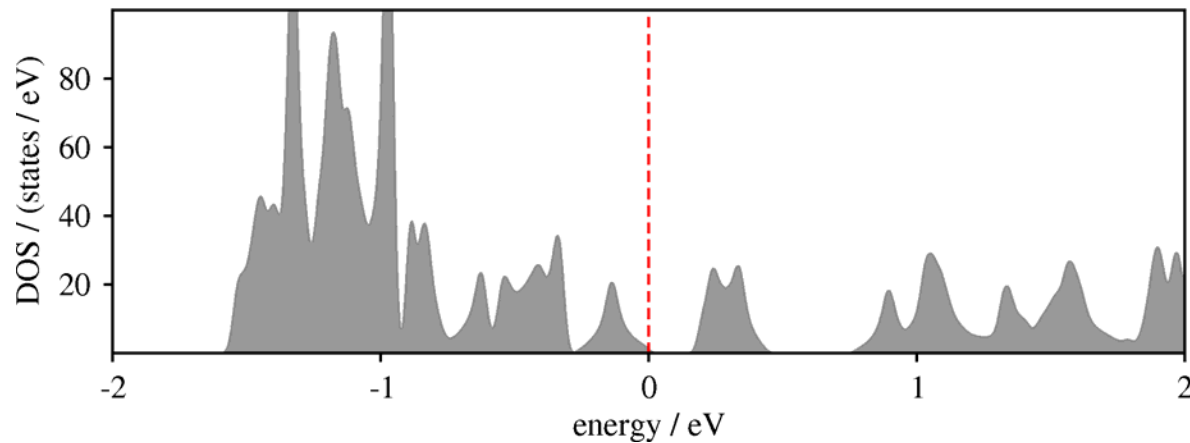
$\text{Cs}_{18}\text{Tl}_8\text{O}_6$ – Density of States



non-spinpolarized - without spin-orbit coupling



non-spinpolarized - with spin-orbit coupling



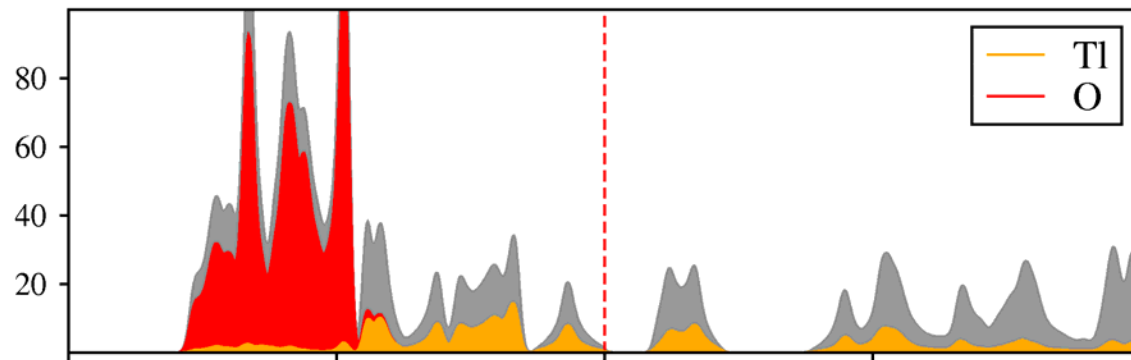
Including spin-orbit coupling → no spin-polarization → closed shell system



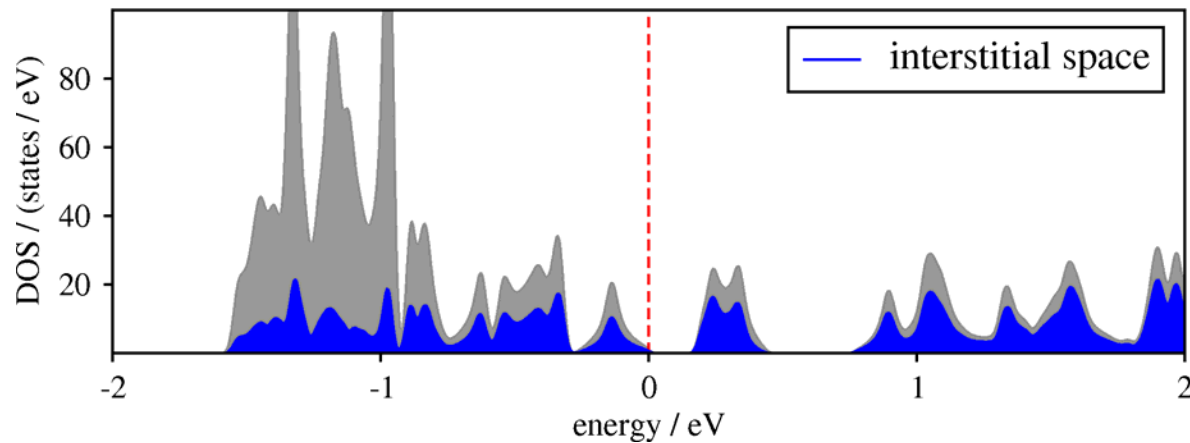
$\text{Cs}_{18}\text{Tl}_8\text{O}_6$ – Density of States



non-spinpolarized - with spin-orbit coupling



non-spinpolarized - with spin-orbit coupling



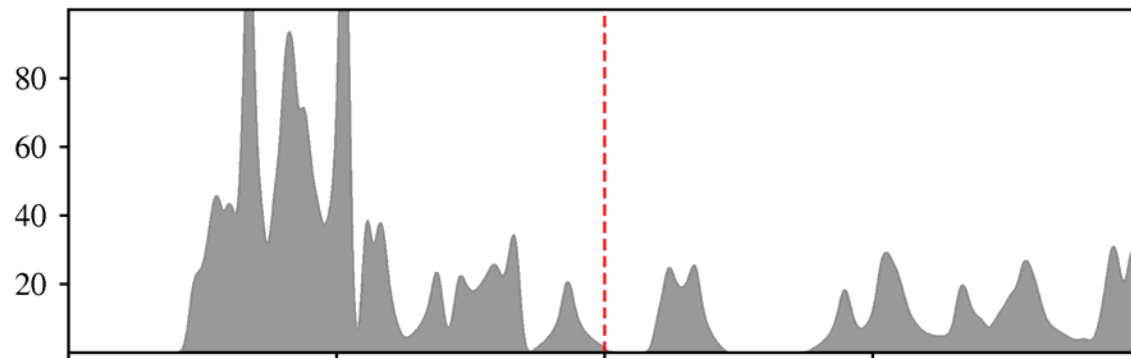
Contributions of the plane waves (interstitial space) to the DOS



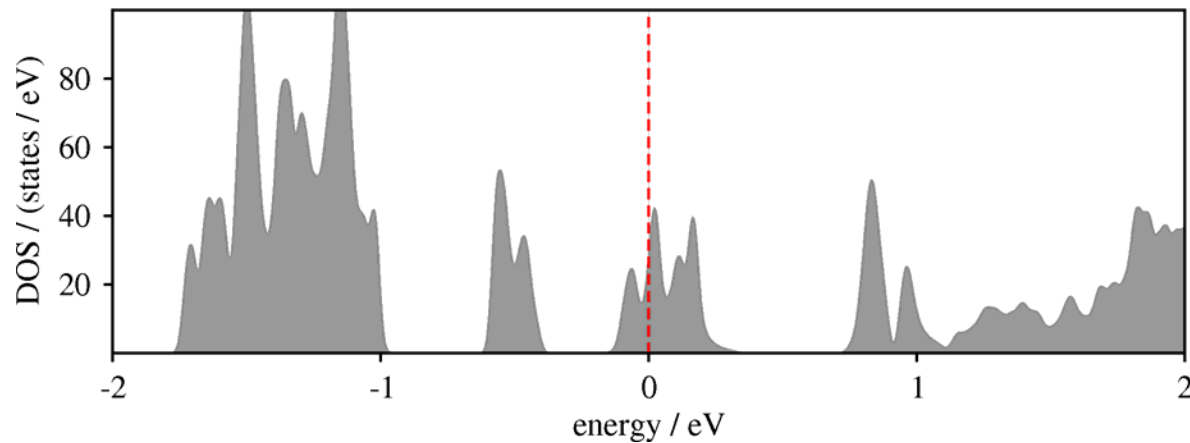
$\text{Cs}_{18}\text{Tl}_8\text{O}_6$ – Density of States



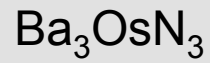
non-spinpolarized - with spin-orbit coupling



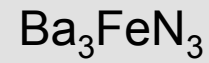
non-spinpolarized - with spin-orbit coupling - ideal cube



Including spin-orbit coupling → the tetrahedral star, a Jahn-Teller distorted cube



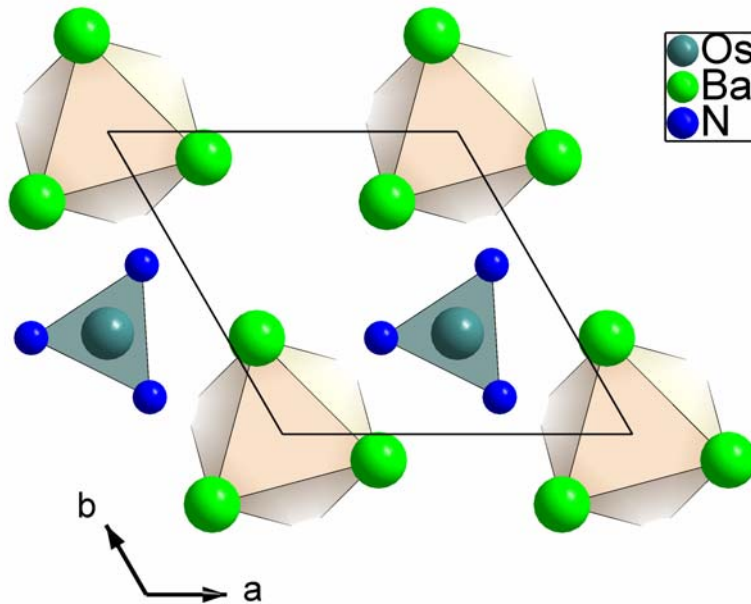
vs.



$R\bar{3}$

$a = 811.0 \text{ pm}$

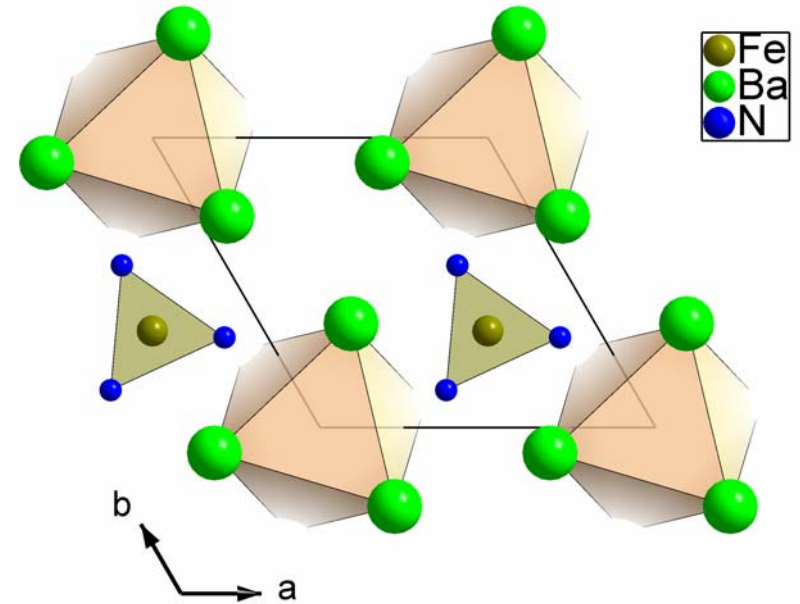
$c = 1739.0 \text{ pm}$



$P6_3/m$

$a = 801.4 \text{ pm}$

$c = 560.8 \text{ pm}$



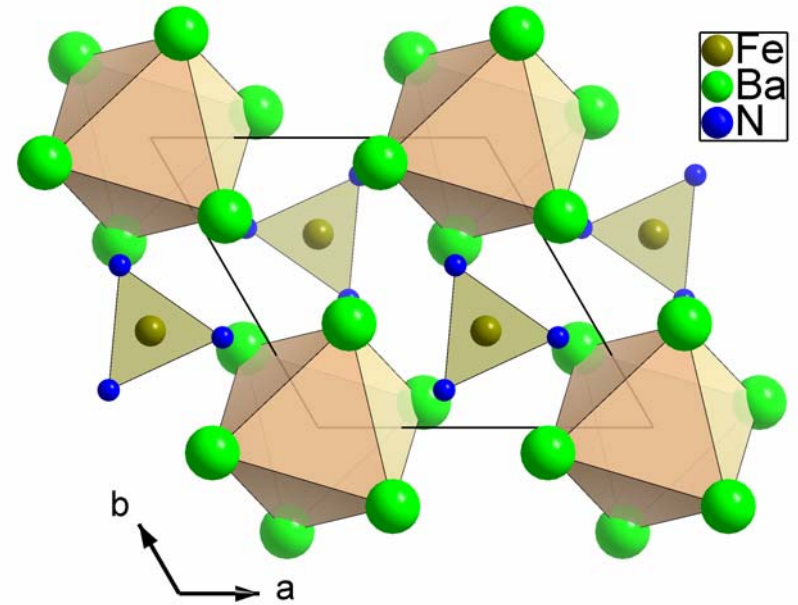
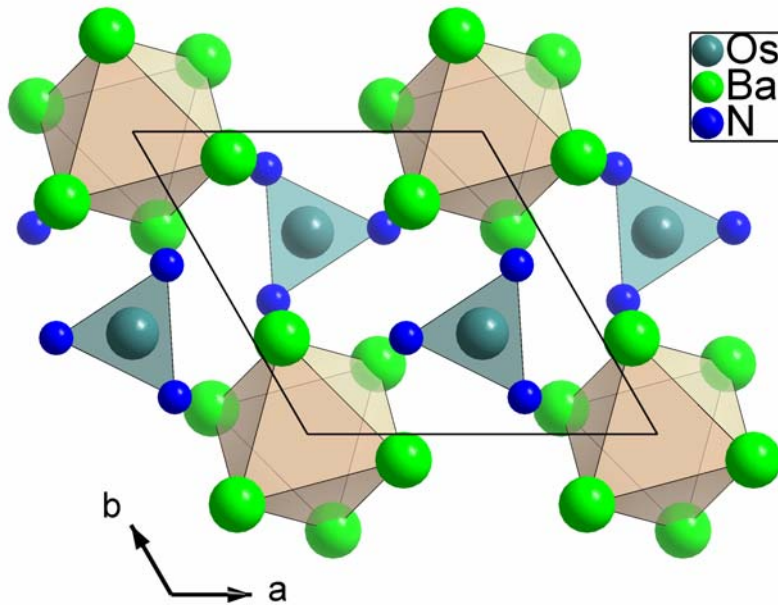
P. Höhn, R. Kniep, A. Rabenau
Z. Krist. 196 (1991) 153



“Ba₃OsN₃”

vs.

Ba₃FeN₃

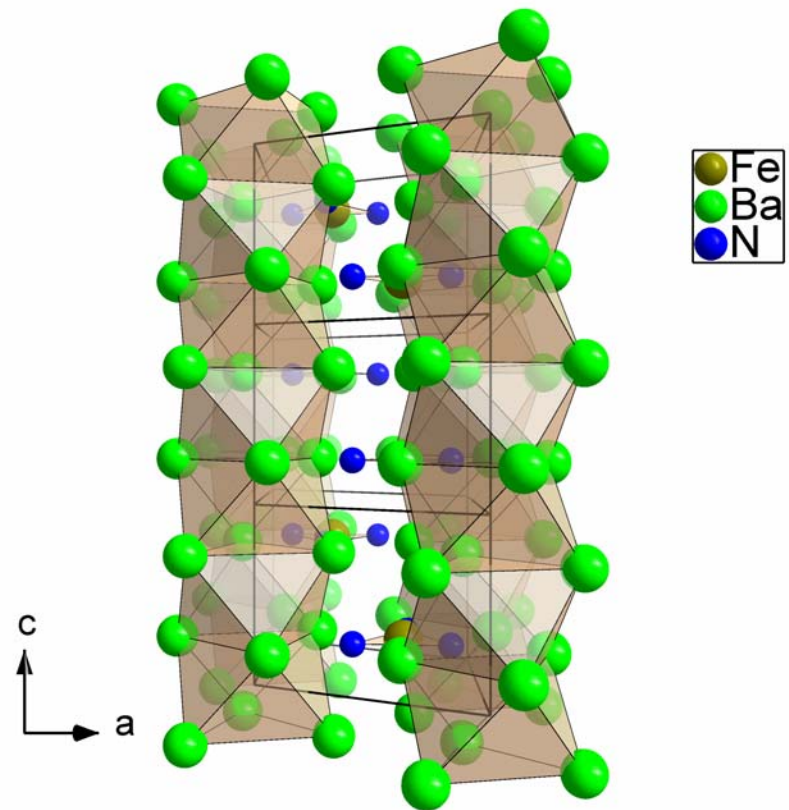
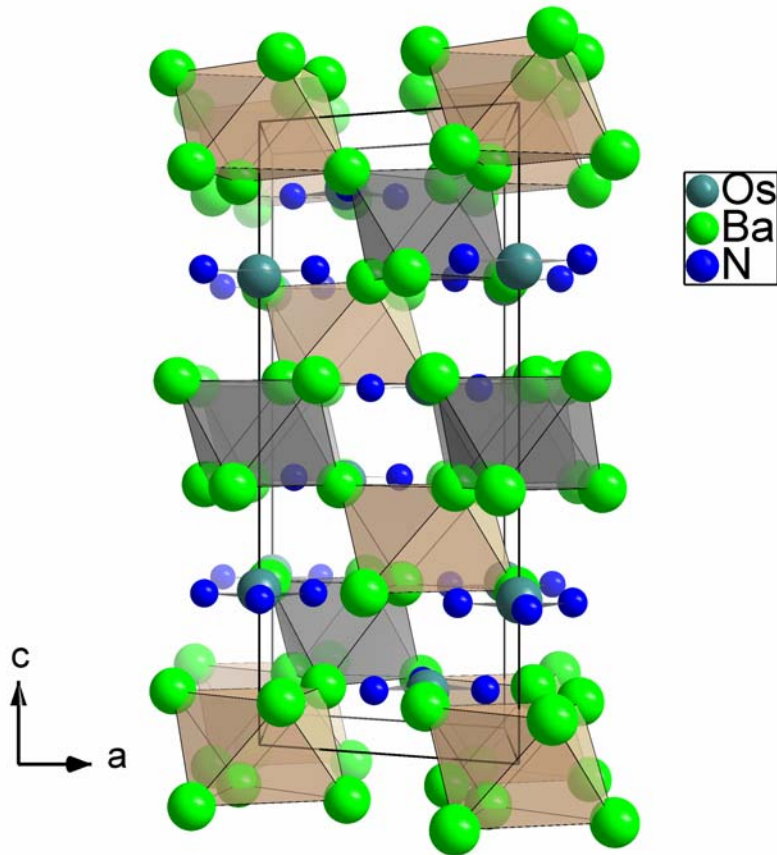


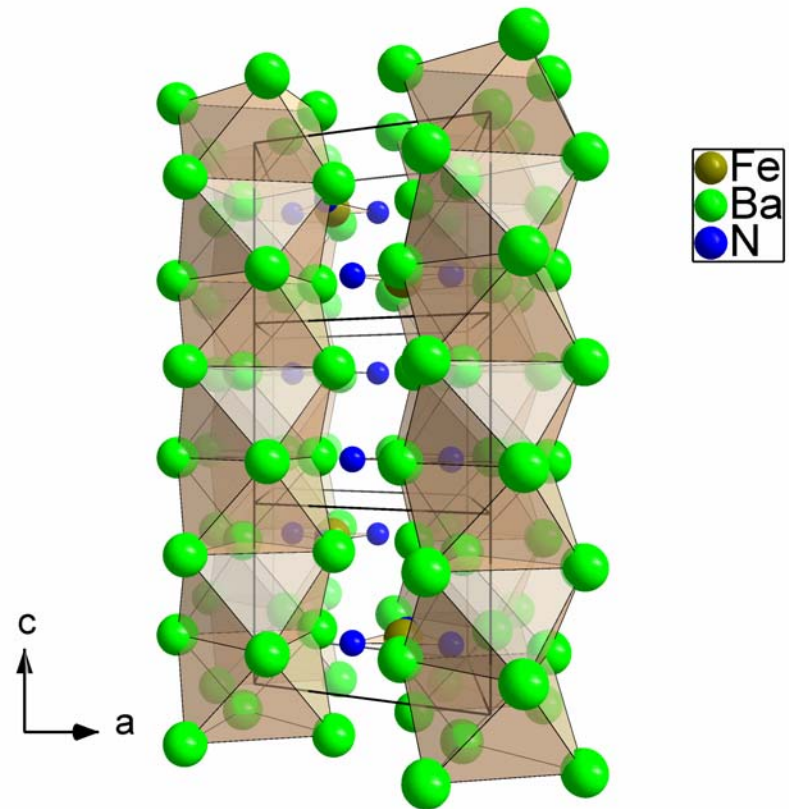
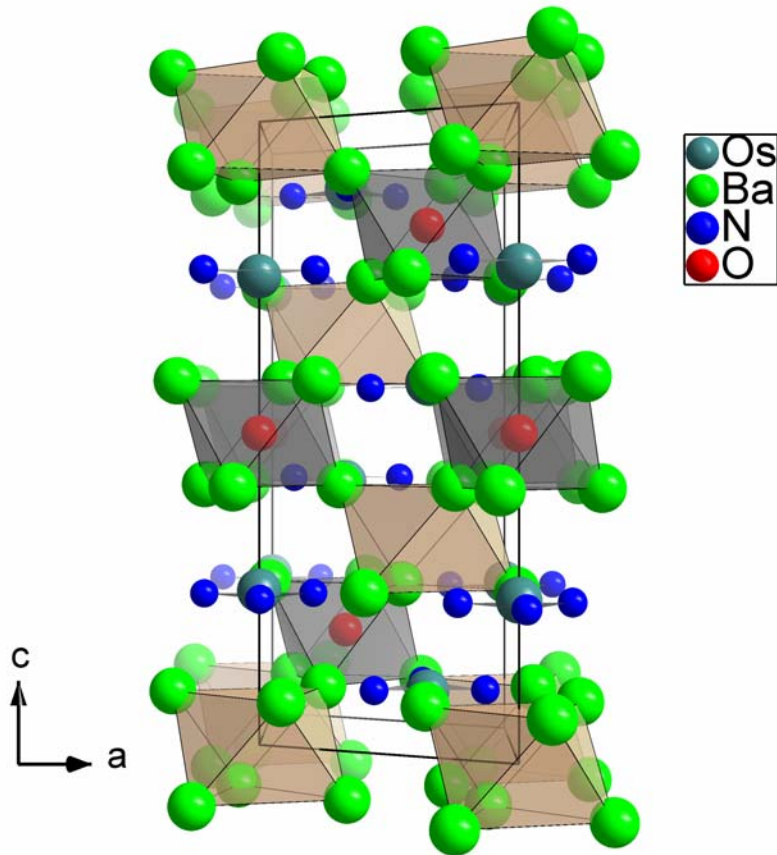
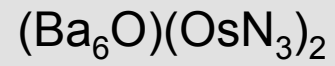


“Ba₃OsN₃”

vs.

Ba₃FeN₃



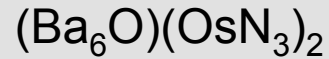




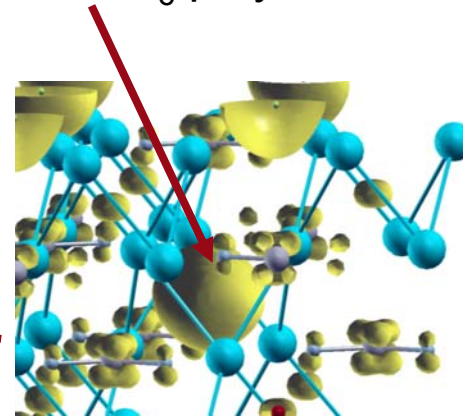
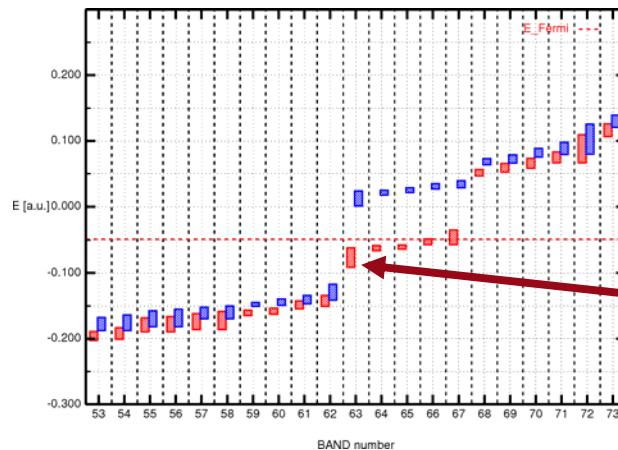
Calculations with CRYSTAL06, hybrid functional B3PW



		expt.	computed			
		(Ba ₆ O)(OsN ₃) ₂	(Ba ₆ □)(OsN ₃) ₂	(Ba ₆ O)(OsN ₃) ₂	(Ba ₆ N)(OsN ₃) ₂	(Ba ₆ O ₂)(OsN ₃) ₂
positions	3b	O	-	O	N	O
	3a	-	-	-	-	O
lattice parameter / Å	a	8.112	8.077	8.085	8.135	8.094
	c	17.390	17.348	17.414	17.599	17.359
distances / Å	Ba – 3b	2.73	2.82	2.71	2.70	2.80
	Ba – 3a	2.91	2.82	2.92	2.96	2.80
binding energy / (kJ / mole)	O / N in 3a / 3b			822	578	1586
partial charges / spin charges	OsN ₃ ^{-δ}		-2.8 / +1.9	-2.6 / +1.6	-2.4 / +1.1	-2.4 / +1.0
	Ba		+1.2 / -0.1	+1.3 / +0.1	+1.4 / +0.1	+1.4 / 0
	Pos. 3b		-0.7 / -0.6	-1.9 / 0	-2.8 / 0	-1.8 / 0
	Pos. 3a		-0.7 / -0.6	-0.5 / +0.5	-0.5 / +0.4	-1.8 / 0



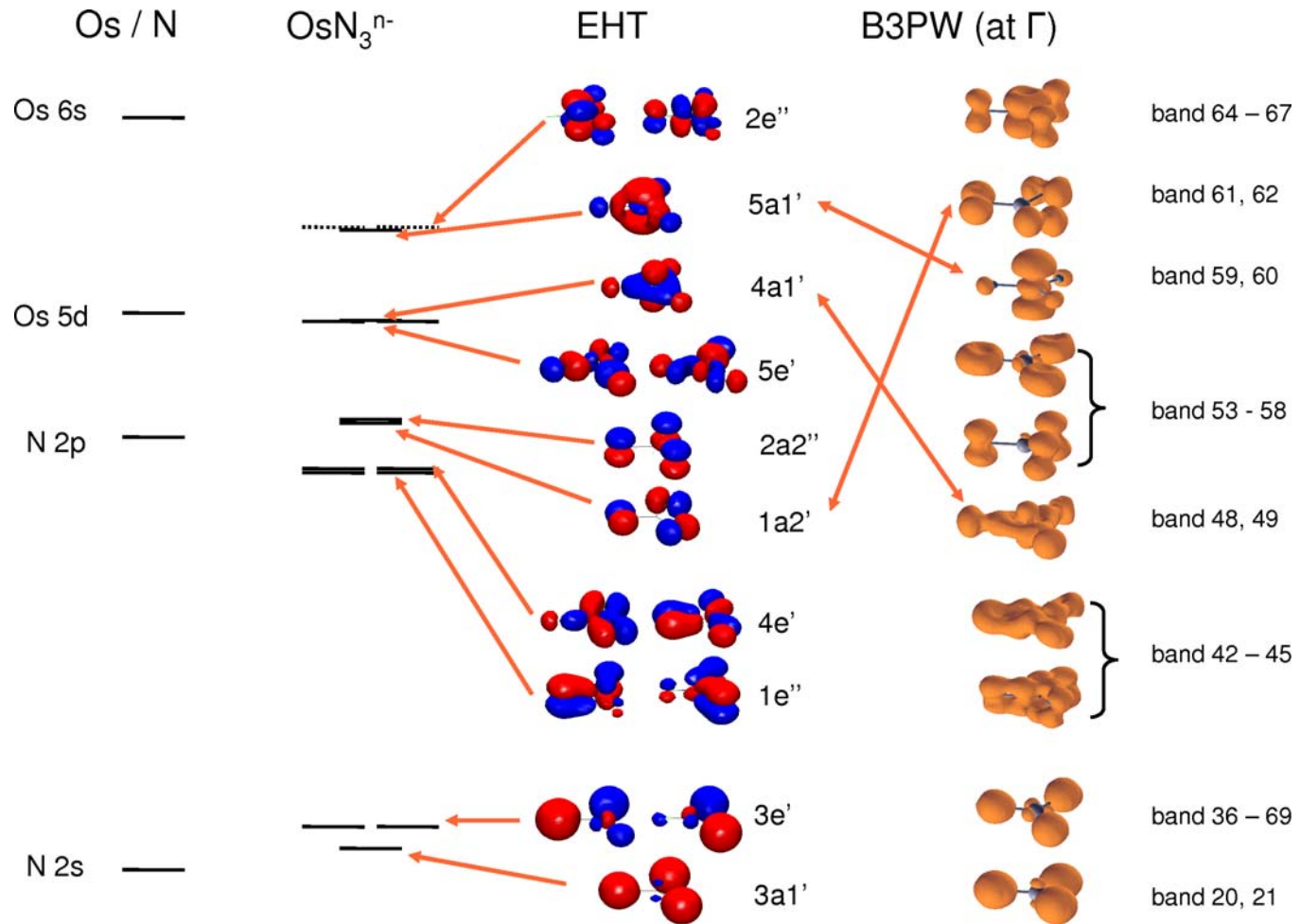
- $(\text{Ba}_6\text{O})(\text{OsN}_3)_2$ is the most probable composition
- Oxygen at position 3b (0,0,1/2) within Ba_6 polyhedra
- OsN_3^{5-} -units with osmium in oxidation state +4
powder X-ray diffraction, ESCA, calculations
- Spin density at position 3a (0,0,0) within Ba_6 polyhedra



- Conductivity: semiconductor, variable range hopping, $\sigma \sim T^{-1/n}$
- Magnetism: paramagnetic, magnetic moment: $1,7 \mu_B$



OsN₃⁵⁻-units

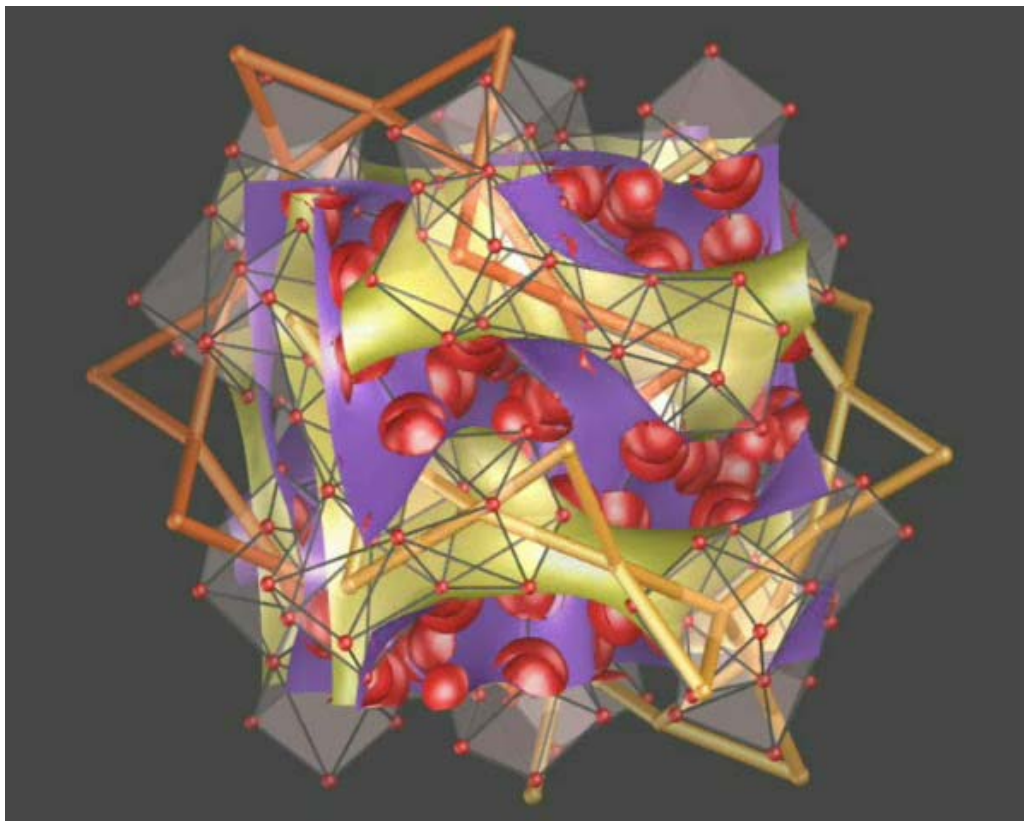




Chemical Bonding in Crystalline Compounds



Why are metal atoms in a crystal arranged in a certain manner ?



RhBi₄:

Ia3d

a=14.928 Å

120 atoms / cell

A description:

Two catena-like interpenetrating enantiomorphic frameworks of tetragonal antiprisms RhBi_{8/2}, separated by hyperbolic layers of Bi lone pair.

Y. Grin, U. Wedig, H. G. v. Schnering, *Angew. Chem. Int Ed. Engl.* **34** (1995) 1204