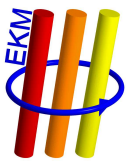
New Perspectives in Efficient Large-Scale Modeling

Volker Eyert

Center for Electronic Correlations and Magnetism
Institute for Physics, University of Augsburg

September 24, 2009



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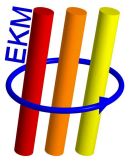

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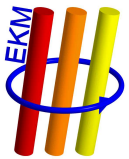

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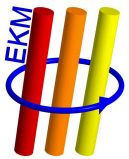

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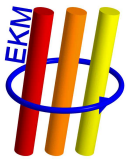
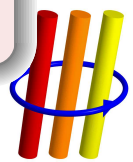


Materials Design

Computational Modeling and Data Driven Materials Discovery

- on-the-fly calculation $\Longleftrightarrow$ storage in databases
  - calculational approaches?
  - functional indicators?



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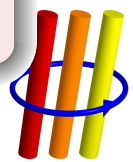

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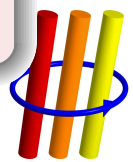
  $\Longleftrightarrow$ identifying common phenomena across materials



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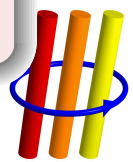
- knowledge $\Longleftrightarrow$ understanding
  - where does scientific experience/intuition enter?



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Computational Modeling — A Zoo of Options

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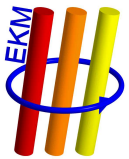

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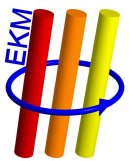

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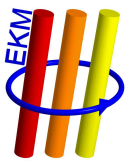

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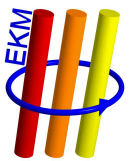

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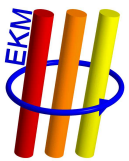

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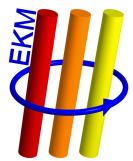

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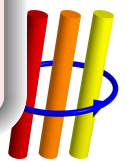

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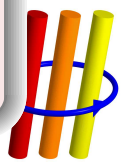

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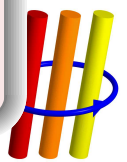

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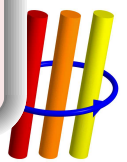

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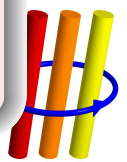

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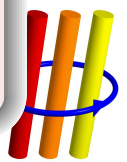

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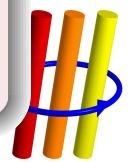

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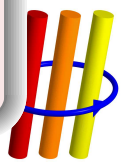

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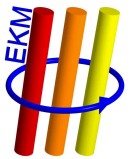

Back in the 1930's . . .

John C. Slater

Full Potential

$$v_\sigma(\mathbf{r}) : \begin{cases} \text{spherical symmetric near nuclei} \\ \text{flat outside the atomic cores} \end{cases}$$

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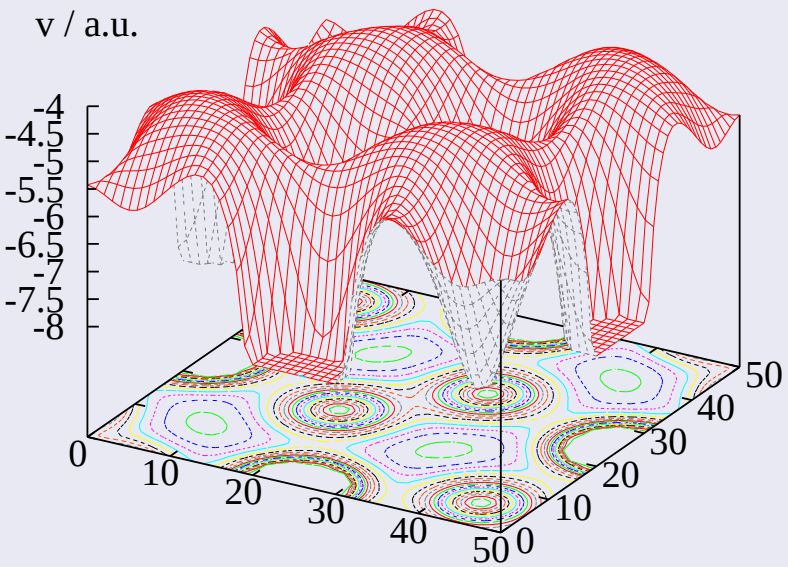
Muffin-Tin Approximation

$$v_\sigma^{MT}(\mathbf{r}) = \begin{cases} \text{spherical symmetric in spheres} \\ \text{constant in interstitial region} \end{cases}$$

Back in the 1930's . . .

Full Potential (FeS_2)



Muffin-Tin Potential

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Partial Waves

- muffin-tin spheres
  - $v_{eff,\sigma}(\mathbf{r}) = v_{eff,\sigma}(|\mathbf{r}|)$
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    - plane waves
    - spherical waves

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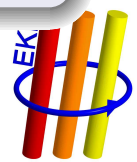
Basis Functions

- matched partial waves
  - augmented plane waves (APWs)
  - „muffin-tin orbitals" (MTOs), augmented spherical waves (ASWs)



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expand in basis functions

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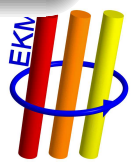

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Core States

all-electron methods

- fully included
- orthogonal to partial waves

Basis Functions

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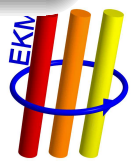
- used to describe valence states



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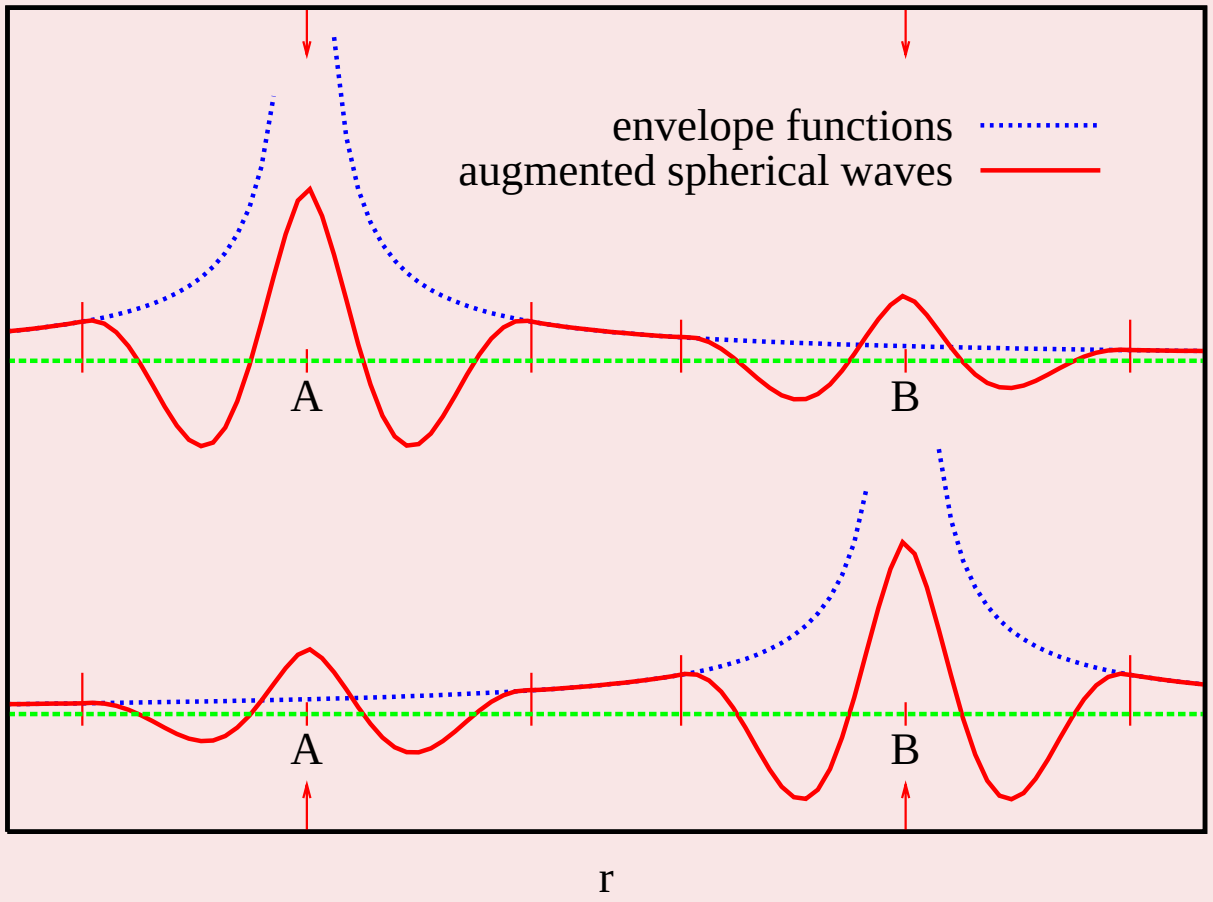
Augmented Spherical Waves



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"Linear Methods in Band Theory"

- energy dependence of basis functions almost linear $\rightarrow$ linearize $(\varphi, \dot{\varphi})$
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Linear Augmented Plane Wave (LAPW)

- muffin-tin approximation
- easy to implement — good!
- full-potential at a low price
  - basis functions from muffin-tin potential
  - wave functions from full potential
  - example: Wien2k
- large basis set ($\approx$ 100 pw's/atom) — bad!

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Linear Muffin-Tin Orbital (LMTO)

- based on spherical waves
  - does not require crystalline periodicity
  - natural interpretation of results
- difficult to implement bad!
- full-potential extension extremely difficult
- muffin-tin approximation (?)
  - finite interstitial region
  - large basis set:
    two functions per *s*-, *p*-, *d*-state
  - still inefficient bad!

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  - make spheres space-filling!
    - interstitial region formally removed
    - only numerical functions in spheres
  - minimal basis set (s, p, d)
    - very high computational efficiency $\rightarrow \mathcal{O}$(ASA) speed!!!
  - makes potential more realistic
  - systematic error in total energy bad!

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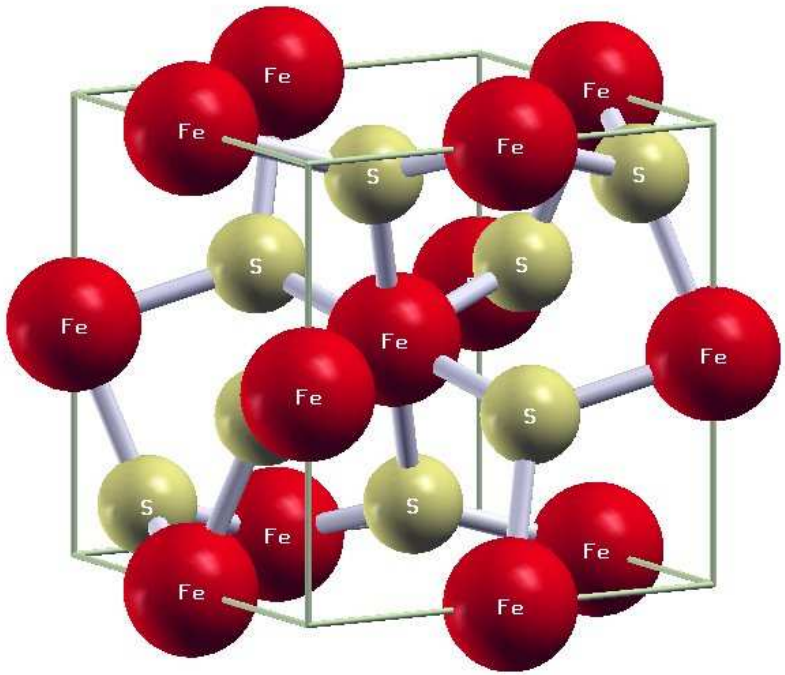
Iron Pyrite: FeS_2

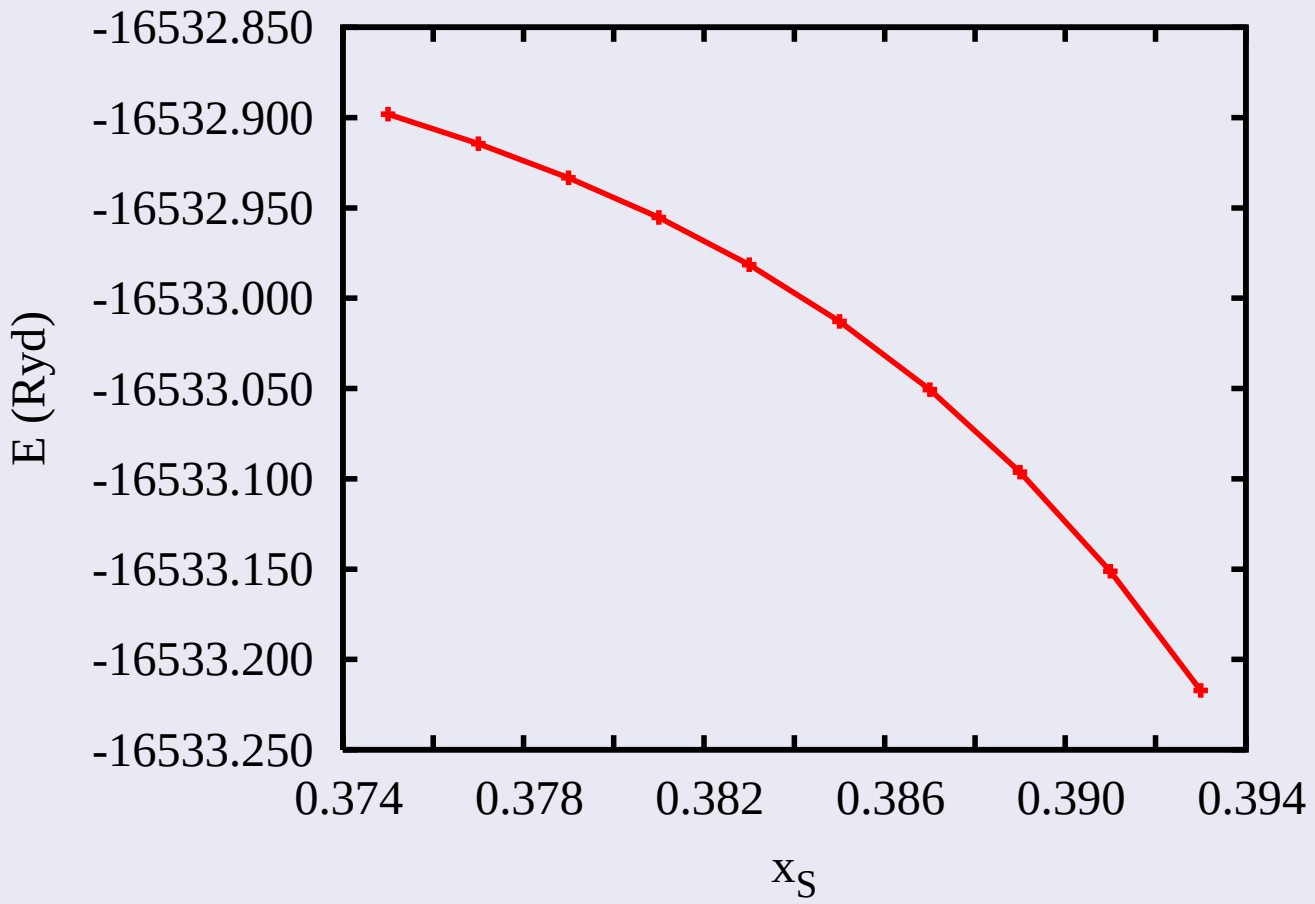


Pyrite

- $Pa\bar{3}$ (T_h^6)
- a = 5.4160 Å
- "NaCl structure" sublattices occupied by
  - iron atoms
  - sulfur pairs
- sulfur pairs $\parallel \langle 111 \rangle$ axes
- x_S = 0.38484
- rotated FeS_6 octahedra

FeS_2: Structure Optimization

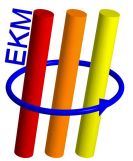
ASA^+ Code



Towards a Full-Potential Spherical-Wave Method

Conclusions

- ASA (space-filling atomic spheres)
  - $\mathcal{O}$(ASA) speed
  - systematic error in total energy
- non-overlapping muffin-tin spheres
  - prerequisite for accurate total energies
  - larger basis set $\longrightarrow$ inefficient



Towards a Full-Potential Spherical-Wave Method

Conclusions

- ASA (space-filling atomic spheres)
  - $\mathcal{O}$(ASA) speed
  - systematic error in total energy
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Requirements

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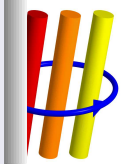
  - go to non-overlapping muffin-tin spheres
  - go beyond constant-potential approximation
- inside muffin-tin spheres
  - non-spherical contributions



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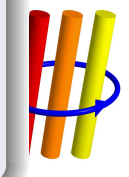
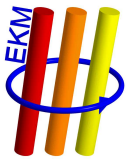


Towards a Full-Potential Spherical-Wave Method

Guidelines

- interstitial quantities expanded in plane waves
  - straightforward to implement
  - inefficient
- interstitial quantities expanded in spherical waves
  - elegant, no periodicity required
  - efficient
  - difficult to implement



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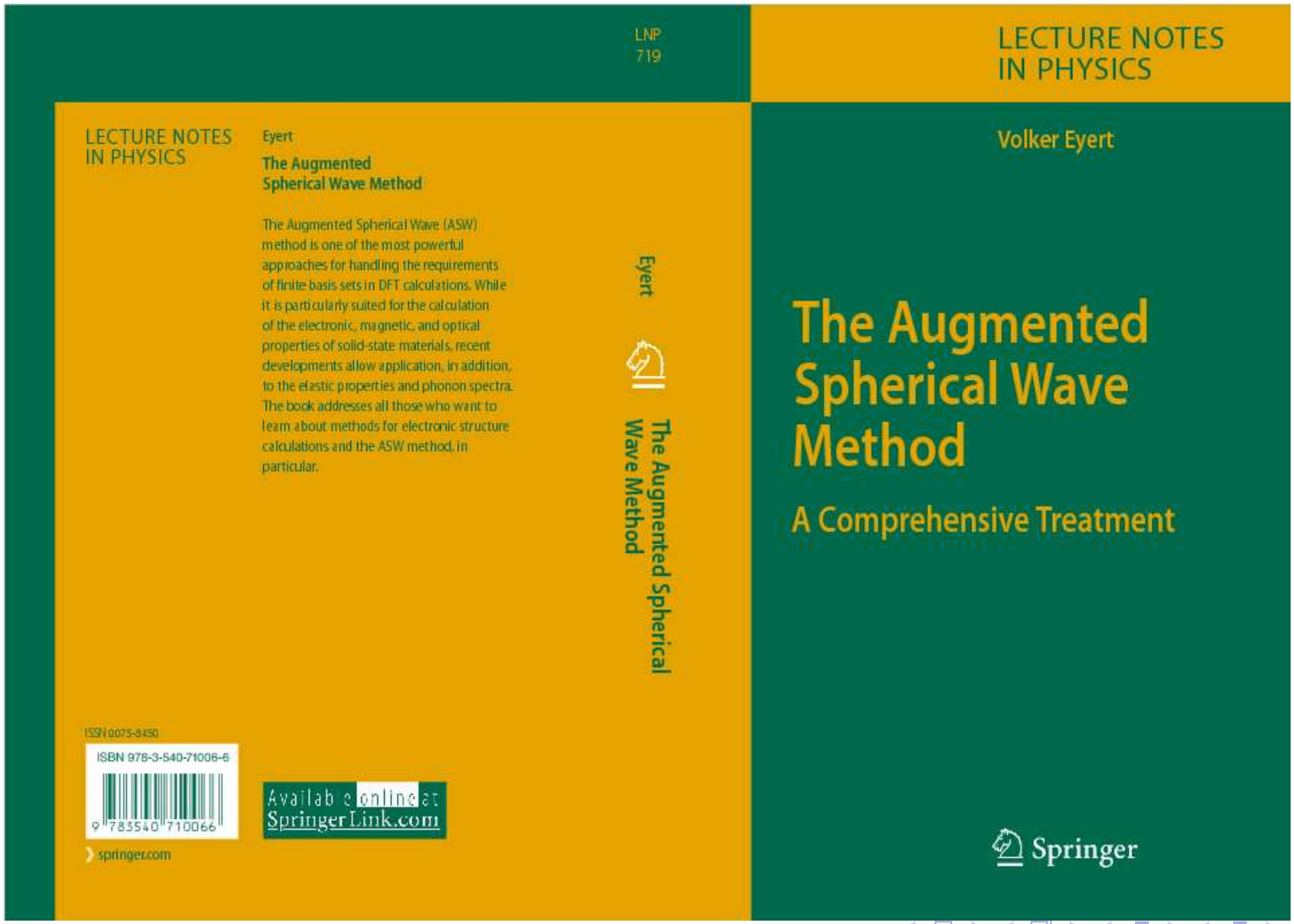
ASW Method: Further Reading



Basic Principles

Steps to be Taken

- remove total energy error due to overlap of atomic spheres
  - reintroduce non-overlapping muffin-tin spheres
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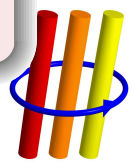

Basic Principles

Steps to be Taken

- remove total energy error due to overlap of atomic spheres
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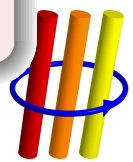
- find representation of electron density and full potential
  - inside muffin-tin spheres
  - in the interstitial region



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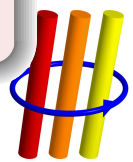

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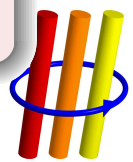

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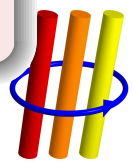
    - use spherical-harmonics expansions
  - in the interstitial region



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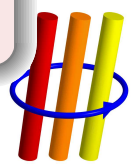
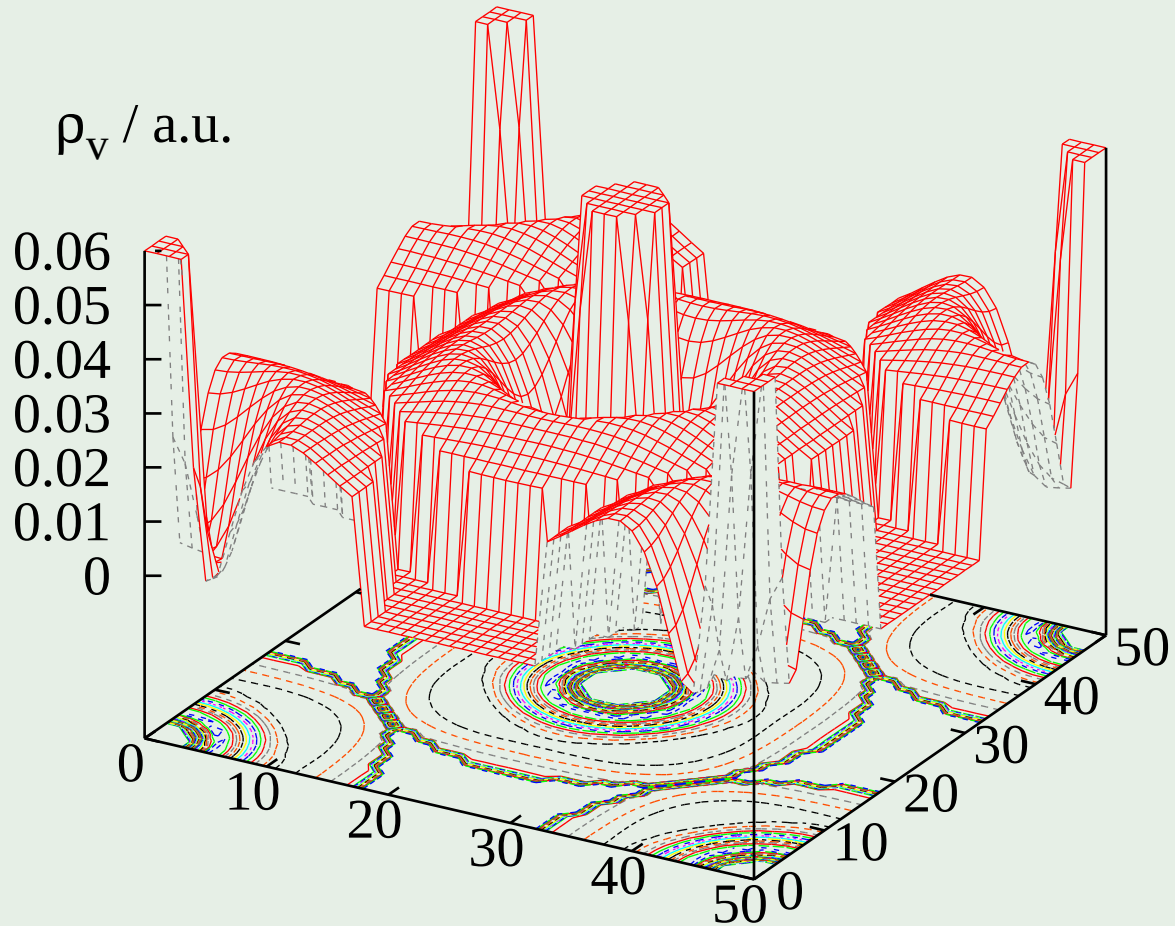
  - inside muffin-tin spheres
    - use spherical-harmonics expansions
  - in the interstitial region
    - no exact spherical-wave representation available!



From Wave Functions to Electron Density

Density inside MT-Spheres (Al)



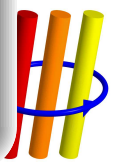
From Wave Functions to Electron Density

Products of Basis Functions in Interstitial Region

$$p^I(\mathbf{r}) = \sum_n d_n F_n(\mathbf{r})$$

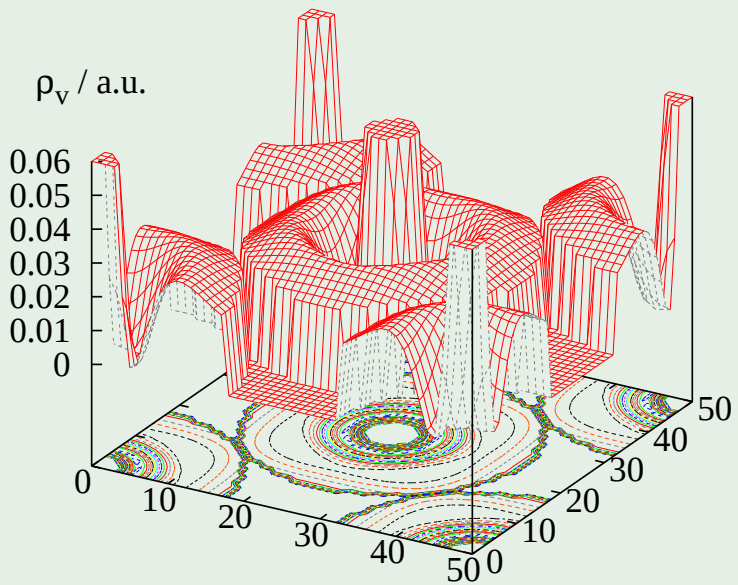
$$\int d^3\mathbf{r}\, F^*_{n'}(\mathbf{r}) p^I(\mathbf{r}) = \sum_n d_n \int d^3\mathbf{r}\, F^*_{n'}(\mathbf{r}) F_n(\mathbf{r})$$

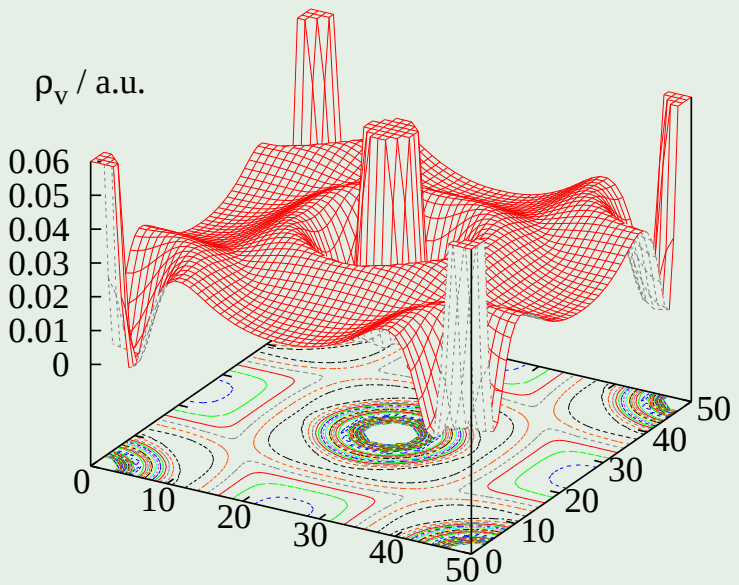
- $F_n(\mathbf{r})$: spherical waves
  - would be efficient
  - integrals not known analytically
  - Springborg/Andersen 1987, Methfessel 1988, VE 2002, VE 2006
  - Methfessel 1988:
    match values and slopes at MT-sphere surfaces



From Wave Functions to Electron Density

Density from Value/Slope Matching at MT-Radii (Al)





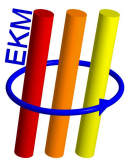
From Electron Density to Full Potential

Inside Muffin-Tin Spheres

- density, Hartree-potential and xc-potential numerically

Interstitial Region

- density from value/slope matching
- Hartree-potential analytically
- xc-potential from value/slope matching



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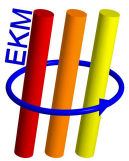


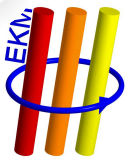
From Full Potential to Basis Functions

Previous Approaches

- project full potential to muffin-tin potential
- construct basis functions from muffin-tin potential
- no minimal basis set! (large basis set!)

Present Approach

- project full potential to ASA potential
- construct basis functions from ASA potential
- minimal basis set!



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Comparison of Approaches

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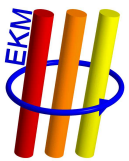
- ASA geometry used for basis functions
  $\rightarrow$ minimal basis set good!
- ASA geometry used for density and potential
  $\rightarrow$ error in total energy bad!



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- MT geometry used for density and potential
  $\longrightarrow$ accurate total energy — good!
- MT geometry used for basis functions
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present approach

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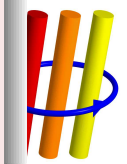
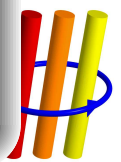


Implementation

2nd Generation ASW (VE, 2000s)

- based on 1st generation code
- full-potential ASW method — at $\mathcal{O}$(ASA) speed!
  - electron densities, spin densities
  - electric field gradients
  - elastic properties, phonon spectra
- optical properties
  - based on linear-response theory
  - direct calculation of $\Re\sigma$ and $\Im\sigma$
  - no Kramers-Kronig relations needed
- transport properties, thermoelectrics
- LDA+U method
  - all „flavours“ for double-counting terms (AMF, FLL, DFT)



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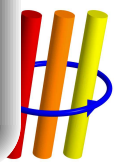

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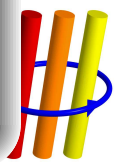

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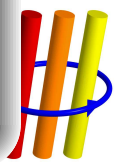
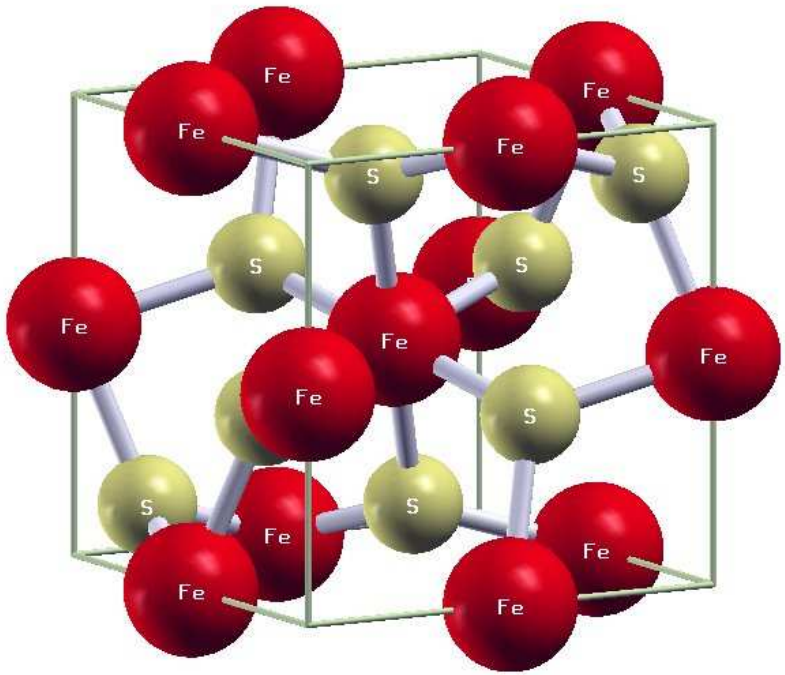


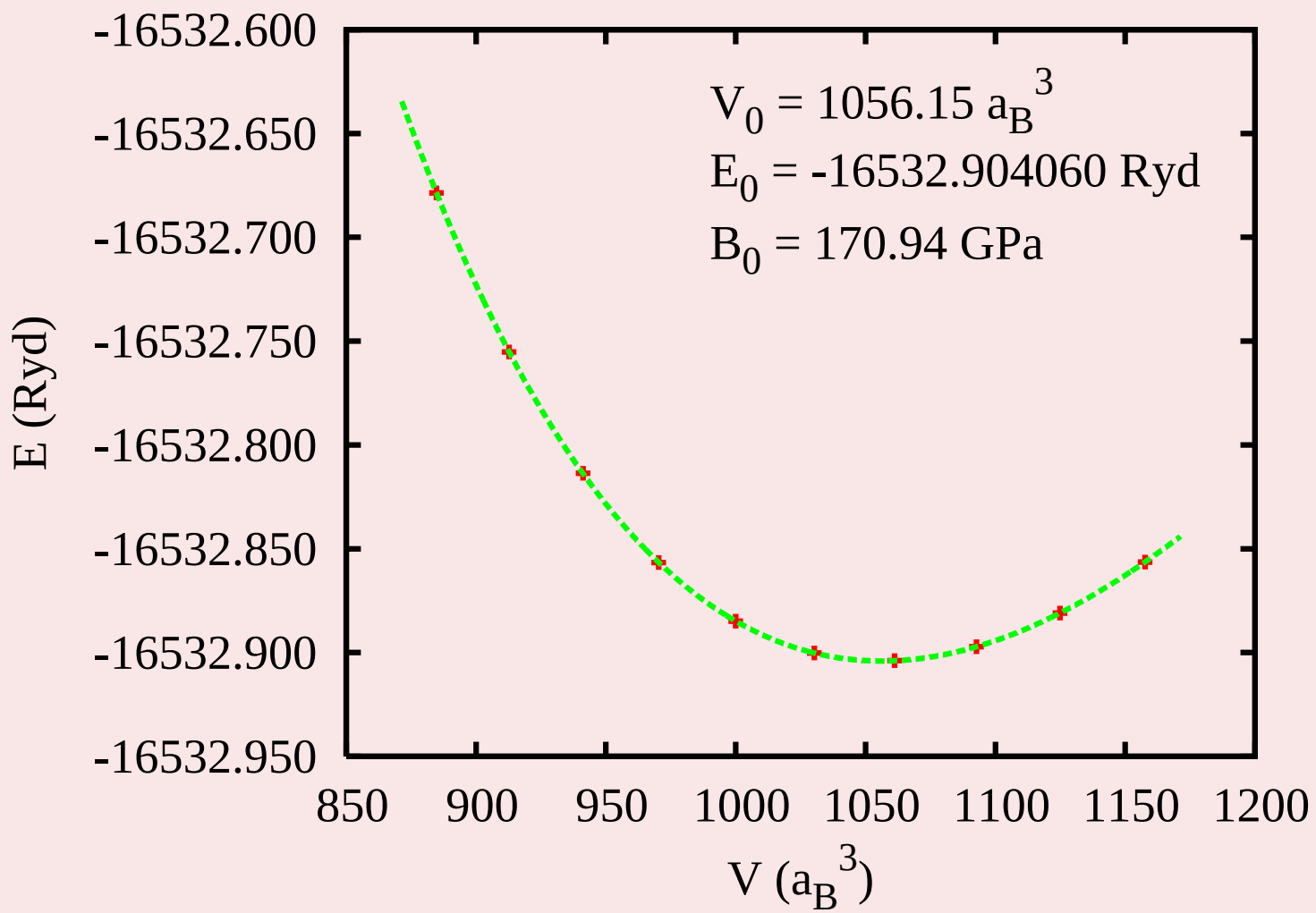
Iron Pyrite: FeS_2



Pyrite

- $Pa\bar{3}$ (T_h^6)
- a = 5.4160 Å
- "NaCl structure" sublattices occupied by
  - iron atoms
  - sulfur pairs
- sulfur pairs $\parallel \langle 111 \rangle$ axes
- x_S = 0.38484
- rotated FeS_6 octahedra

FeS_2: Equilibrium Volume and Bulk Modulus



FeS_2: Equilibrium Volume and Bulk Modulus

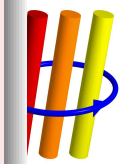
Lattice Constant

10.28	NCPP	Zeng and Holzwarth '94
10.02	FPLO	Opahle *et al.* '99
10.17	CRYSTAL98	Muscat *et al.* '02
9.92	CASTEP	Muscat *et al.* '02
10.18	FPASW	present work
10.23	exp.	Finklea *et al.* '76
10.22	exp.	Will *et al.* '84
10.23	exp.	Stevens *et al.* '91

FeS_2: Equilibrium Volume and Bulk Modulus

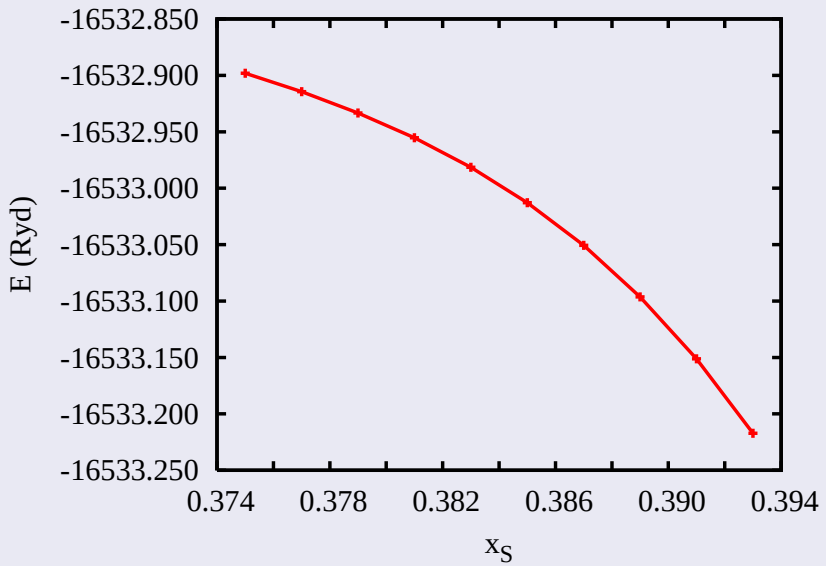
Bulk Modulus

187	LMTO	Nguyen-Manh *et al.* ’98
185	FPLO	Opahle *et al.* ’99
209	CRYSTAL98	Muscat *et al.* ’02
208	CASTEP	Muscat *et al.* ’02
171	FPASW	present work
148	exp.	Drickamer *et al.* ’66
118	exp.	Will *et al.* ’84
215	exp.	Chattopadhyay and von Schnering ’85
157	exp.	Fujii *et al.* ’86
143	exp.	Jephcoat and Olson ’87
162	exp.	Ahrens and Jeanloz ’87
145	exp.	Blachnik *et al.* ’98



FeS_2: Structure Optimization

ASA^+ Code



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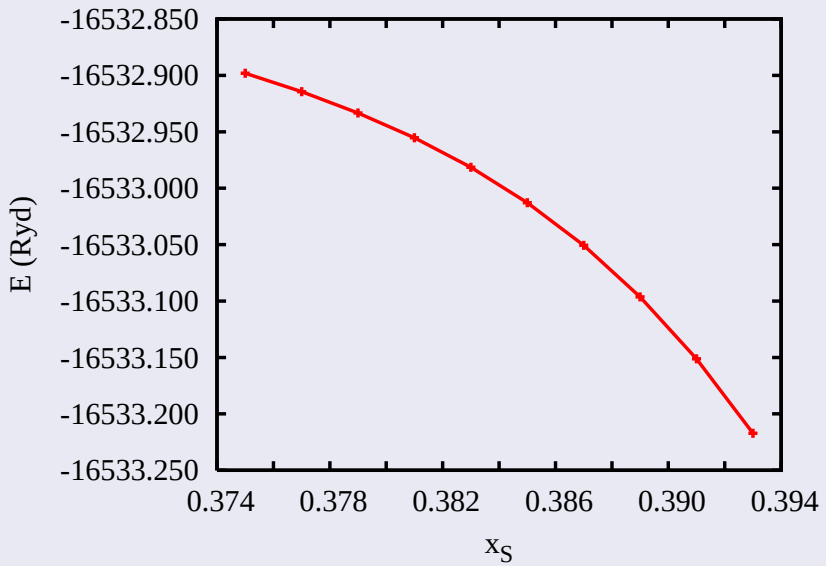
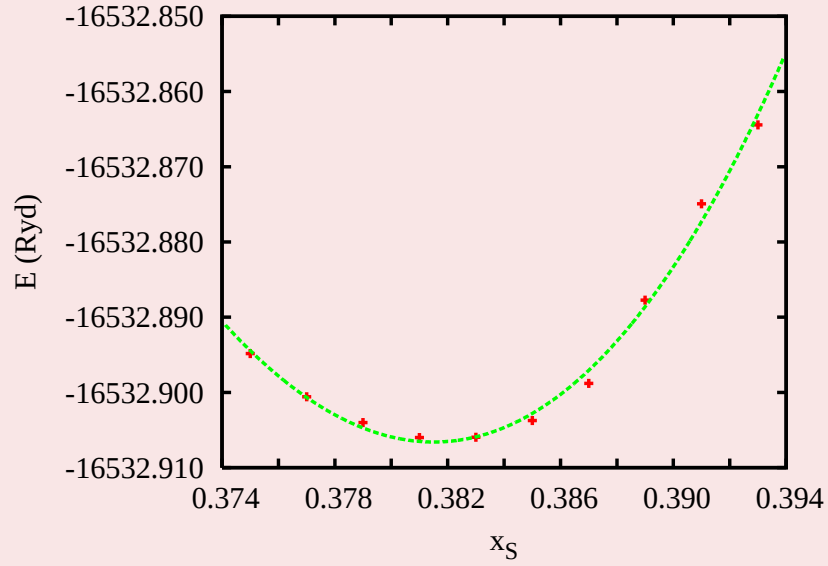


Full-Potential Code



FeS_2: Structure Optimization

Sulfur Position

0.378	NCPP	Zeng and Holzwarth '94
0.377	FPLO	Opahle *et al.* '99
0.378	CRYSTAL98	Muscat *et al.* '02
0.382	CASTEP	Muscat *et al.* '02
0.382	FPASW	present work
0.386	exp.	Finklea *et al.* '76
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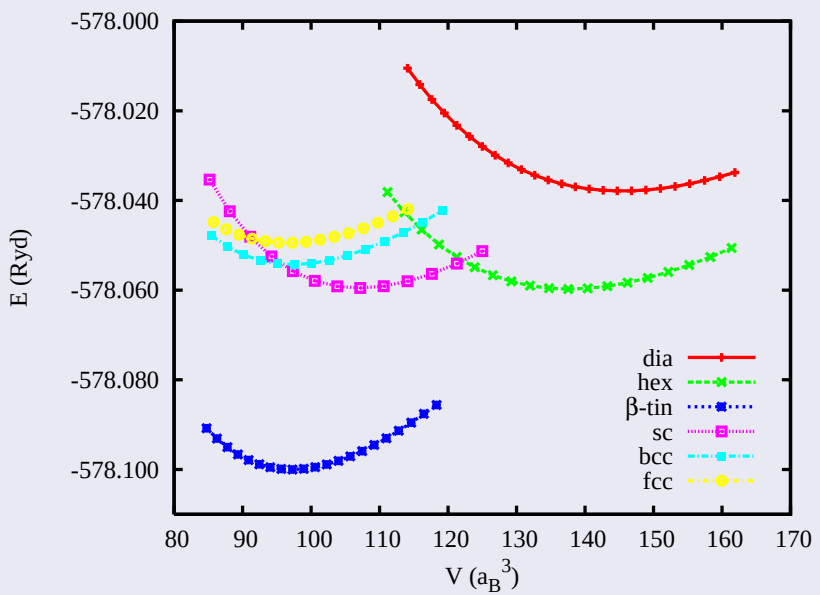
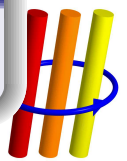
Phase Stability in Silicon

ASA$^+$ Code



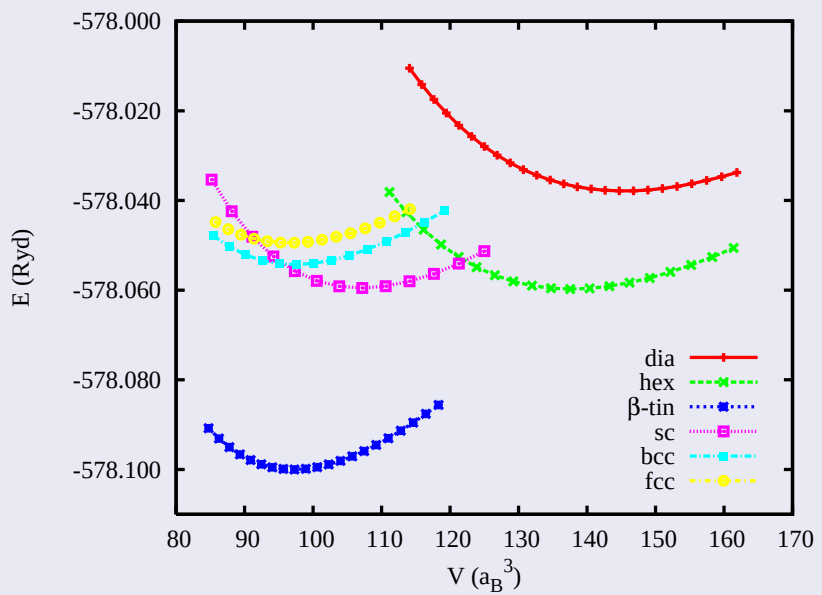
Bad

- β-tin structure most stable # nature (diamond structure)

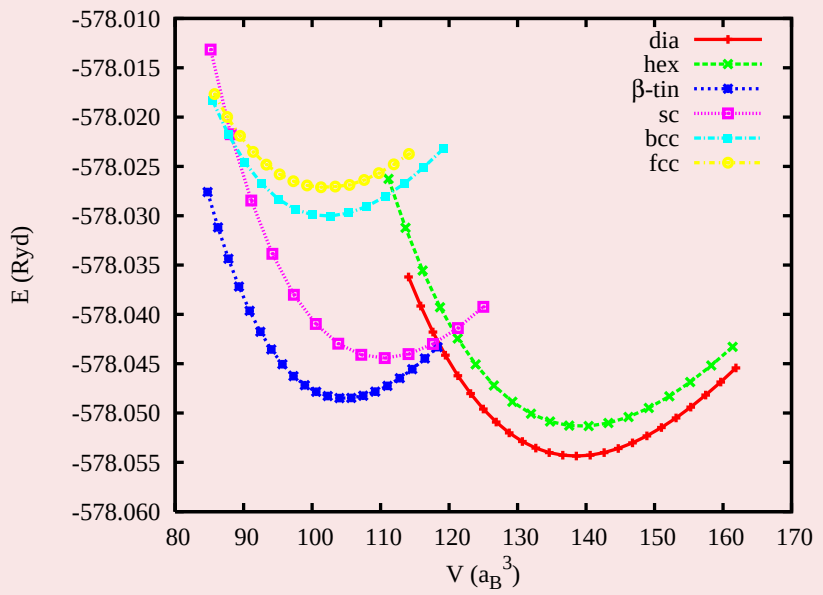


Phase Stability in Silicon

ASA$^+$ Code

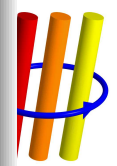


Full-Potential Code



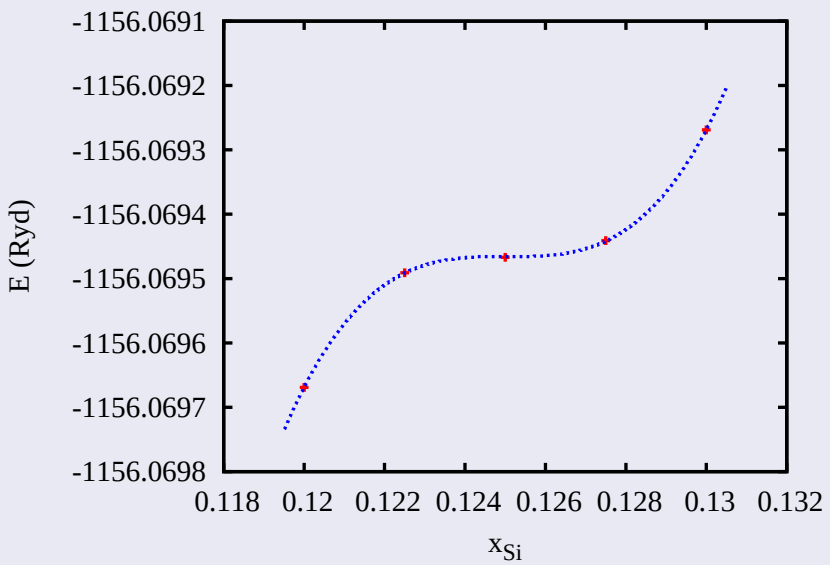
New!

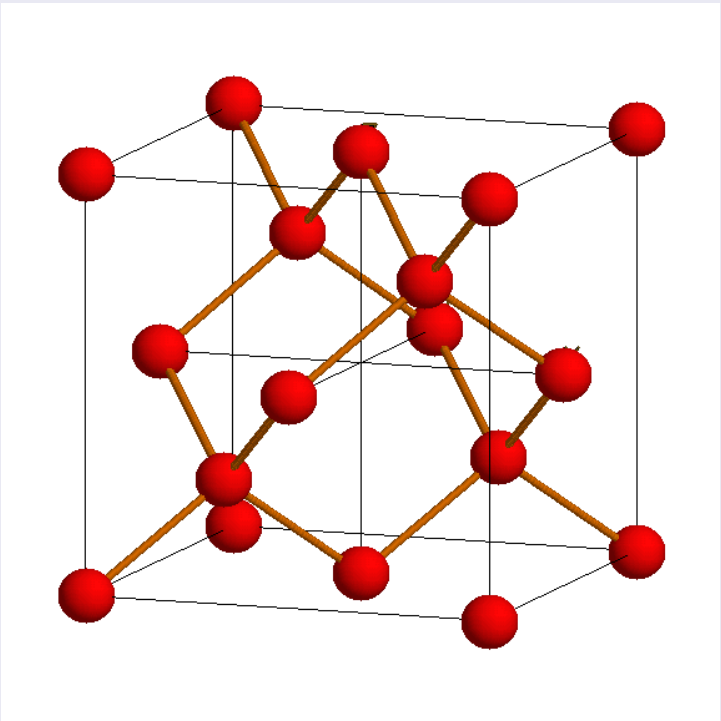
- diamond structure most stable
- pressure induced phase transition to β-tin structure



LTO(Γ)-Phonon in Silicon

ASA$^+$ Code





Bad

- no stable Si position # nature

LTO(Γ)-Phonon in Silicon

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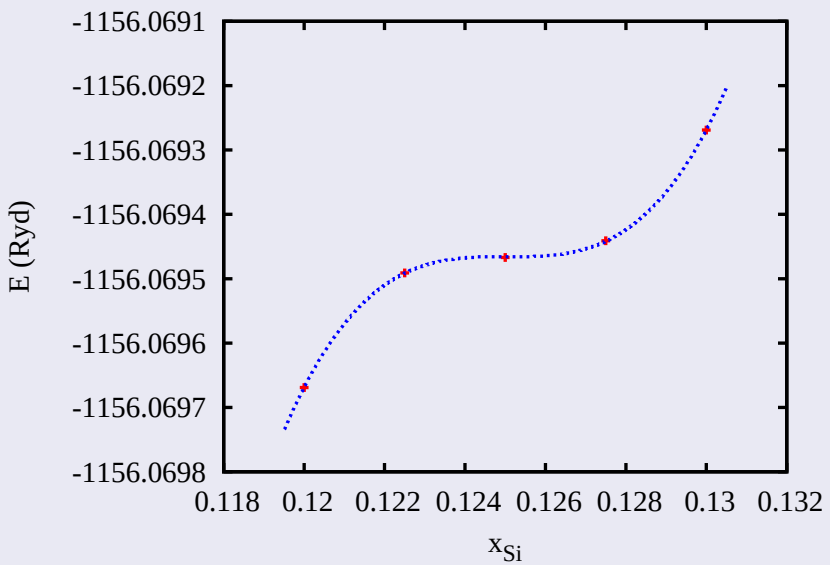

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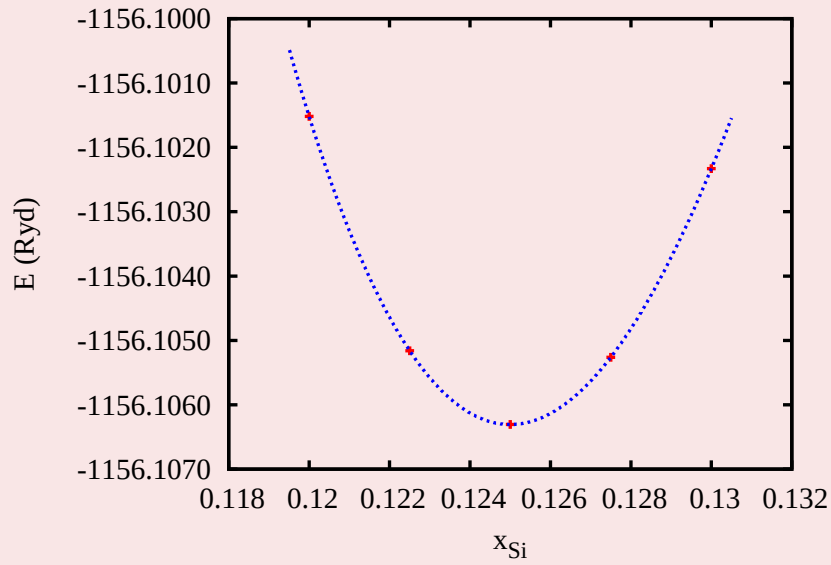
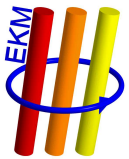


New!

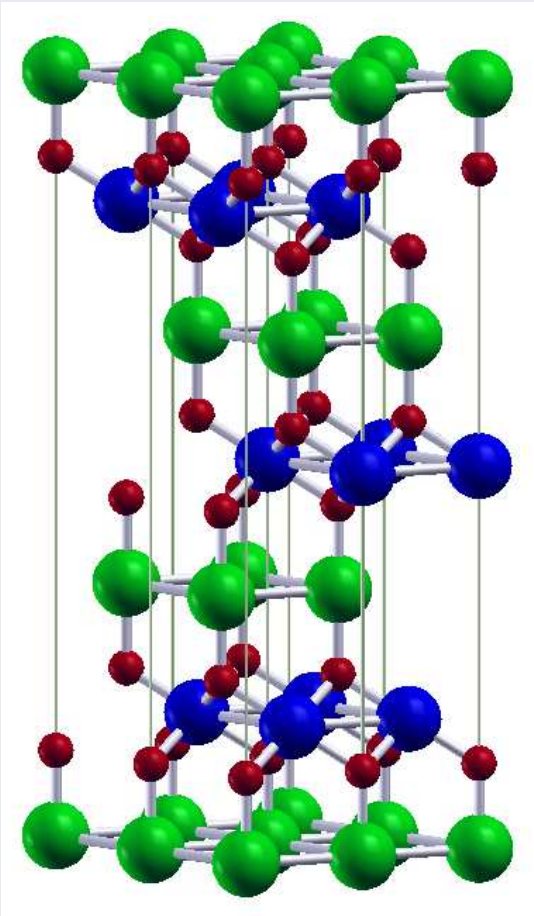
- phonon frequency: $f_{calc} = 15.34\,\mathrm{THz}$ ($f_{exp} = 15.53\,\mathrm{THz}$)

Outline



ABO_2

Delafossite Structure

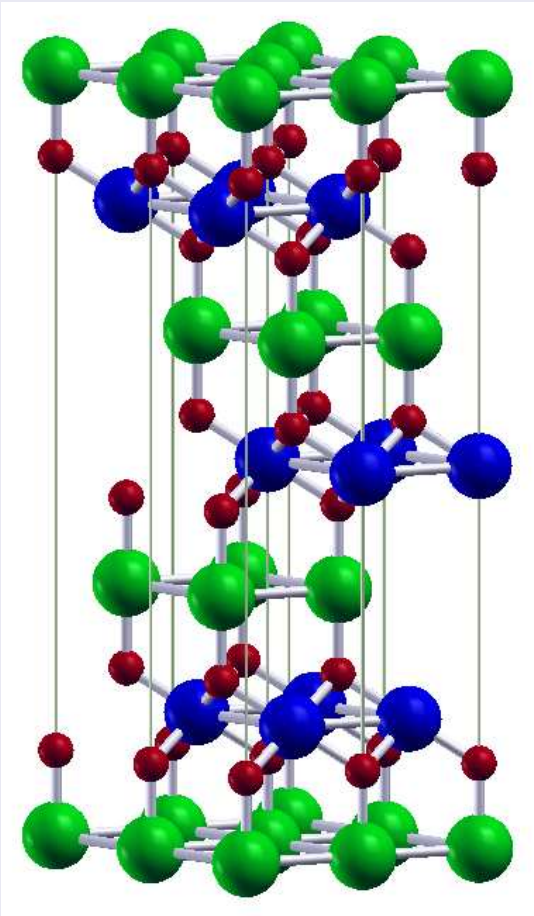


Building Blocks

- rhombohedral lattice
- triangular A-atom layers
- BO_2 sandwich layers
- B-atoms octahedrally coordinated
- linear O–A–O bonds

ABO_2

Delafossite Structure



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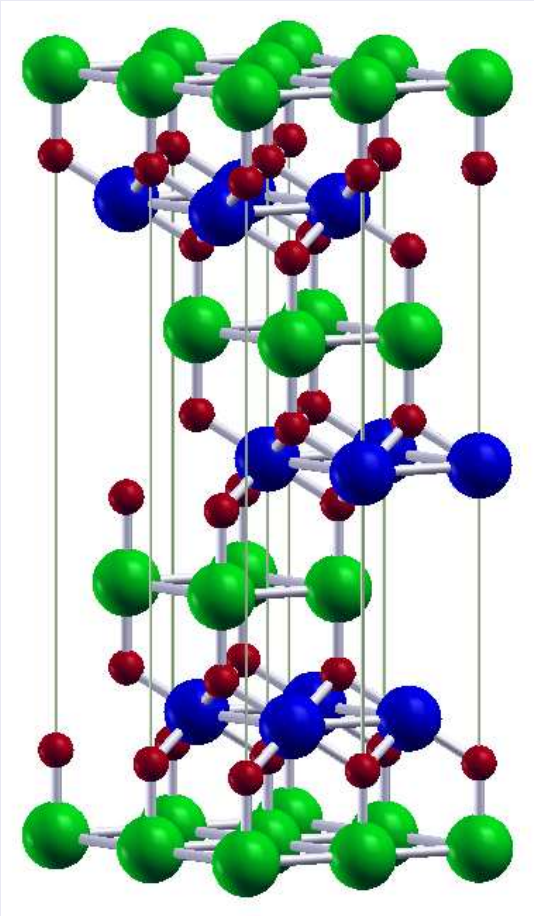
Issues

- dimensionality
- geometric frustration
- play chemistry

ABO_2

Delafossite Structure



Prototype Materials

- $CuFeO_2$, $CuCrO_2$
- $CuCoO_2$, $CuRhO_2$
- $CuAlO_2$, $CuGaO_2$, $CuInO_2$, ...
- $PdCrO_2$, $PdCoO_2$, $PdRhO_2$, $PtCoO_2$

Properties

- semiconductors, AF interactions, (distorted) triangular
- non-mag. semicond., high TEP
- wide-gap semicond., p-type TCO
- very good metals, high anisotropy

ABO_2

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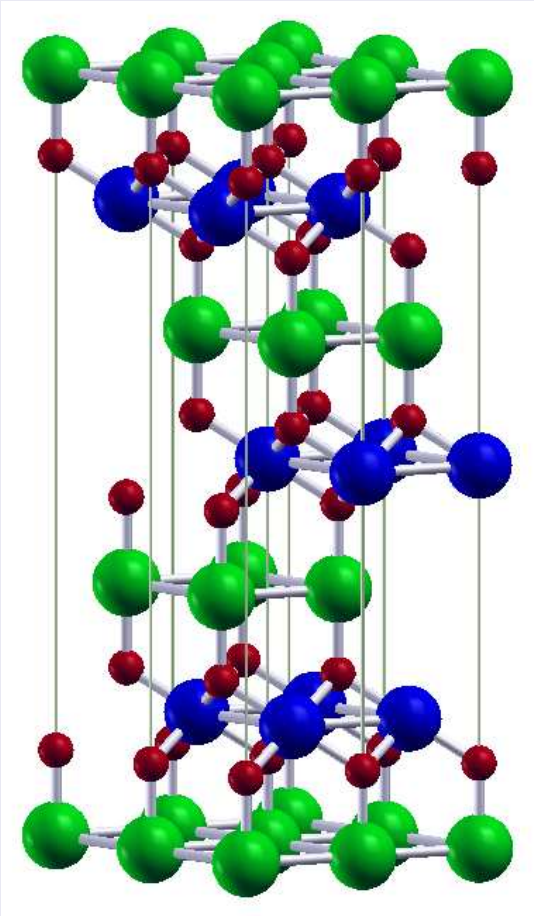

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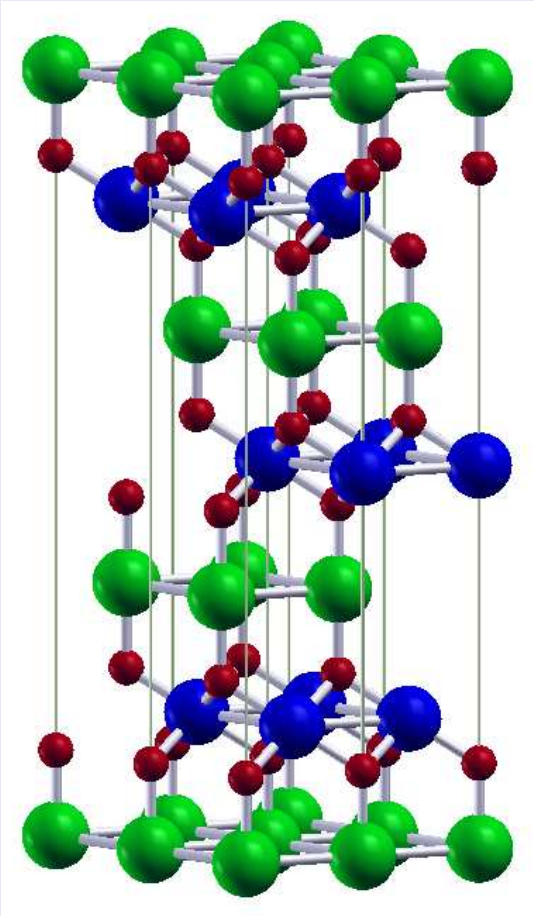

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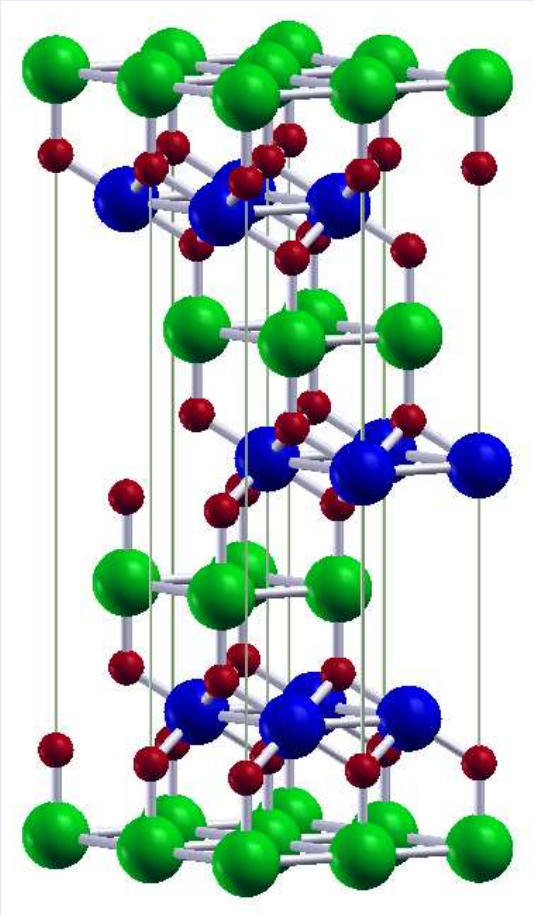

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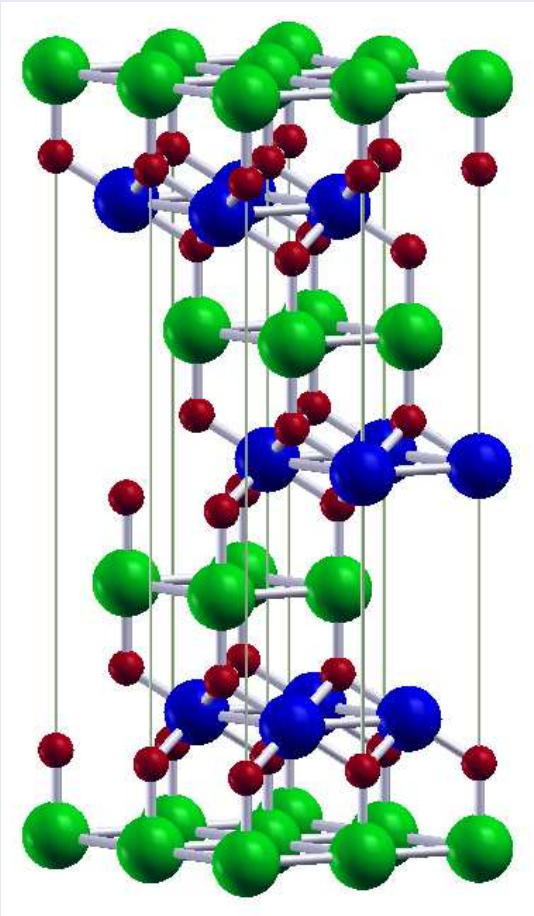
$PdCoO_2$ and $PtCoO_2$

Delafossite Structure

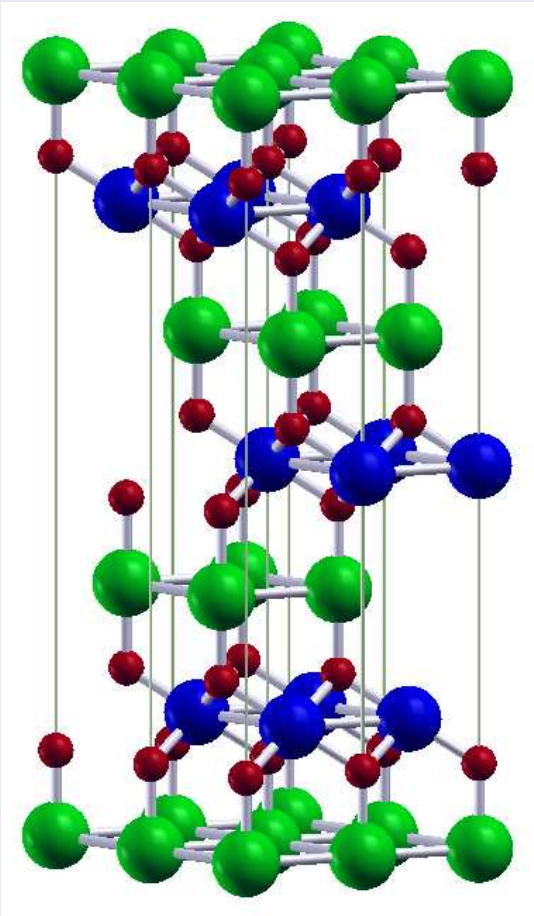


Experimental Results

- very low resistivity
- anisotropy ratio ≈ 200
- PES: only Pd $4d$ states at E_F
- PES/IPES: E_F in shallow DOS minimum
  - high TEP on doping?

$PdCoO_2$ and $PtCoO_2$

Delafossite Structure



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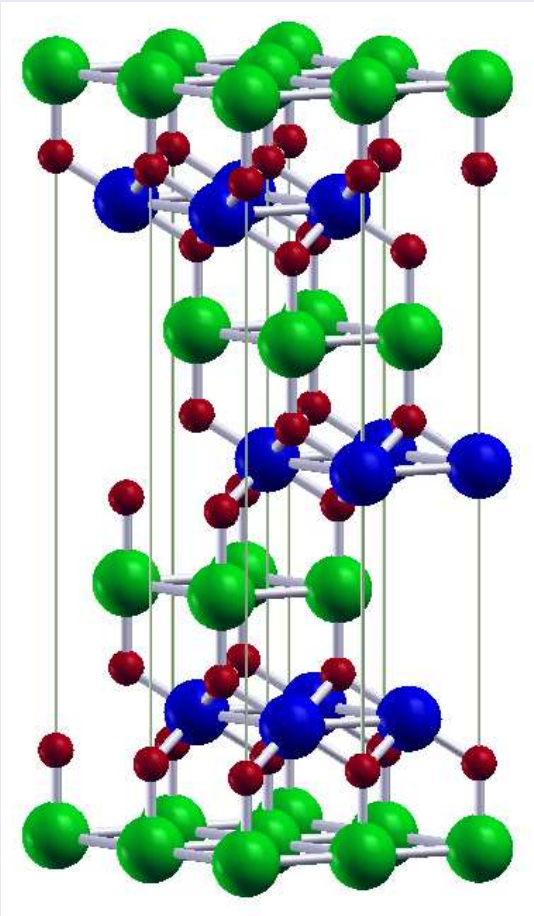
Open Issues

role of Pd $4d$, Co $3d$, and O $2p$ orbitals?

Structure Optimization in $PdCoO_2$

Delafossite Structure



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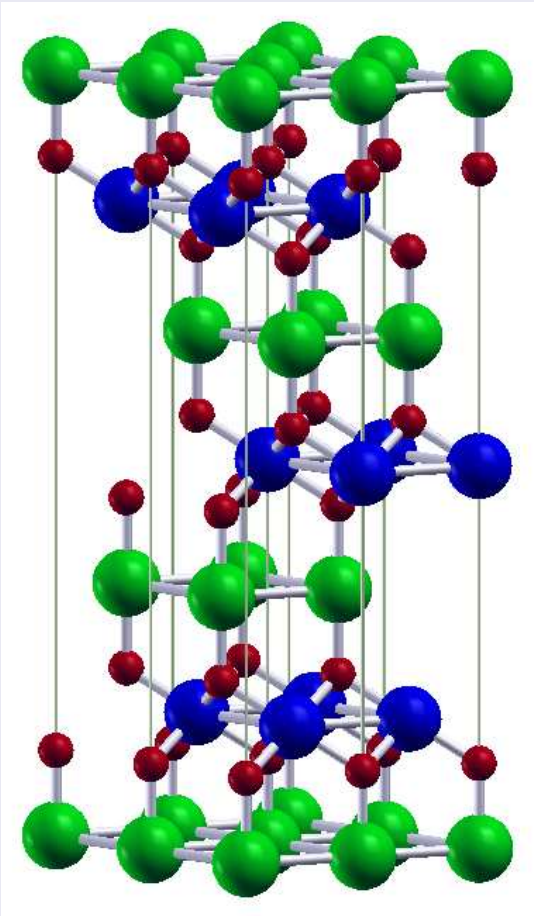
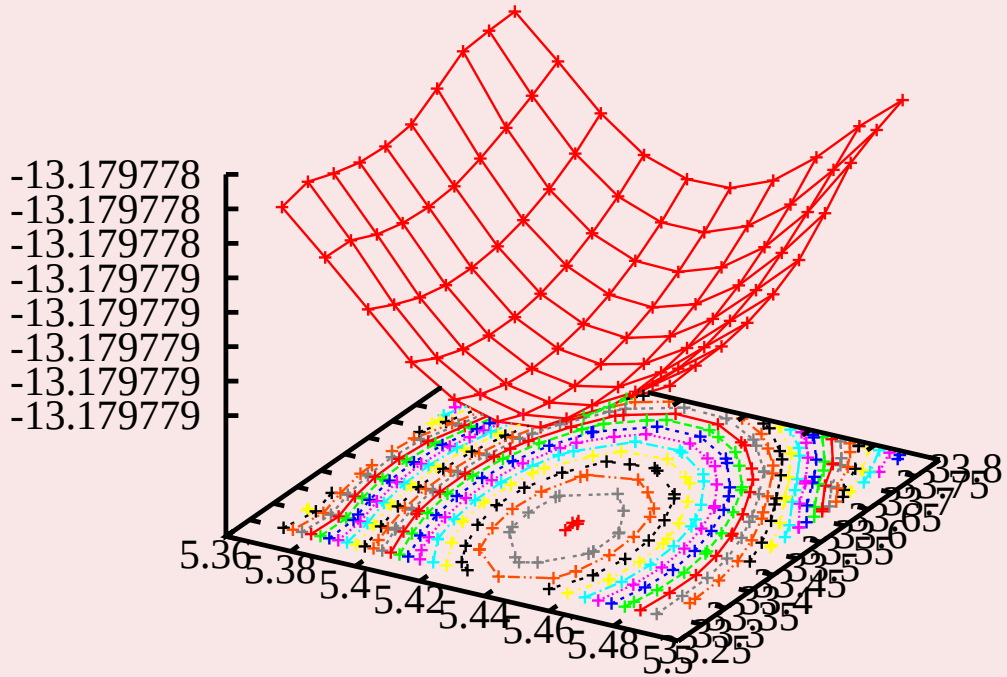


Total energy surface



Structure Optimization in $PdCoO_2$

Structural Data

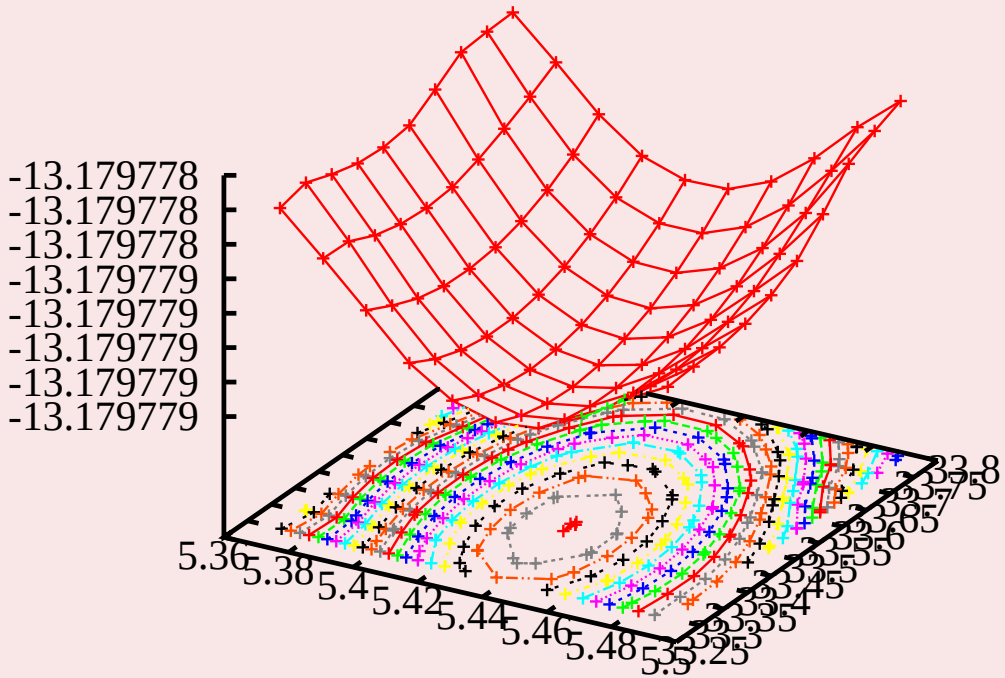
experiment

- $a = 2.83\,\text{Å}$
- $c = 17.743\,\text{Å}$
- $z_O = 0.1112$

theory

- $a = 2.8767\,\text{Å}$
- $c = 17.7019\,\text{Å}$
- $z_O = 0.1100$

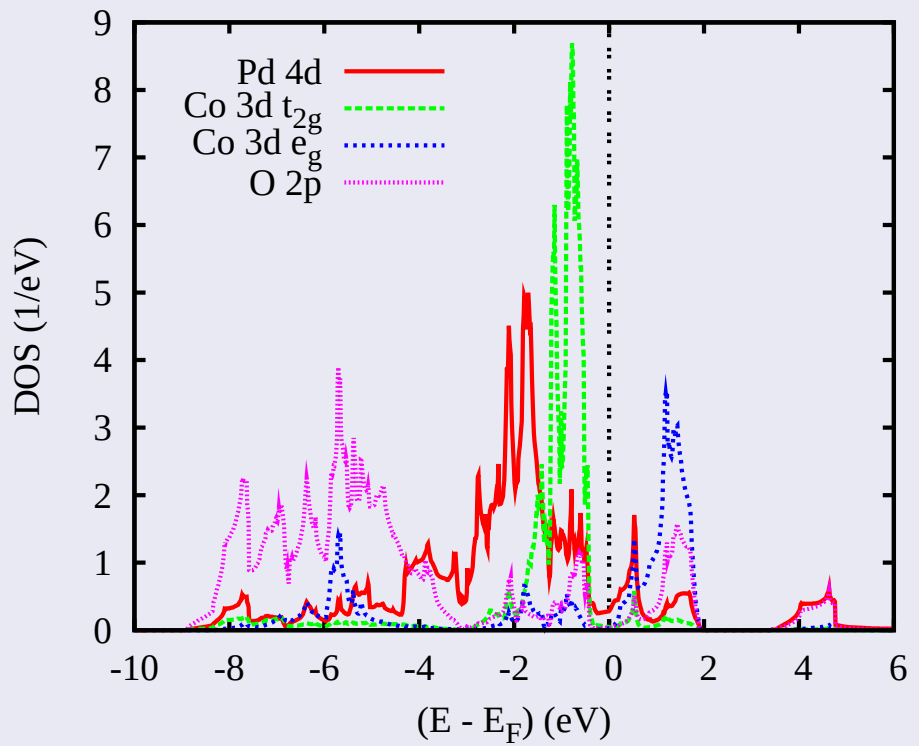
Total energy surface



VE, R. Frésard, A. Maignan, Chem. Mat. **20**, 2370 (2008)

Electronic Properties of $PdCoO_2$

Partial Densities of States



Results

- Co 3*d*-O 2*p* hybridization
- CoO_6 octahedra: Co 3*d* $\Rightarrow$ t_{2g} and e_g
- Co $3d^6$ (Co^{3+}) LS
- Pd $4d^9$ (Pd^{1+})
- Co 3*d*, O 2*p*: very small DOS at E_F

VE, R. Frésard, A. Maignan, Chem. Mat. **20**, 2370 (2008)

Electronic Properties of $PdCoO_2$

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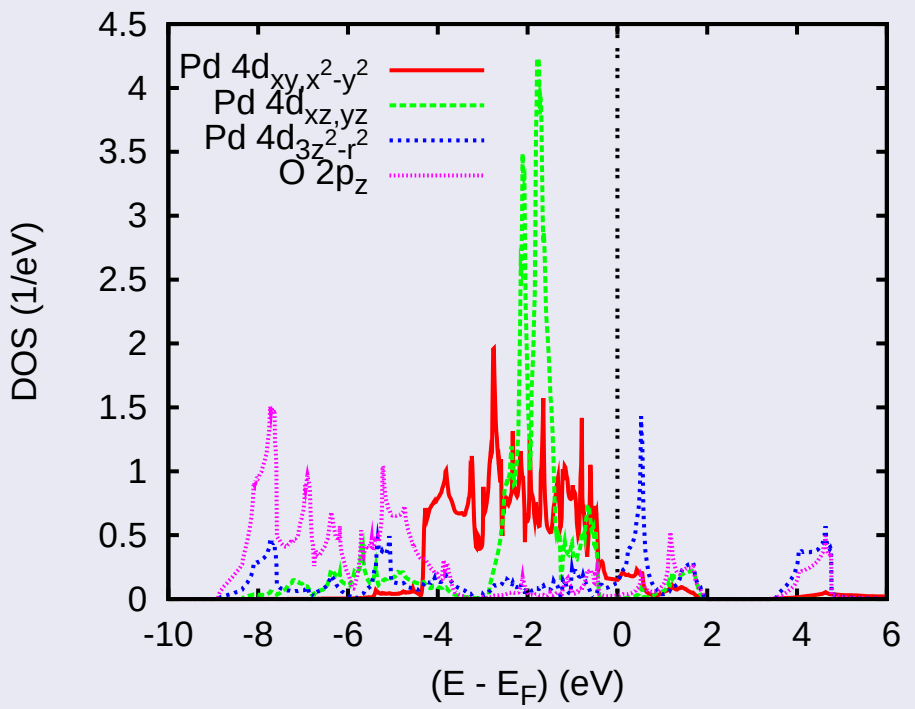


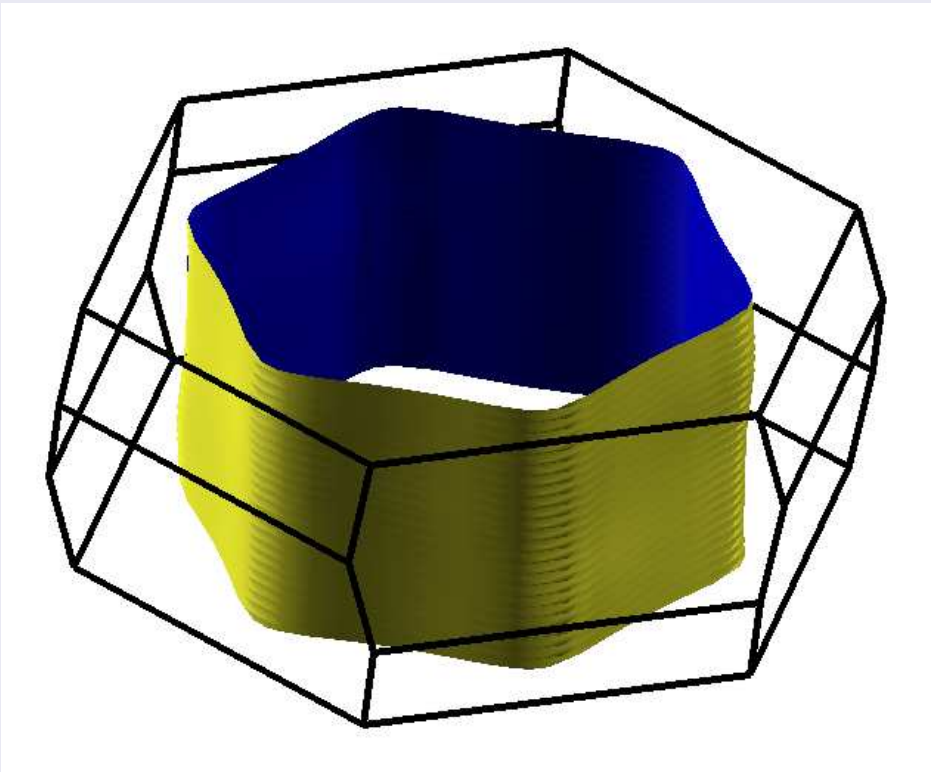
Results

- broad Pd d_{xy,x^2-y^2} bands
  - short in-plane Pd-Pd distance
- non-bonding Pd $d_{xz,yz}$ bands
- strong Pd $4d_{3z^2-r^2}$-O $2p$ hybridization
- states at E_F: Pd d_{xy,x^2-y^2}, $d_{3z^2-r^2}$

VE, R. Frésard, A. Maignan, Chem. Mat. **20**, 2370 (2008)

Electronic Properties of $PdCoO_2$

Fermi Surface



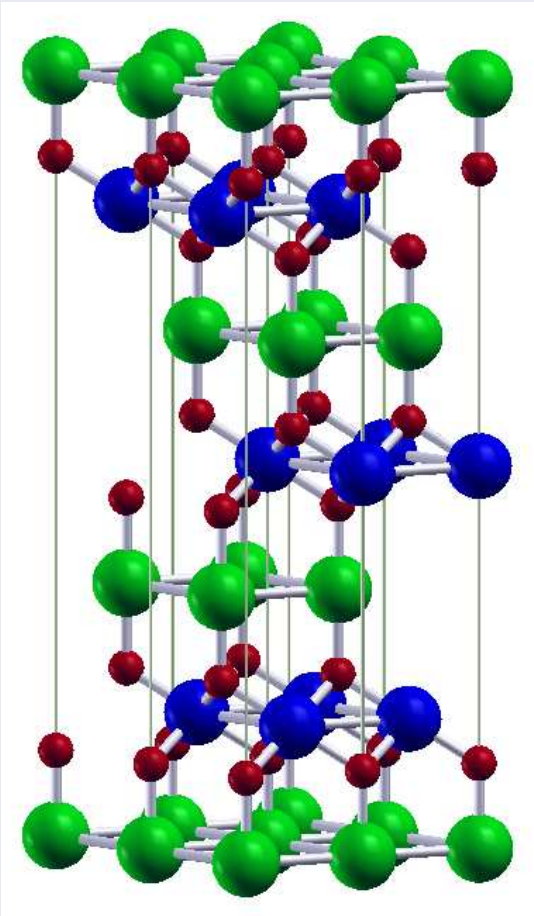
Results

- quasi-2D
- single band crossing E_F
- but: bands below E_F disperse along Γ-A

VE, R. Frésard, A. Maignan, Chem. Mat. **20**, 2370 (2008)

$CuFeO_2$

Delafossite Structure



Basics

- semiconductor
- AF interactions
- triangular lattice

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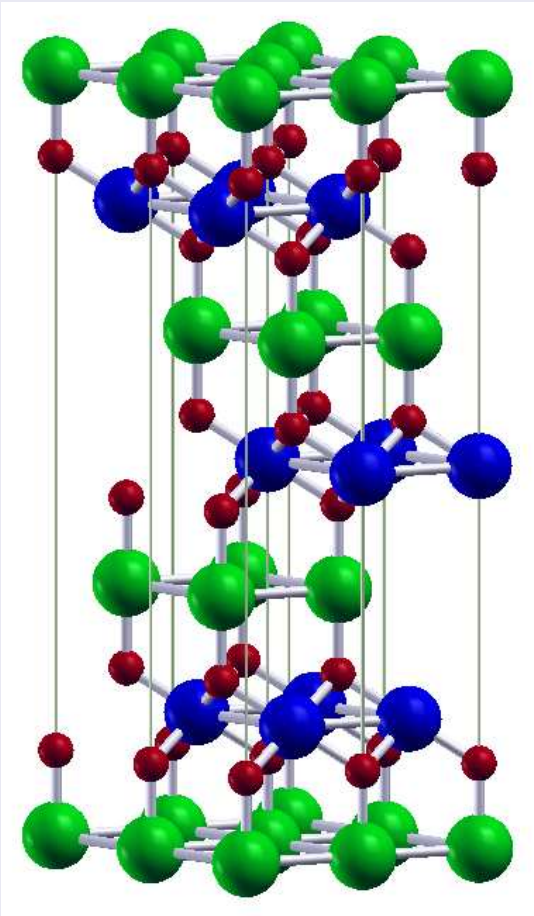

Basics

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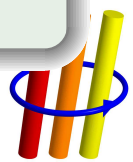
Open Issues

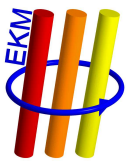
- frustration vs. long-range order
- role of Cu 3*d* orbitals?
- role of Fe 3*d* and O 2*p* orbitals?



$CuFeO_2$

Previous Neutron Data

- $T_{N_1} = 16\,\mathrm{K}$, $T_{N_2} = 11\,\mathrm{K}$
- $\Theta_{CW} = -90\,\mathrm{K}$
- magnetic supercells
- no structural distortion
- $m_{Fe^{3+}} = 4.4\,\mu_B$



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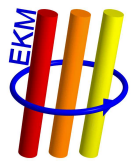
Band Calculations

- rhombohedral structure
- $m_{Fe} = 0.9\,\mu_B$, $m_{Fe} = 3.8\,\mu_B$
- $E_g = 0$ in LDA, GGA
- $\sharp$ PES, XES



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New Neutron Data

- magnetic supercells
- monoclinic structure below 4 K

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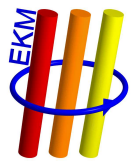

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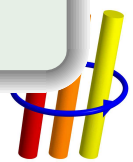
- ♯ PES, XES

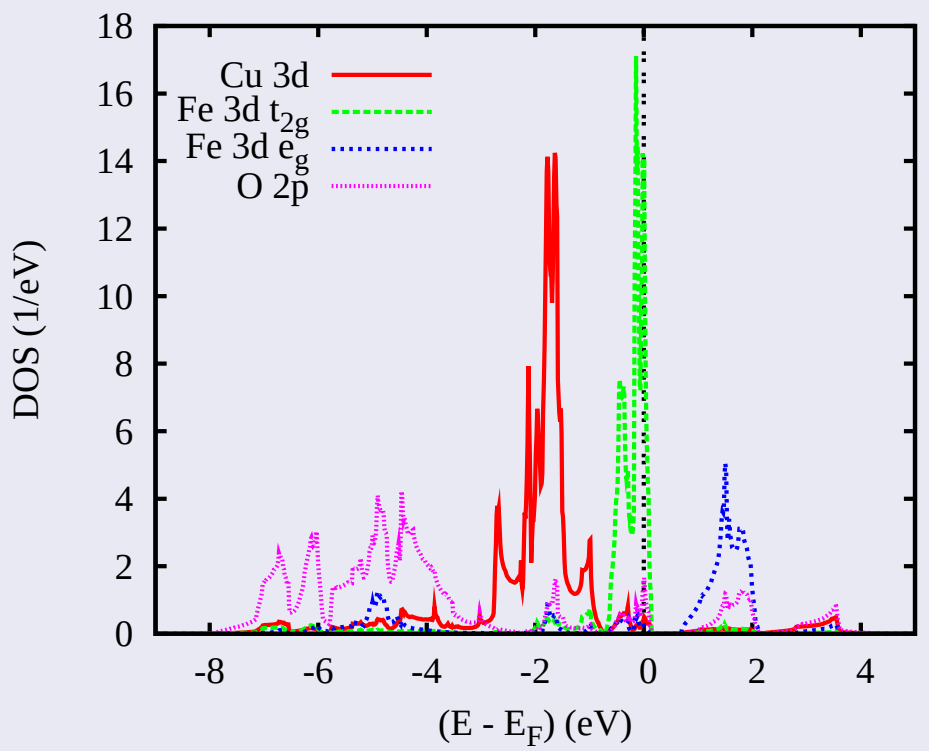
Open Issues

- spin-state of Fe?
- influence of monoc. structure?



Electronic Properties of $CuFeO_2$

Partial Densities of States



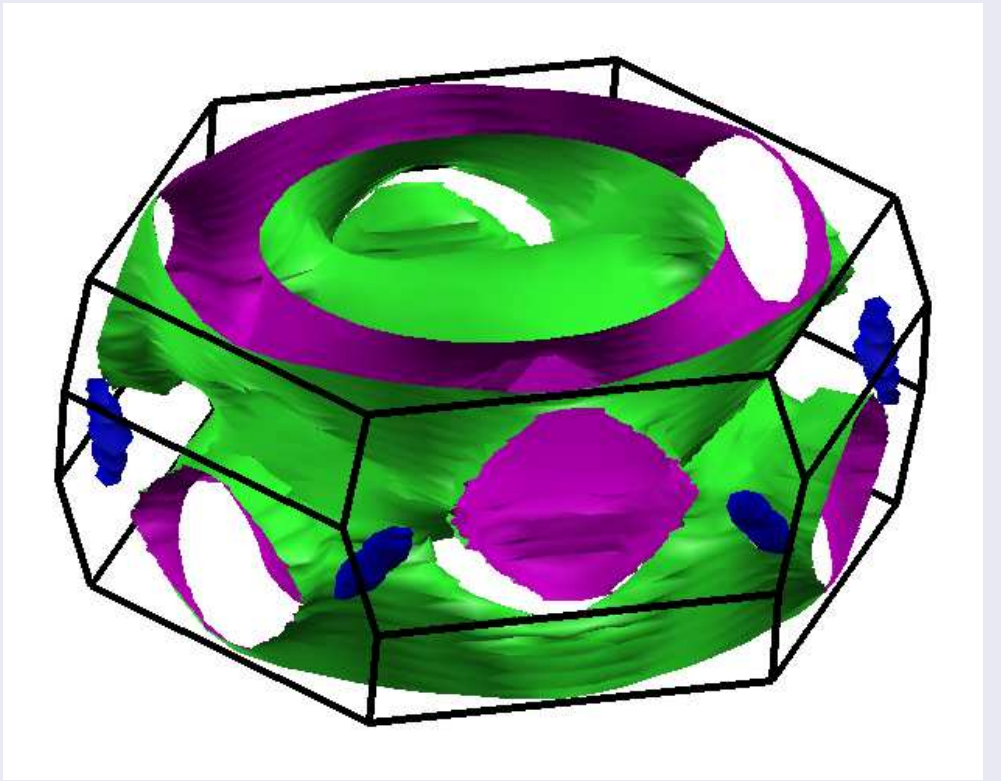
Results

- Fe $3d$-O $2p$ hybridization
- FeO_6 octahedra: Fe $3d \Rightarrow t_{2g}$ and e_g
- Cu $4d^{10}$ (Cu^{1+})
- Fe $3d$ t_{2g}
  - sharp peak at E_F

VE, R. Frésard, A. Maignan, Phys. Rev. B **78**, 052402 (2008)

Electronic Properties of $CuFeO_2$

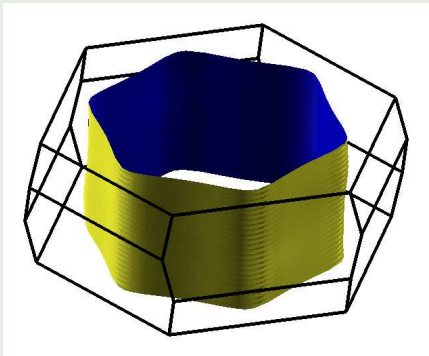
Fermi Surface



Results

- strongly 3D

FS $PdCoO_2$



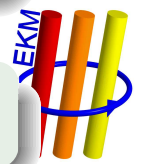
VE, R. Frésard, A. Maignan, Phys. Rev. B **78**, 052402 (2008)

Magnetic Properties of $CuFeO_2$

Total Energies (mRyd/f.u.), Magn. Moms. (μ_B), Band Gaps (eV)

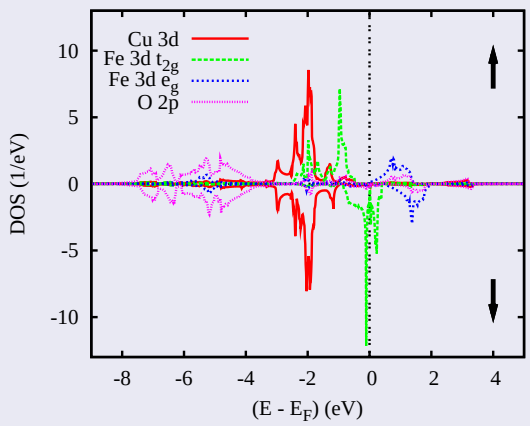
structure	magn. order	ΔE	m_{Fe}	m_{O}	E_g
rhomb.	spin-deg.	0.0			-
rhomb.	ferro (LS)	-16.7	1.03	-0.02	-
rhomb.	ferro (IS)	-12.0	2.02	-0.02	-
rhomb.	ferro (HS)	-19.2	3.73	0.21	-

VE, R. Frésard, A. Maignan, Phys. Rev. B **78**, 052402 (2008)

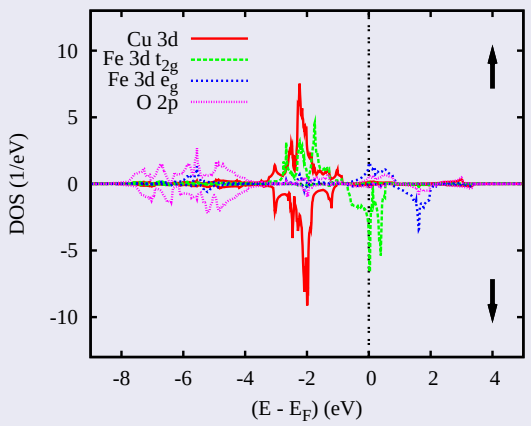


Magnetic Properties of $CuFeO_2$

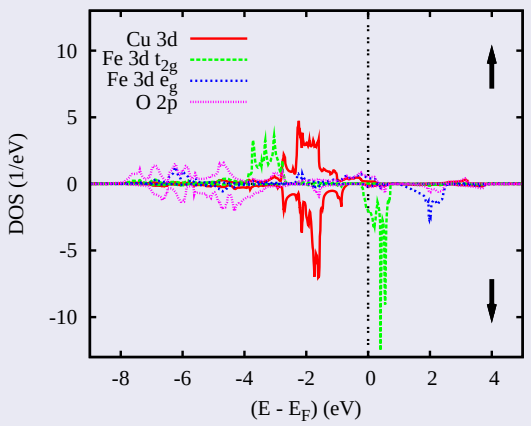
LS Ferromagnet



IS Ferromagnet



HS Ferromagnet



Results

- LS, IS, HS in rhombohedral structure
- HS: O 2*p* polarization via Fe 3*d* e_g

VE, R. Frésard, A. Maignan, Phys. Rev. B **78**, 052402 (2008)

Magnetic Properties of $CuFeO_2$

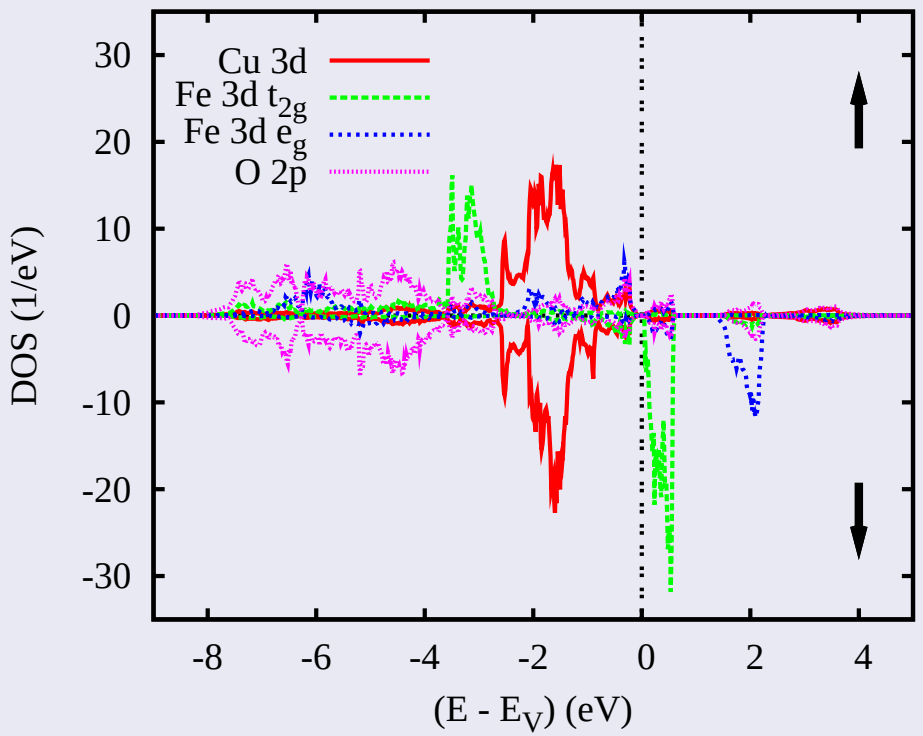
Total Energies (mRyd/f.u.), Magn. Moms. (μ_B), Band Gaps (eV)

structure	magn. order	ΔE	m_{Fe}	m_{O}	E_g
rhomb.	spin-deg.	0.0			-
rhomb.	ferro (LS)	−16.7	1.03	−0.02	-
rhomb.	ferro (IS)	−12.0	2.02	−0.02	-
rhomb.	ferro (HS)	−19.2	3.73	0.21	-
monoc.	spin-deg.	−6.0			-
monoc.	ferro (LS)	−21.5	1.04	−0.02	-
monoc.	ferro (IS)	−19.0	2.08	−0.02	-
monoc.	ferro (HS)	−32.0	3.62	0.19	-

VE, R. Frésard, A. Maignan, Phys. Rev. B **78**, 052402 (2008)

Magnetic Properties of $CuFeO_2$

Antiferromagnet



Results

- monoc. structure
- Fe^{3+} HS
- O $2p$ polarization via Fe $3d$ e_g
- $E_g > 0$ in GGA

VE, R. Frésard, A. Maignan, Phys. Rev. B **78**, 052402 (2008)

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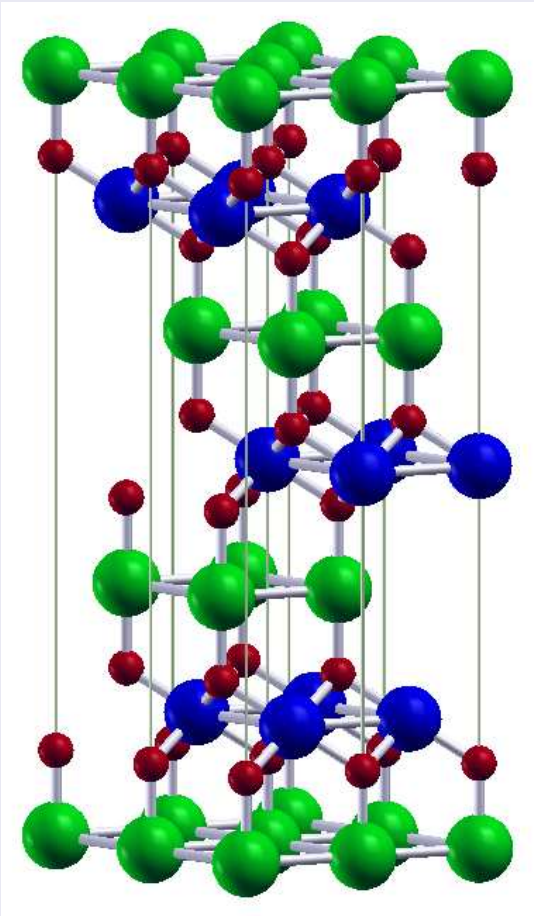
monoc.	ferro (HS)	-32.0	3.62	0.19	-
monoc.	antiferro	-46.0	± 3.72	± 0.08	0.05

VE, R. Frésard, A. Maignan, Phys. Rev. B **78**, 052402 (2008)

$CuRhO_2$

Delafossite Structure

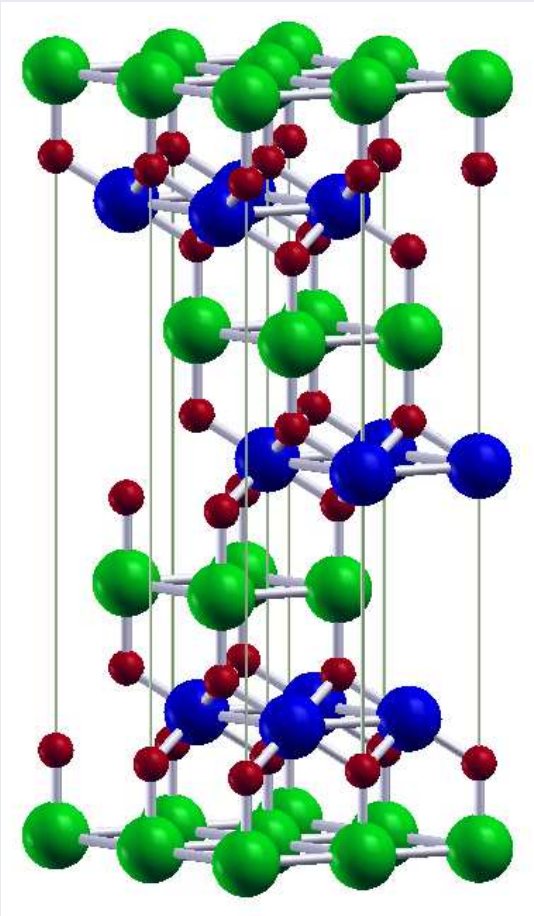


Experimental Findings

- semiconductor
- high TEP on hole doping
  - $Rh^{3+} \longrightarrow Mg^{2+}$ up to 12%
- high T-independent PF

$CuRhO_2$

Delafossite Structure



Experimental Findings

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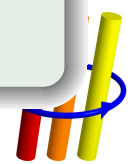
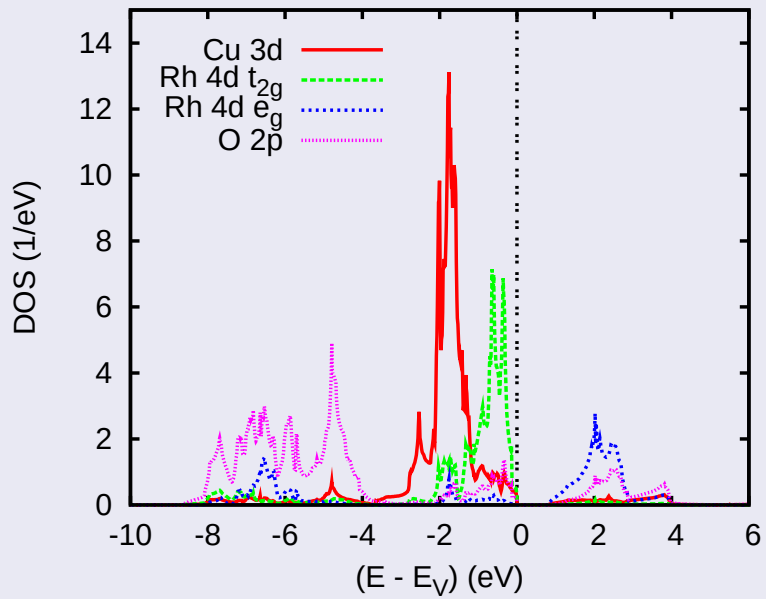
Open Issues

- origin of high TEP
- role of Cu 3*d* orbitals?
- role of Rh 4*d* and O 2*p* orbitals?



Electronic Properties of $CuRhO_2$

Partial Densities of States



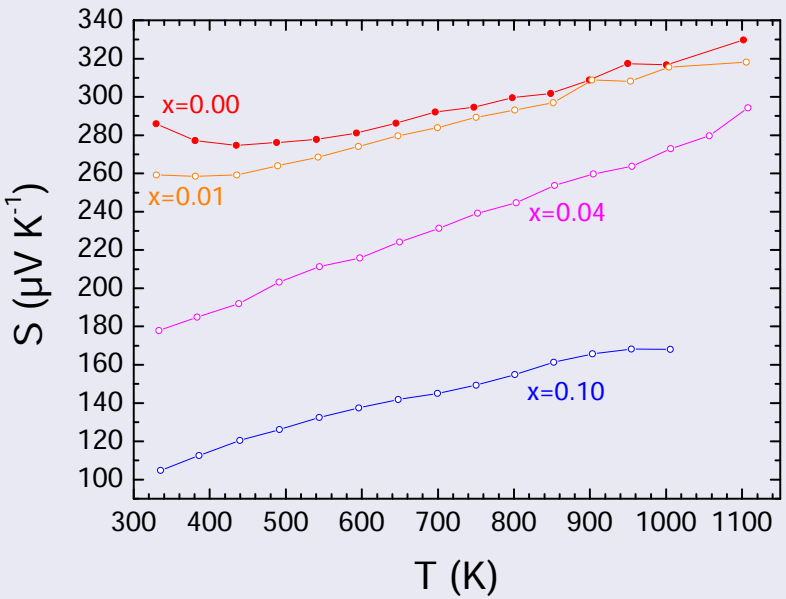
Results

- Rh $4d$-O $2p$ hybridization
- RhO_6 octahedra: Rh $4d \Rightarrow t_{2g}$ and e_g
- $E_g \approx 0.75\,eV$
- Cu $4d^{10}$ (Cu^{1+})
- electronic structure: strongly 3D

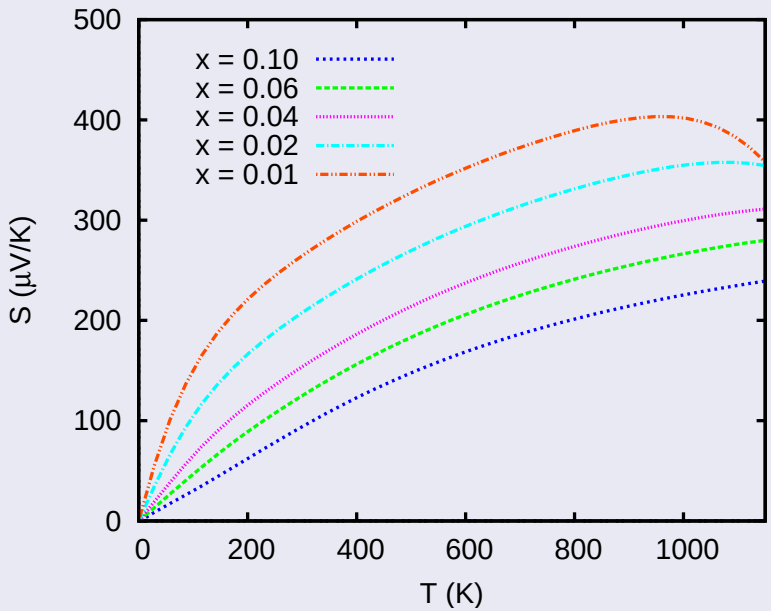
A. Maignan, VE, *et al.*, Phys. Rev. B **80**, 115103 (2009)

Thermoelectric Power of $CuRhO_2$

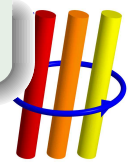
Experiment



Theory: S_{xx}



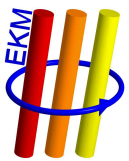
A. Maignan, VE, *et al.*, Phys. Rev. B **80**, 115103 (2009)



Summary

Computational Modeling . . . Full-Potential ASW Method

- Highly Accurate Total Energies
- $\mathcal{O}$(ASA) Speed!
- Optical and Transport Properties Available

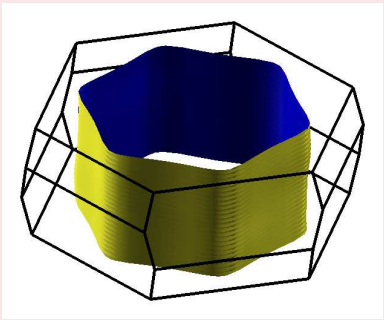


Summary

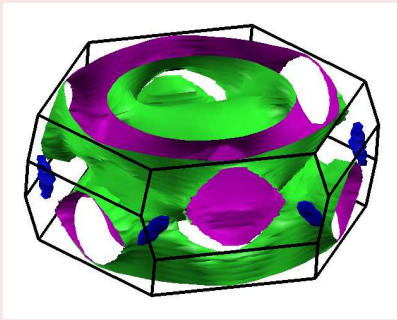
Computational Modeling . . . Full-Potential ASW Method

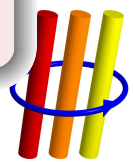
- Highly Accurate Total Energies
- $\mathcal{O}$(ASA) Speed!
- Optical and Transport Properties Available

. . . and Materials Discovery Delafossites



- high conductivity
- high TEP
- magnetism
- p-type TCOs





Acknowledgments

Caen

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Darmstadt/Jülich

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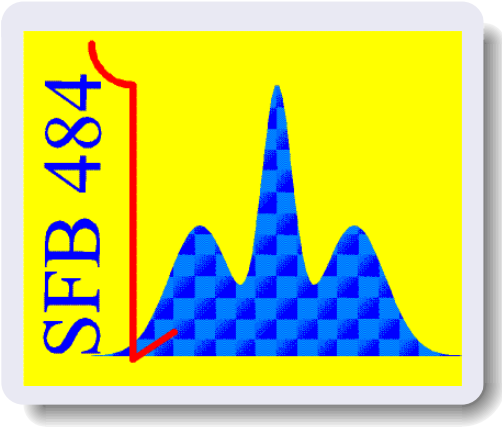
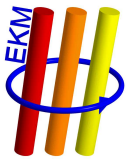
J. Sticht †



Augsburg

K.-H. Höck, T. Kopp, J. Mannhart



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Rio de Janeiro

Thank You for Your Attention!