TECHNISCHE UNIVERSITÄT WIEN

Electronic structure, atomic forces and structural relaxations by WIEN2k

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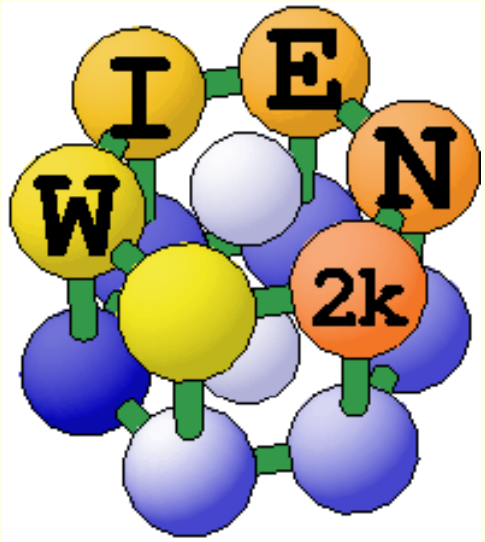
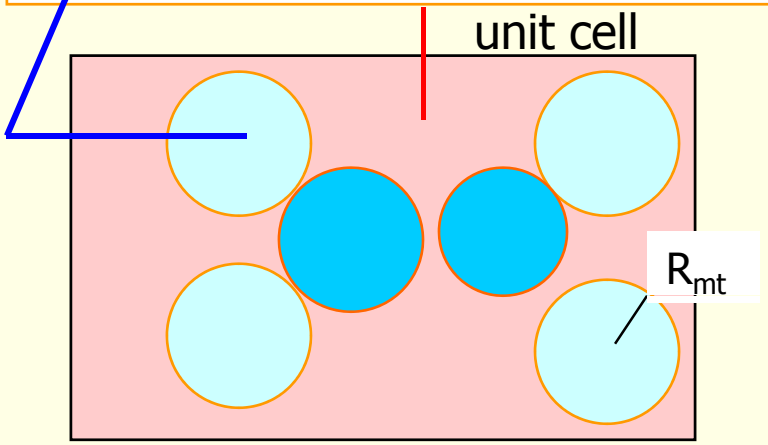


Outline:

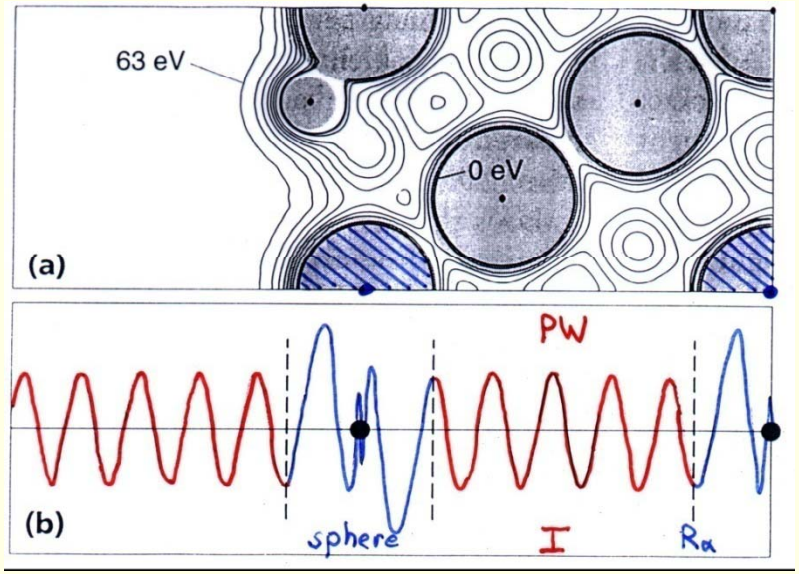
- APW-based methods (history and state-of-the-art)
- WIEN2k
  - *program structure + usage*
  - *forces, structure relaxation*
- Applications
  - *Phonons in matlockite PbFI*
  - *Phasetransitions in Aurivillius phases*
  - *Structure of Pyrochlore $Y_2Nb_2O_7$*

APW Augmented Plane Wave method

The unit cell is partitioned into:
- atomic spheres
- Interstitial region



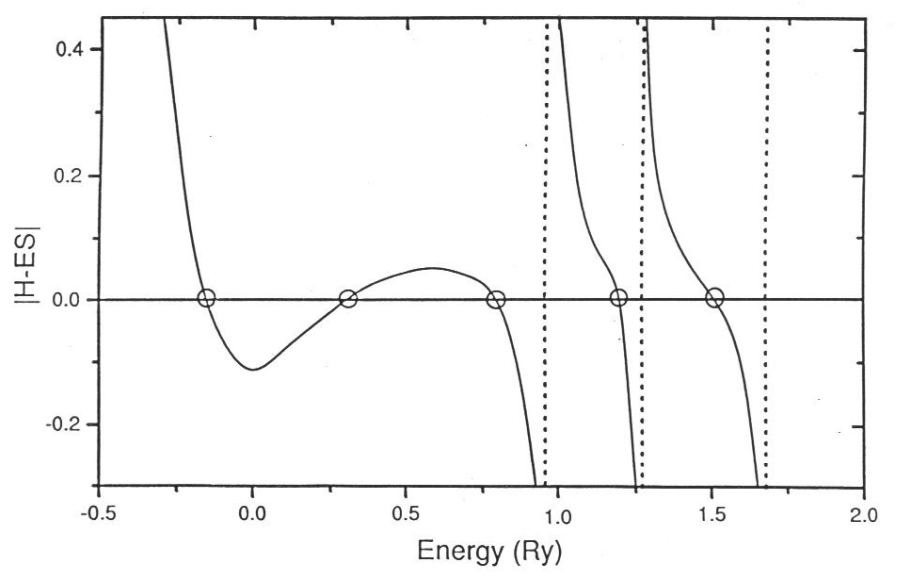
Bloch wave function:
- atomic partial waves
- Plane Waves (PWs)



PW: $e^{i(\vec{k}+\vec{K}).\vec{r}}$ — join — Atomic partial waves $\sum_{\ell m} a_{\ell m}^{K} u_\ell(r',\varepsilon) Y_{\ell m}(\hat{r}')$

matching coefficient, radial function, spherical harmonics

Slater's APW (1937)



Atomic partial waves

$$\sum_{\ell m} a_{\ell m}^{K} u_{\ell}(r', \varepsilon) Y_{\ell m}(\hat{r}')$$

Energy dependent

Radial basis functions lead to

H Hamiltonian
S Overlap matrix

Non-linear eigenvalue problem

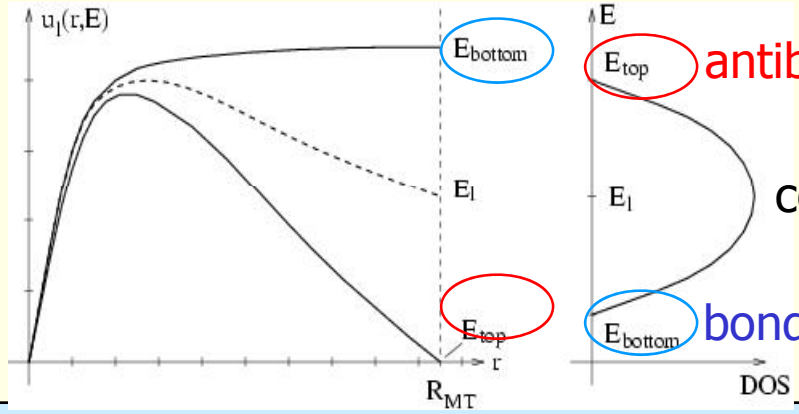
Numerically search for the energy, for which det|H-ES| vanishes.

Computationally very demanding
"Exact" solution for a given (spherical) potential!

Linearization of energy dependence

LAPW suggested by

O.K.Andersen,
Phys.Rev. B 12, 3060 (1975)



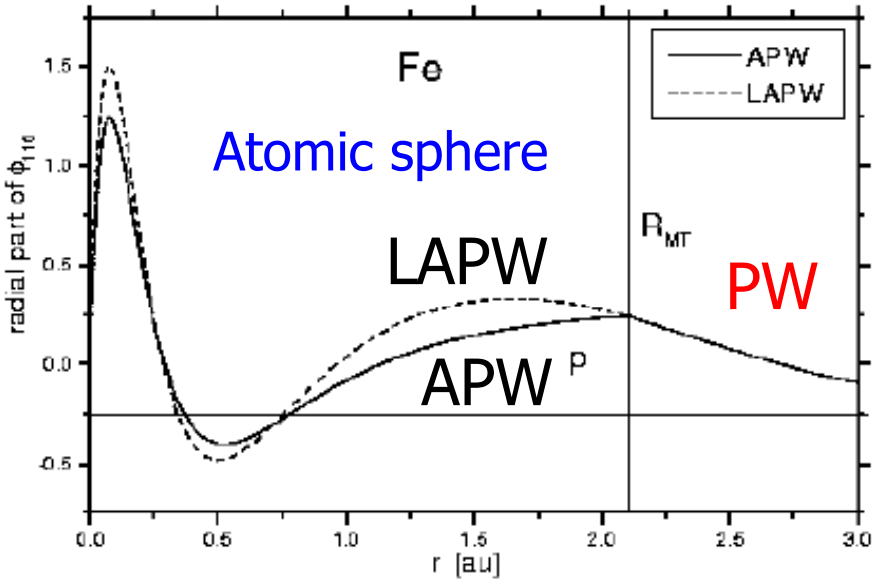
$$\Phi_{k_n} = \sum_{\ell m} [A_{\ell m}(k_n) u_\ell(E_\ell, r) + B_{\ell m}(k_n) \dot{u}_\ell(E_\ell, r)] Y_{\ell m}(\hat{r})$$

expand u_l at fixed energy E_l and add $\dot{u}_l = \partial u_l / \partial \varepsilon$

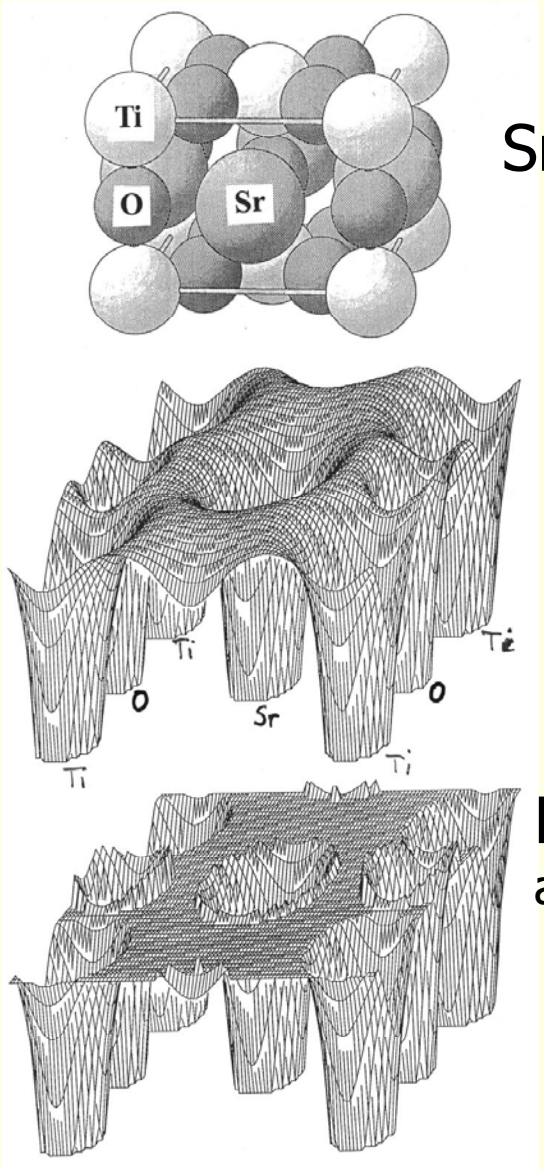
A_{lm}^k, B_{lm}^k: join PWs in value and slope

→ General eigenvalue problem (diagonalization)

→ additional constraint requires more PWs than APW



Full-potential total-energy (A.Freeman etal.)



$SrTiO_3$

Full potential

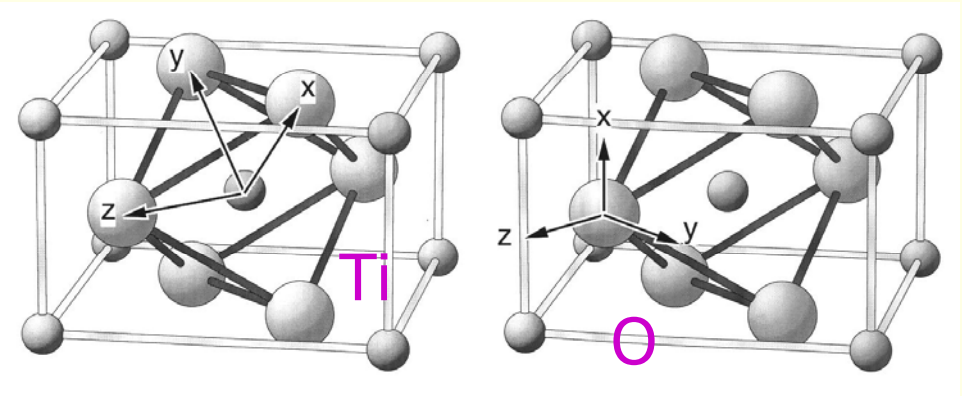
Muffin tin approximation

TiO_2 rutile

- The potential (and charge density) can be of general form (no shape approximation)

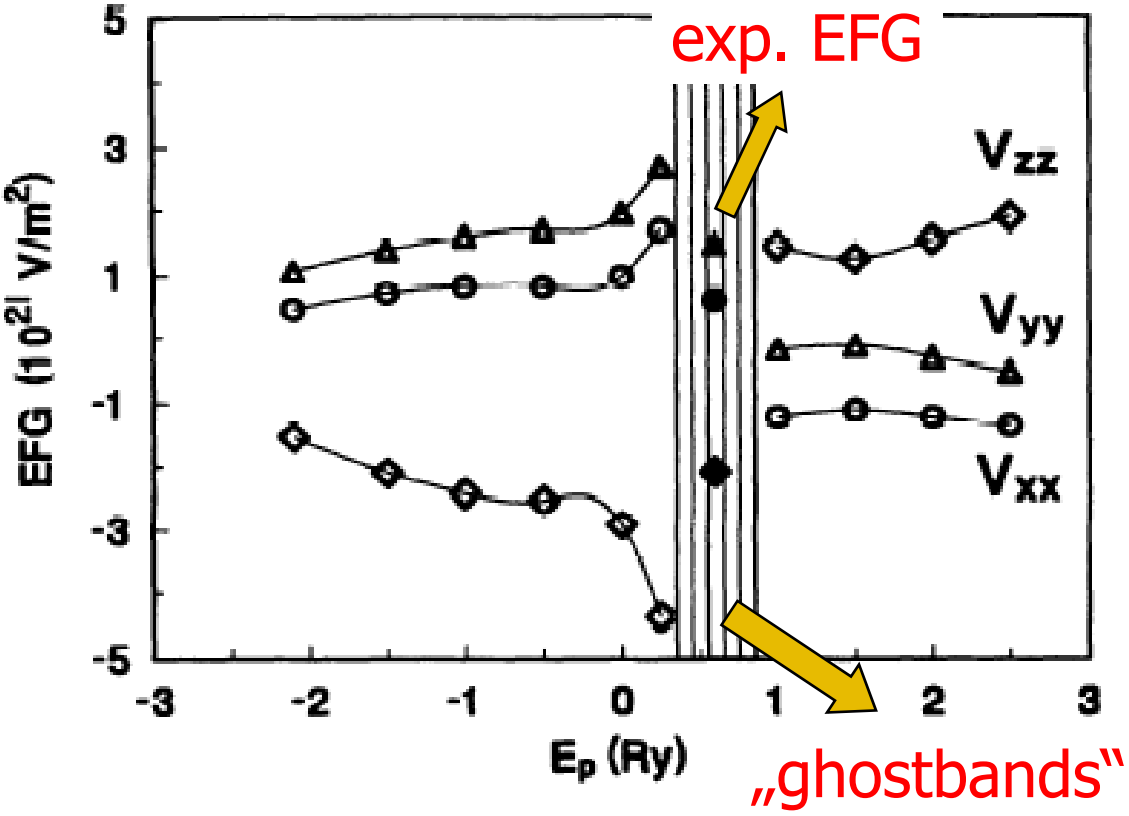
$$V(r) = \begin{cases} \sum_{LM} V_{LM}(r) Y_{LM}(\hat{r}) & r < R_\alpha \\ \sum_{K} V_K e^{i\vec{K}.\vec{r}} & r \in I \end{cases}$$

- Inside each atomic sphere a local coordinate system is used (defining LM)

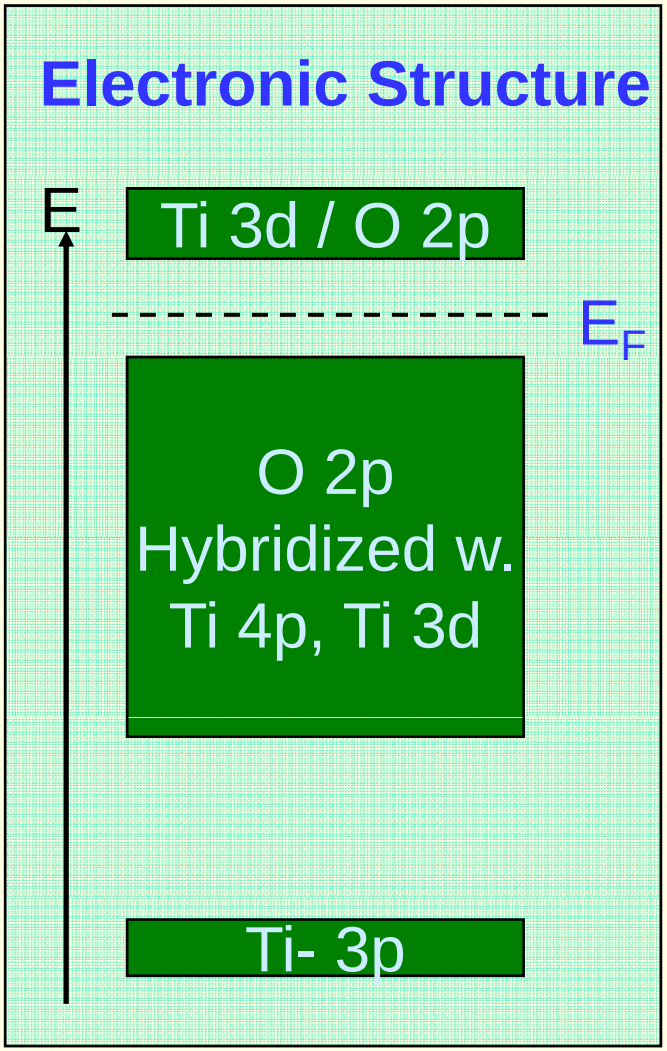


Problems of the LAPW method:

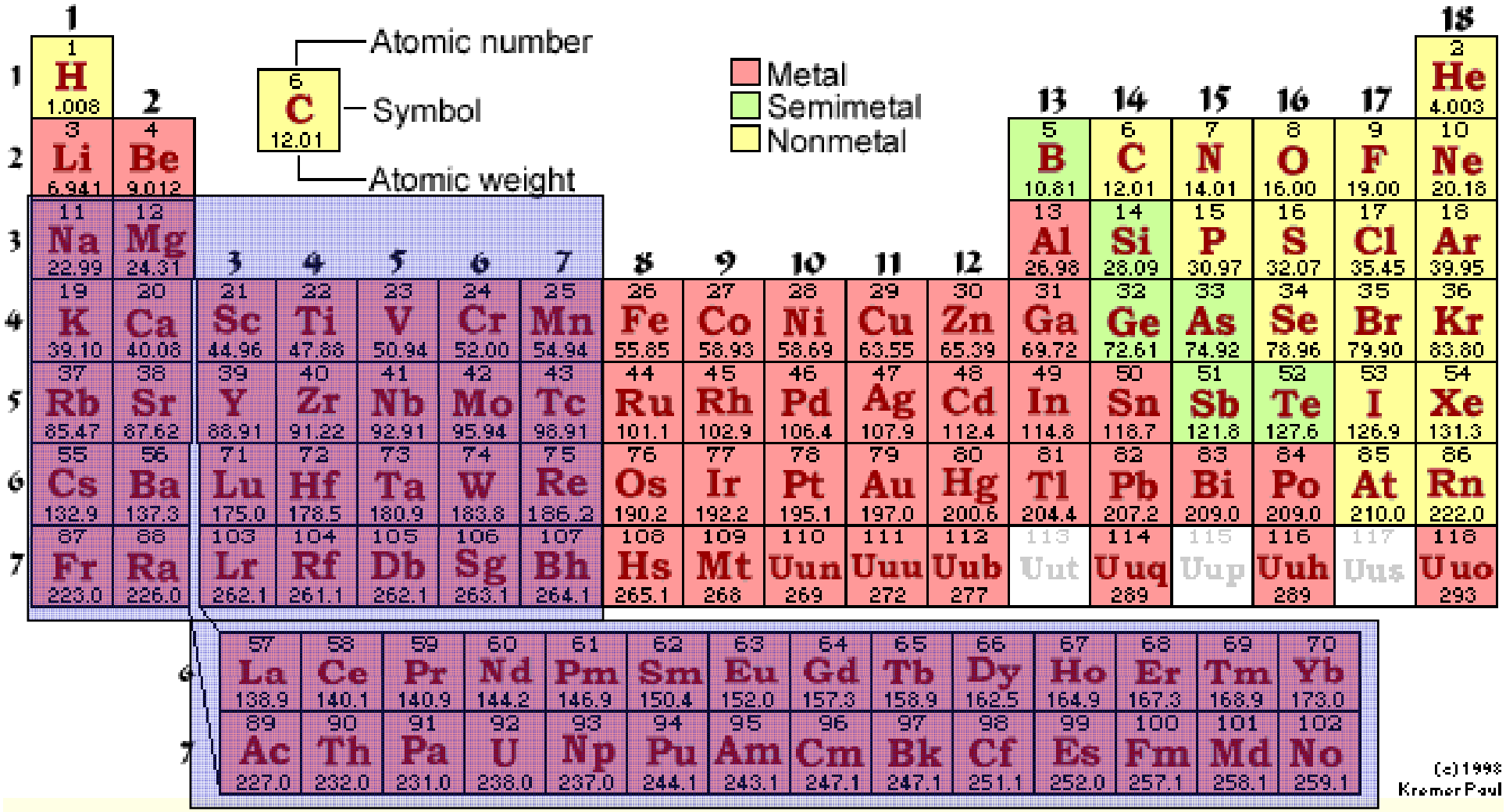
EFG Calculation for Rutile TiO_2 as a function of the Ti-*p* linearization energy E_p



P. Blaha, D.J. Singh, P.I. Sorantin and K. Schwarz, Phys. Rev. B **46**, 1321 (1992).

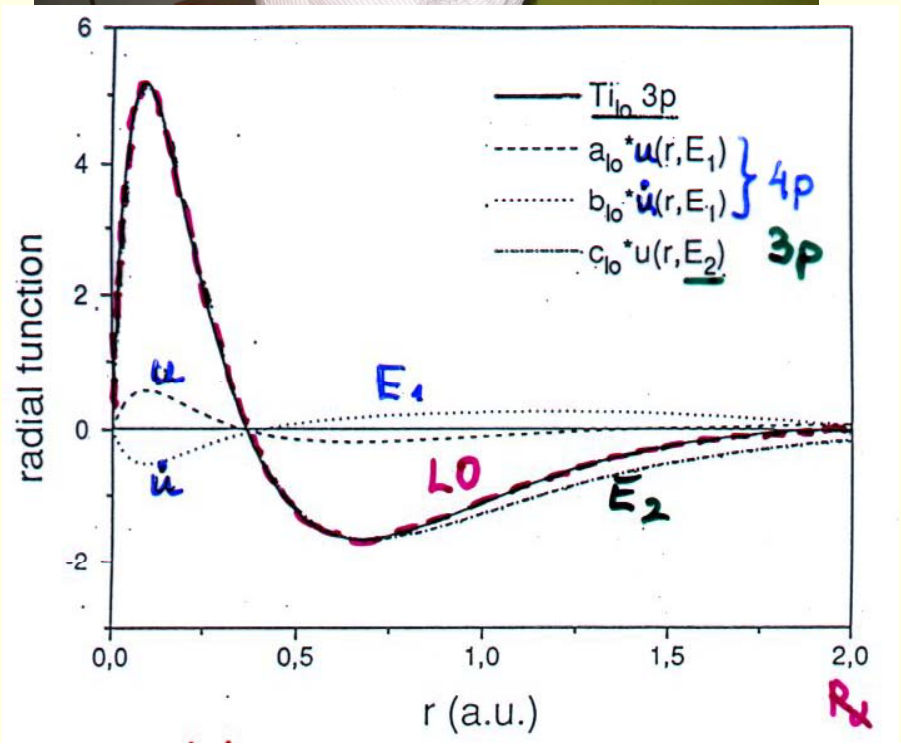


Problems of the LAPW method



Problems with semi-core states

Extending the basis: Local orbitals (LO)



$$\Phi_{LO} = [A_{\ell m} u_\ell^{E_1} + B_{\ell m} \dot{u}_\ell^{E_1} + C_{\ell m} u_\ell^{E_2}] Y_{\ell m}(\hat{r})$$

4p 3p

- LO
  - *is confined to an atomic sphere*
  - *has zero value and slope at R*
  - *can treat two principal QN n for each azimuthal QN ℓ (3p and 4p)*
  - *corresponding states are strictly orthogonal (no "ghostbands")*
  - *tail of semi-core states can be represented by plane waves*
  - *only slight increase of basis set (matrix size)*

D.J.Singh,
Phys.Rev. B 43 6388 (1991)

New ideas from Uppsala and Washington

E.Sjöstedt, L.Nordström, D.J.Singh,
An alternative way of linearizing the augmented plane wave method,
Solid State Commun. 114, 15 (2000)

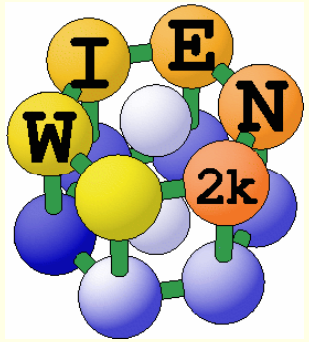
- Use APW, but at fixed E_l (superior PW convergence)
- Linearize with additional lo (add a few basis functions)

$$\Phi_{k_n} = \sum_{\ell m} A_{\ell m}(k_n) u_\ell(E_\ell, r) Y_{\ell m}(\hat{r})$$

$$\Phi_{lo} = [A_{\ell m} u_\ell^{E_1} + B_{\ell m} \dot{u}_\ell^{E_1}] Y_{\ell m}(\hat{r})$$

optimal solution: mixed basis

- use APW+lo for states which are difficult to converge:
(f or d- states, atoms with small spheres)
- use LAPW+LO for all other atoms and ℓ



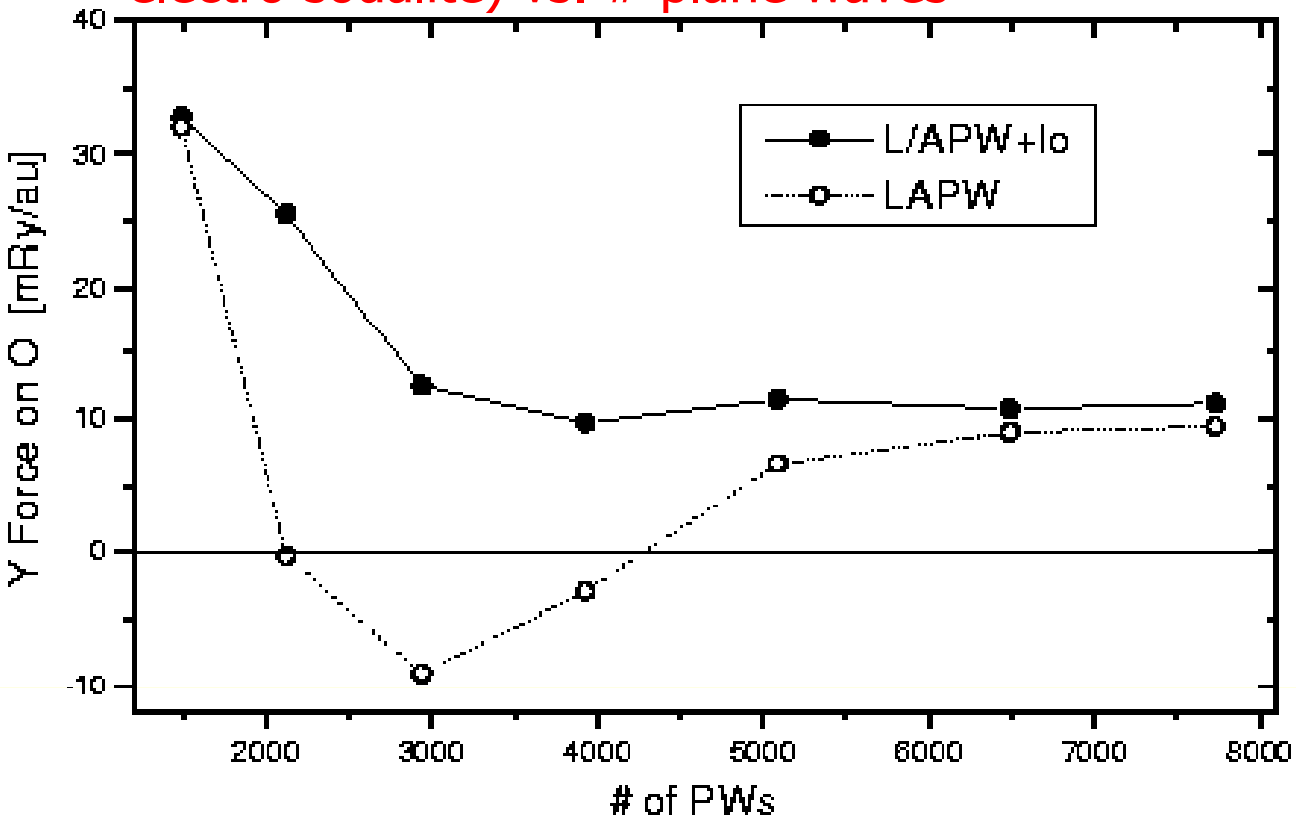
basis for

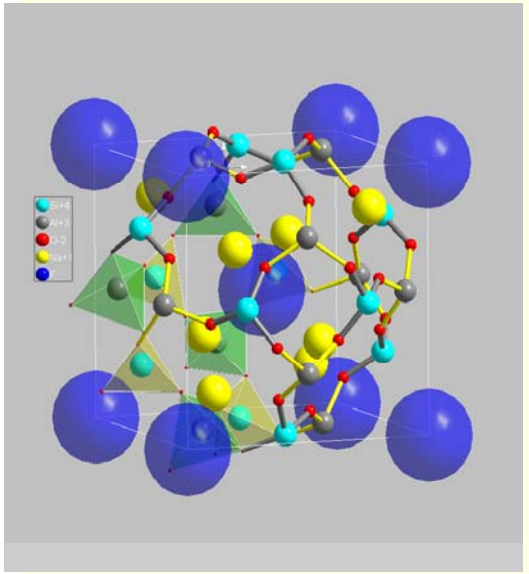
Improved convergence of APW+lo

K.Schwarz, P.Blaha, G.K.H.Madsen,
Comp.Phys.Commun.**147**, 71-76 (2002)

- changes sign and converges slowly in **LAPW**
- better convergence in **APW+lo**

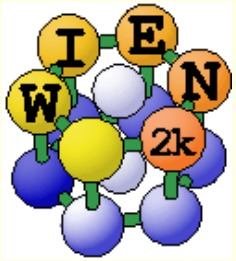
Force (Fy) on oxygen in SES (sodium electro sodalite) vs. # plane waves





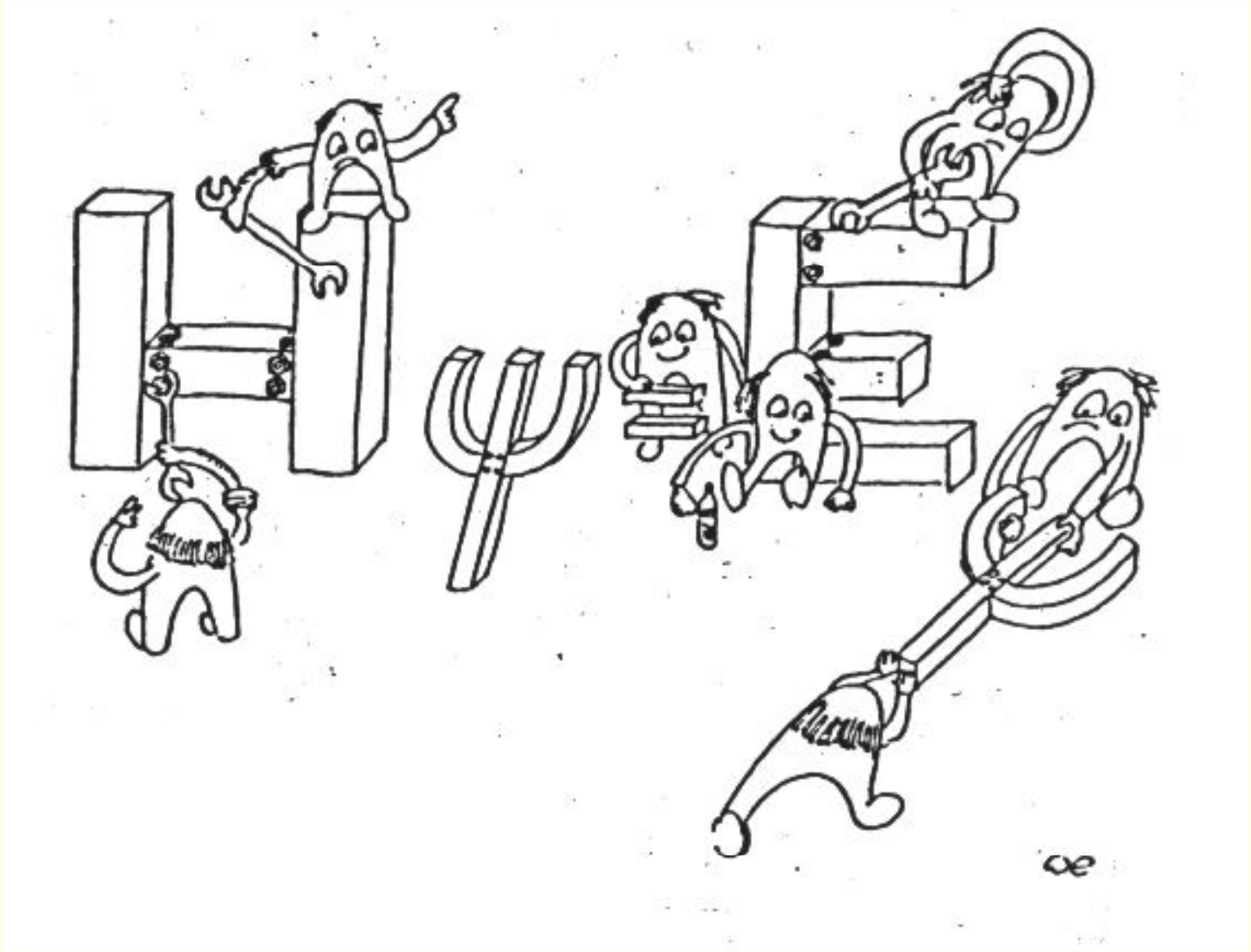
APW based schemes

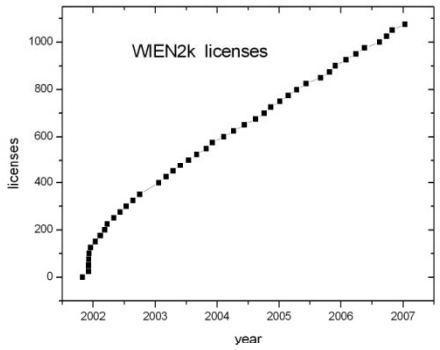
- APW (J.C.Slater 1937)
  - *Non-linear eigenvalue problem*
  - *Computationally very demanding*
- LAPW (O.K.Andersen 1975)
  - *Generalized eigenvalue problem*
  - *Full-potential (A. Freeman et al.)*
- Local orbitals (D.J.Singh 1991)
  - *treatment of semi-core states (avoids ghostbands)*
- APW+lo (E.Sjöstedt, L.Nordstörm, D.J.Singh 2000)
  - *Efficience of APW + convenience of LAPW*
  - *Basis for*



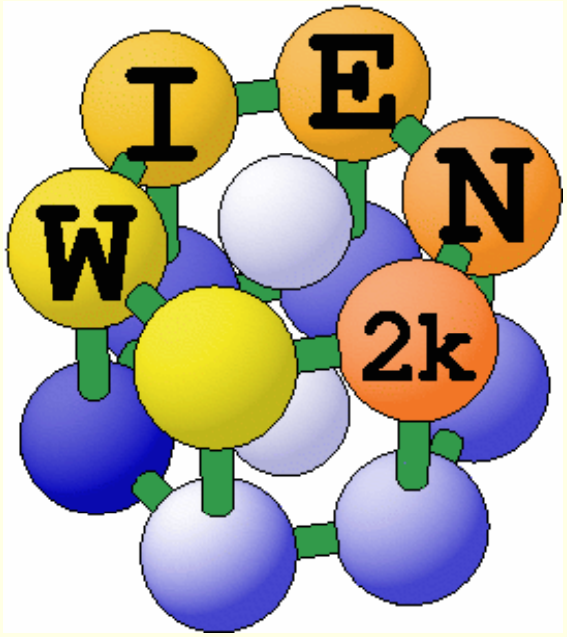
K.Schwarz, P.Blaha, G.K.H.Madsen,
Comp.Phys.Commun.**147**, 71-76 (2002)

Quantum mechanics at work





WIEN2k software package



WIEN97: ~500 users
WIEN2k: ~1190 users
mailinglist: 1800 users

An Augmented Plane Wave Plus Local Orbital Program for Calculating Crystal Properties

Peter Blaha
Karlheinz Schwarz
Georg Madsen
Dieter Kvasnicka
Joachim Luitz

November 2001
Vienna, AUSTRIA
Vienna University of Technology

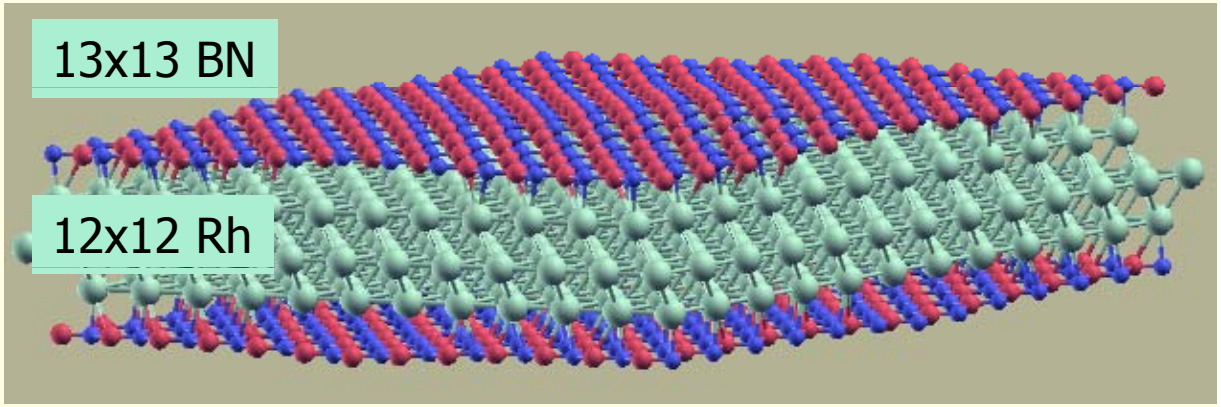
http://www.wien2k.at

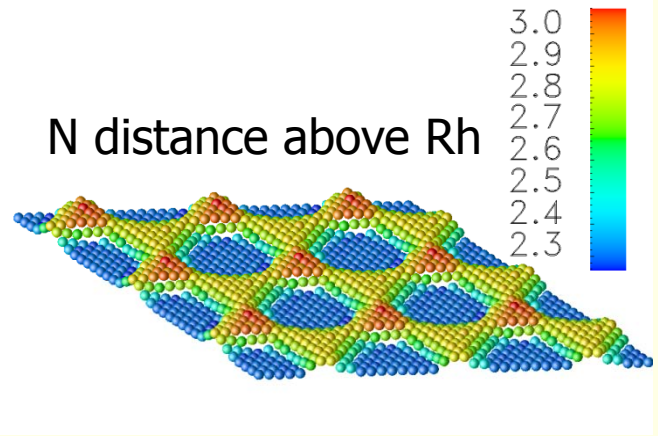
WIEN code as benchmark

General remarks on WIEN2k

- WIEN2k consists of many independent F90 programs, which are linked together via C-shell scripts (needs Unix/Linux)
- real/complex version (inversion)
- 10 atom cells on 256Mb PC / 100 atom cells require 1-2 Gb
- k-point parallel on clusters with common NFS (slow network)
- MPI/Scalapack parallelization for bigger cases (>50 atoms) and fast network

h-BN/Rh(111) nanomesh: 1108 atoms+vacuum on 64 cpus

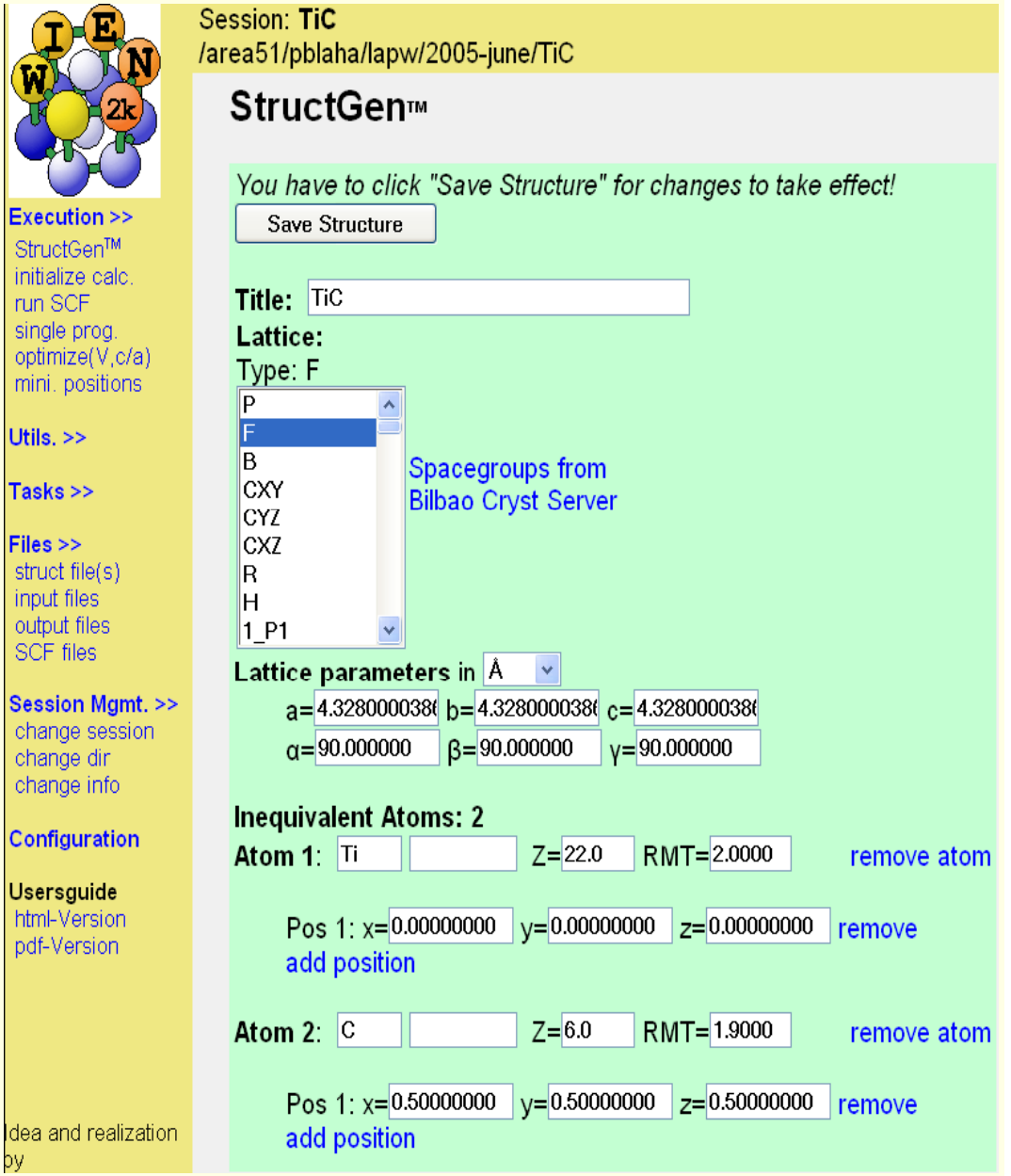




- You can run WIEN2k using any www-browser and the w2web interface, but also at the command line of an xterm.

w2web GUI (graphical user interface)

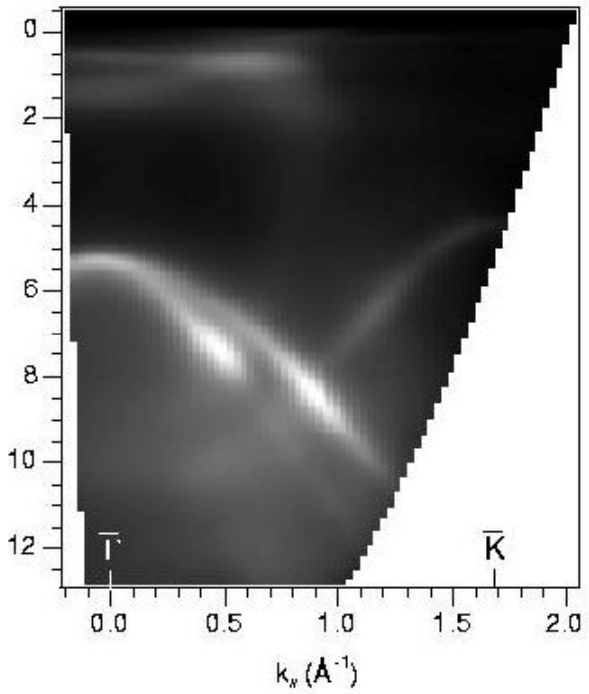
- Structure generator
  - *spacegroup selection*
  - *import cif file*
- step by step initialization
  - *symmetry detection*
  - *automatic input generation*
- SCF calculations
  - *Magnetism (spin-polarization)*
  - *Spin-orbit coupling*
  - *Forces (automatic geometry optimization)*
- Guided Tasks
  - *Energy band structure*
  - *DOS*
  - *Electron density*
  - *X-ray spectra*
  - *Optics*

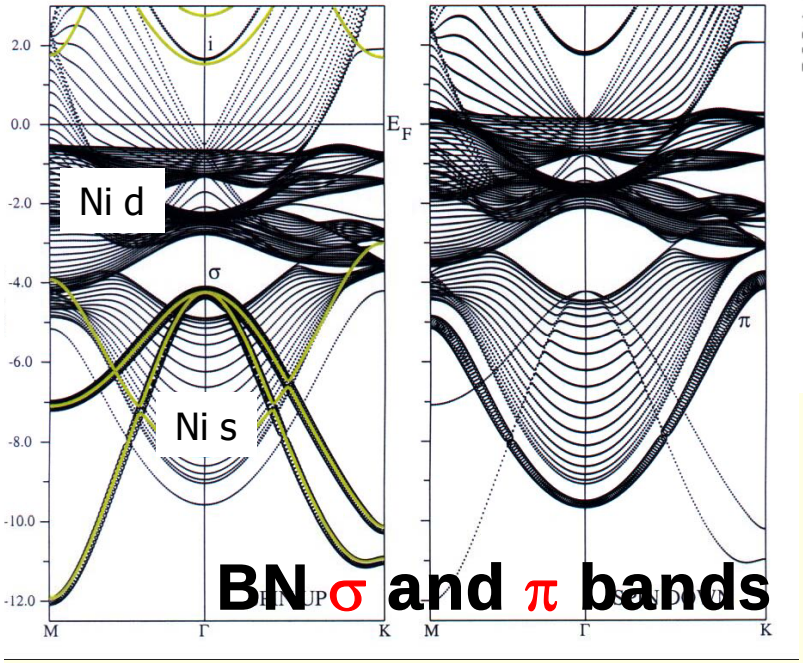


Properties with WIEN2k - I

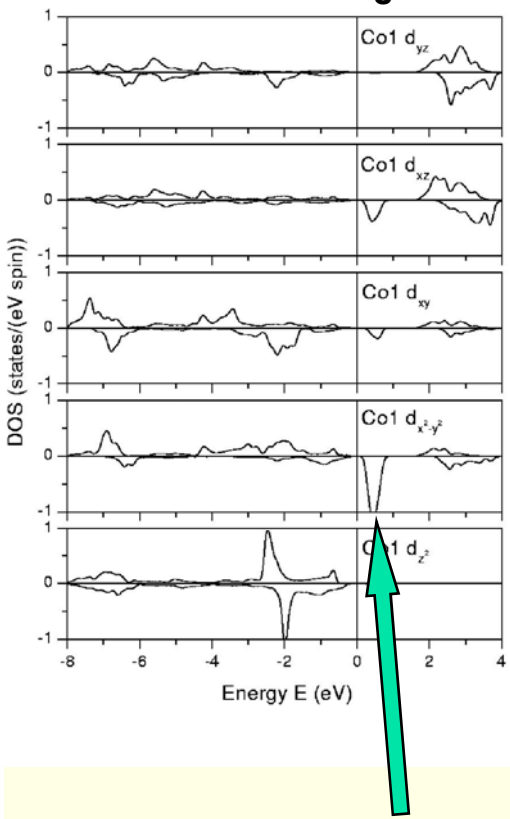
- DFT: LDA, various GGAs; meta-GGA, LDA+U; Hybrid-DFT for „correlated electrons")
- Energy bands
  - *classification of irreducible representations*
  - *´character-plot´ (emphasize a certain band-character)*
- Density of states
  - *including partial DOS with l and m- character*

h-BN / Ni(111): σ and π bands





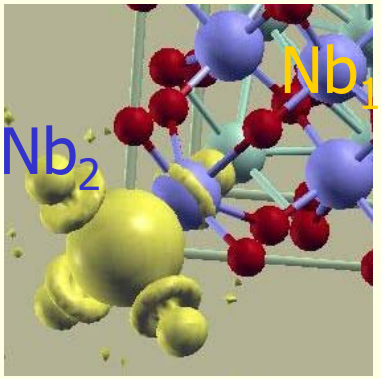
$BaCoO_3$



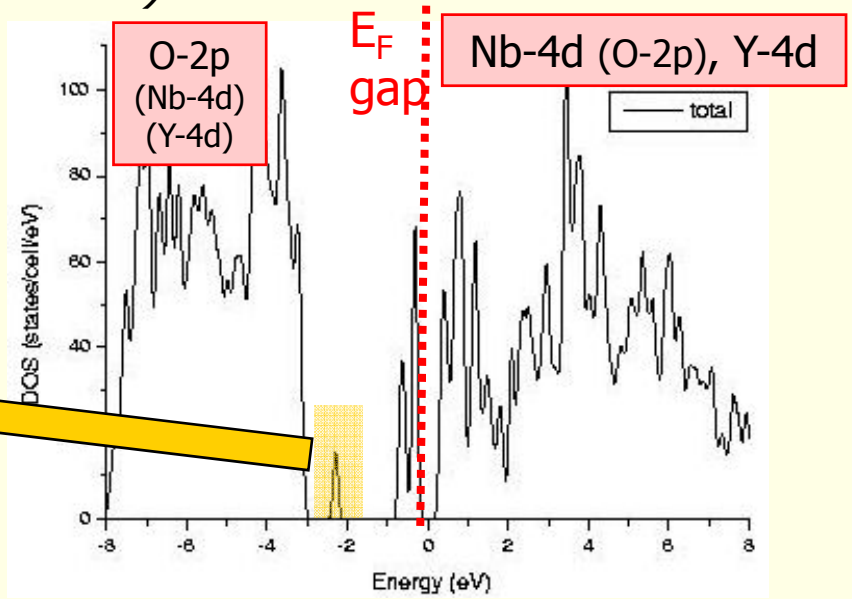
d-x^2-y^2

Properties with WIEN2k - II

- Electron densities, potential
  - *total-, valence-, difference-, spin-densities, ρ of selected states*
  - *1-D, 2D- and 3D-plots (Xcrysden)*
  - *X-ray structure factors, STM pictures*
  - *Bader´s atom-in-molecule analysis, atomic basins and charges ($\nabla\rho.\vec{n}=0$)*
  - *spin+orbital magnetic moments (+ spin-orbit)*



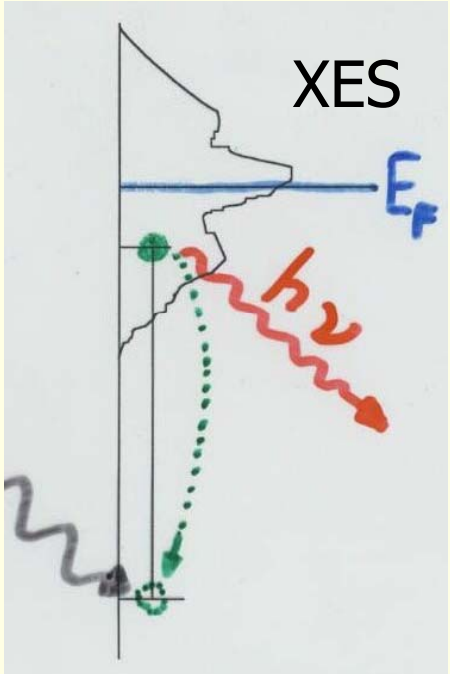
$Y_2Nb_2O_7$



- Hyperfine parameters
  - *Isomer shift*
  - *Electric field gradients*
  - *hyperfine fields (contact + dipolar + orbital contribution)*

Properties with WIEN2k - III

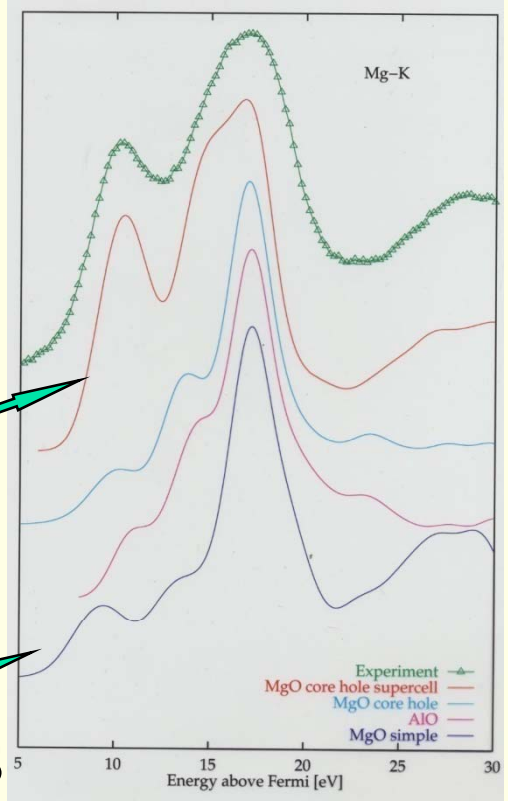
- Spectroscopy
  - *core levels (with core holes)*
  - *X-ray emission, absorption, electron-energy-loss*
    - (core - valence/conduction-band transitions including matrix elements and angular dep.)
    - EELS inclusion of possible non-dipol transitiotons (momentum transfer)
  - *optical properties (dielectric function in RPA, JDOS including momentum matrix elements and Kramers-Kronig)*
  - *fermi surface (2D, 3D)*



Mg-K XAS
probes empty Mg-p

including a core-hole
in supercell
(Final state rule)

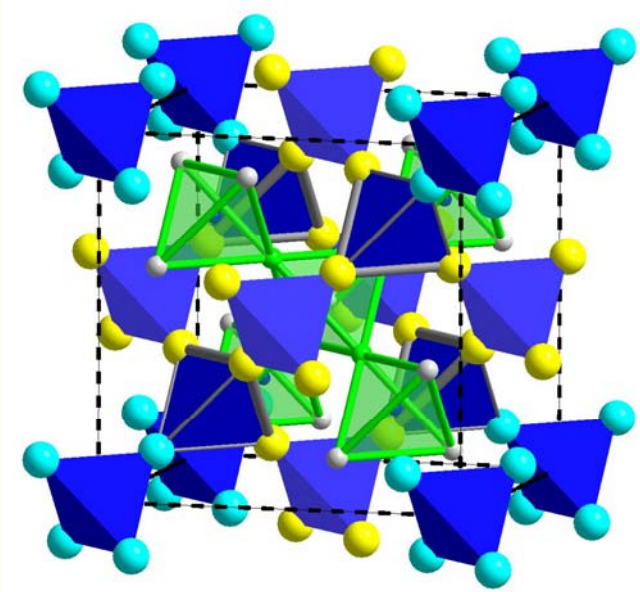
from ground-state DOS

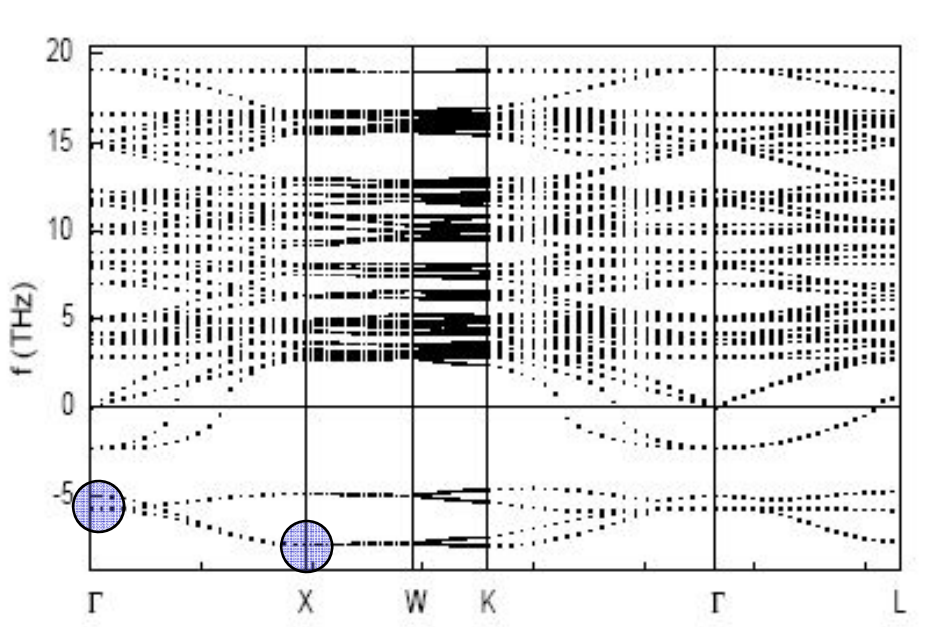


Properties with WIEN2k - IV

- Total energy and forces
  - *optimization of internal coordinates, (damped MD, BROYDEN)*
  - *cell parameter only via E_{tot} (no stress tensor)*
  - *elastic constants for cubic cells*
  - *Phonons via a direct method (based on forces from supercells)*
    - interface to PHONON (K.Parlinski) – bands, DOS, thermodynamics, neutrons

Pyrochlore structure of $Y_2Nb_2O_7$: strong phonon instabilities→ phase transition





Total energies and atomic forces

(Yu et al.; Kohler et al.)

- Total Energy:
  - *Electrostatic energy*
  - *Kinetic energy*
  - *XC-energy*

$$U[\rho] = \tfrac{1}{2}\int d^3\vec{r}\ \rho(\vec{r})V_{es}(\vec{r}) + \tfrac{1}{2}\sum_\alpha Z_\alpha V_{es}^\alpha(\vec{r})$$

$$T[\rho] = \sum_i n_i\varepsilon_i - \int d^3\vec{r}\ \rho(\vec{r})V_{eff}(\vec{r})$$

$$E_{xc}[\rho] = \int d^3\vec{r}\ \rho(\vec{r})\varepsilon_{xc}(\vec{r})$$

- Force on atom α:

$$\vec{F}^\alpha = \frac{-dE_{tot}}{d\vec{R}_\alpha} = F_{HF}^\alpha + F_{core}^\alpha + F_{val}^\alpha$$

  - *Hellmann-Feynman-force*

$$F_{HF}^\alpha = Z_\alpha \sum_{m=-1}^{1} \lim_{r_\alpha\to 0} \frac{V_{1m}^{es}(r_\alpha)}{r_\alpha} \nabla_\alpha\left[r_\alpha Y_{1m}(\hat{r})\right]$$

  - *Pulay corrections*
    - Core

$$F_{core}^\alpha = -\int \rho_{core}(r)\nabla_\alpha V_{eff}(r)\, d\vec{r}$$

    - Valence

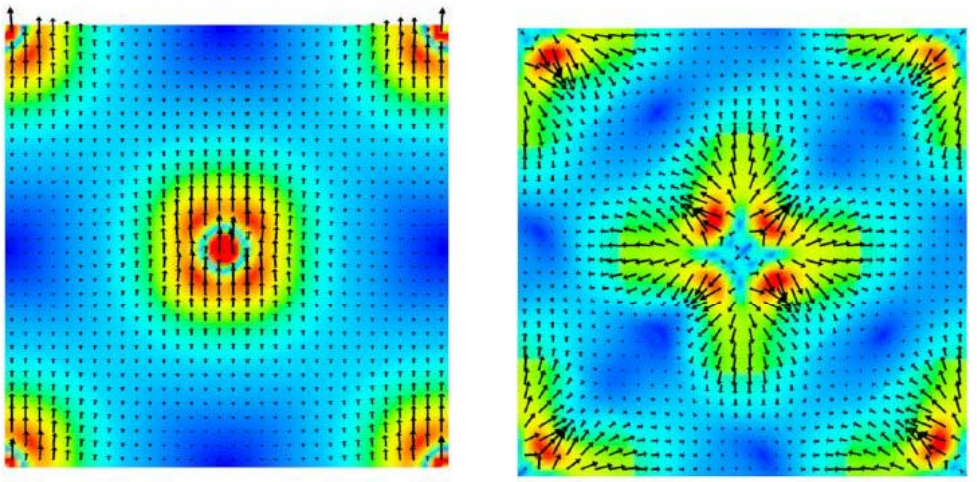
$$F_{val}^\alpha = \int_\alpha V_{eff}(r)\nabla_\alpha\rho_{val}(r)\, d\vec{r} + \sum_{k,i} n_i \sum_{K,K'} c_i^*(K')c_i(K)\times$$
$$\left[(K^2-\varepsilon_i)\oint \phi_{K'}^*(r)\phi_K(r)\, dS_\alpha - i(K-K')\left\langle\phi_{K'}\middle|H-\varepsilon_i\middle|\phi_K\right\rangle_\alpha\right]$$

- expensive, contains a summation of matrix elements over all occupied states (done only in last scf-iteration)

Properties with WIEN2k - V

- New developments (available)
  - *non-linear optics (B.Olejnik)*
  - *non-collinear magnetism (spin-spirals to fully-relativistic) (R.Laskowski)*
  - *transport properties (Fermi velocities, Seebeck, conductivity, thermoelectrics, ..) (G.Madsen)*
  - *GW (M.Scheffler): excited states*
  - *BSE (R.Laskowski) Bethe-Salpether equation for electron-hole interactions; excitons*

Intra-atomic NCM, fcc Pu

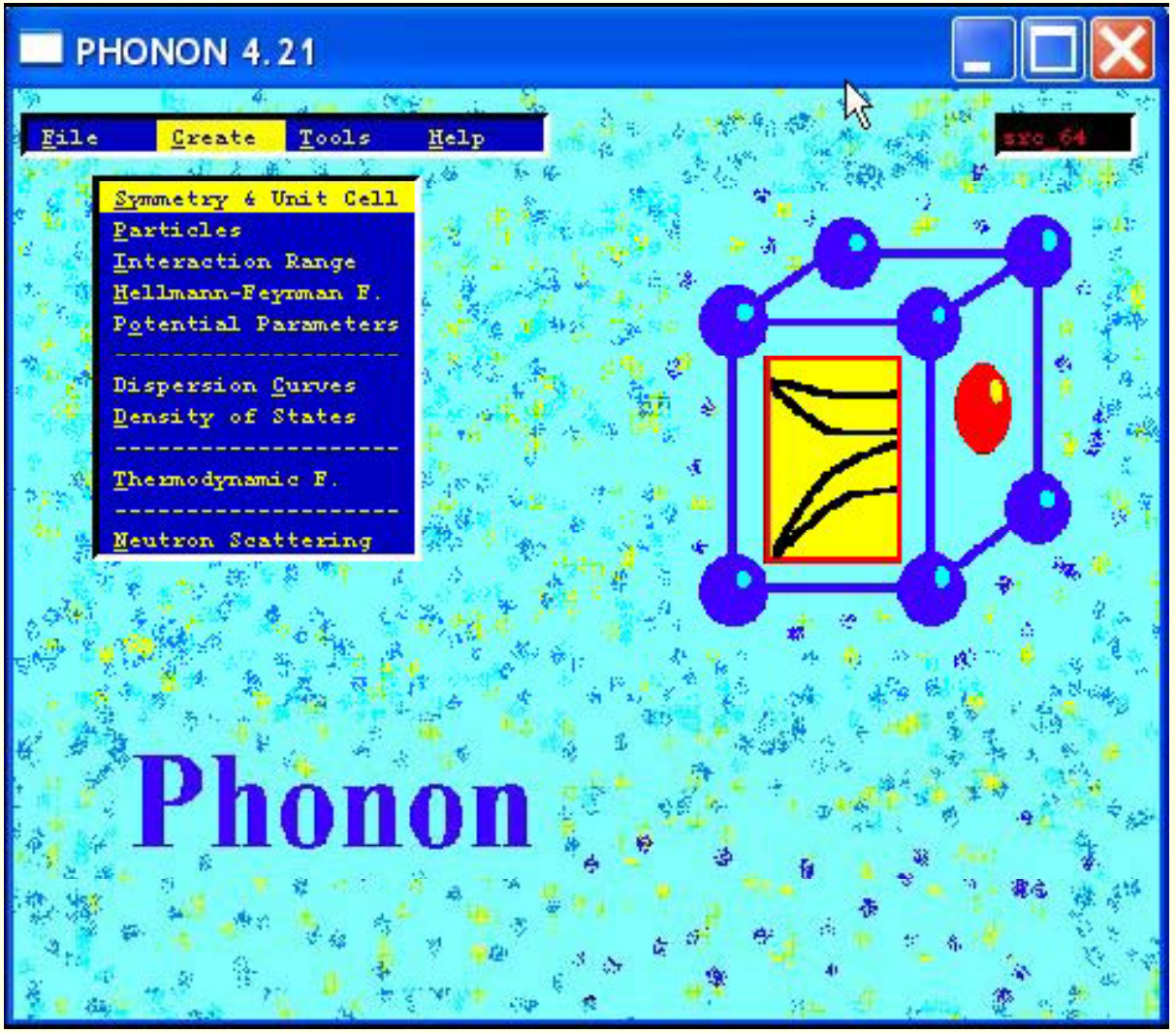


(a) plane $x = 0$ (b) plane $z = 1/10$

Spin density maps of **fcc Pu**. Calculation in FULL mode with SO. Average momenta point to $\langle 001 \rangle$

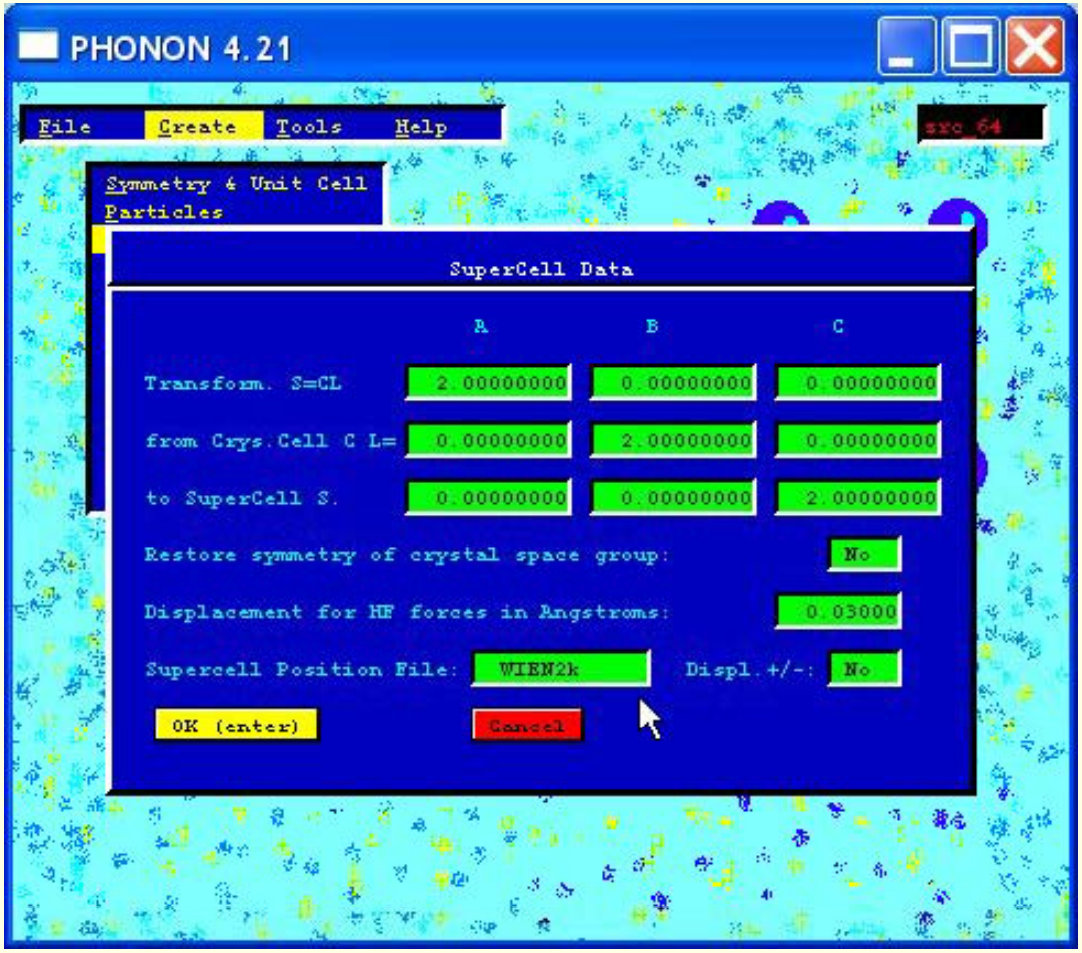
PHONON-I

- PHONON
  - *by K.Parlinski (Crakow)*
  - *runs under MS-windows*
  - *uses a „direct" method to calculate Force-constants with the help of an ab initio program*
  - *with these Force-constants phonons at arbitrary k-points can be obtained*
- Define your spacegroup
- Define all atoms at **previously optimized positions**



PHONON-II

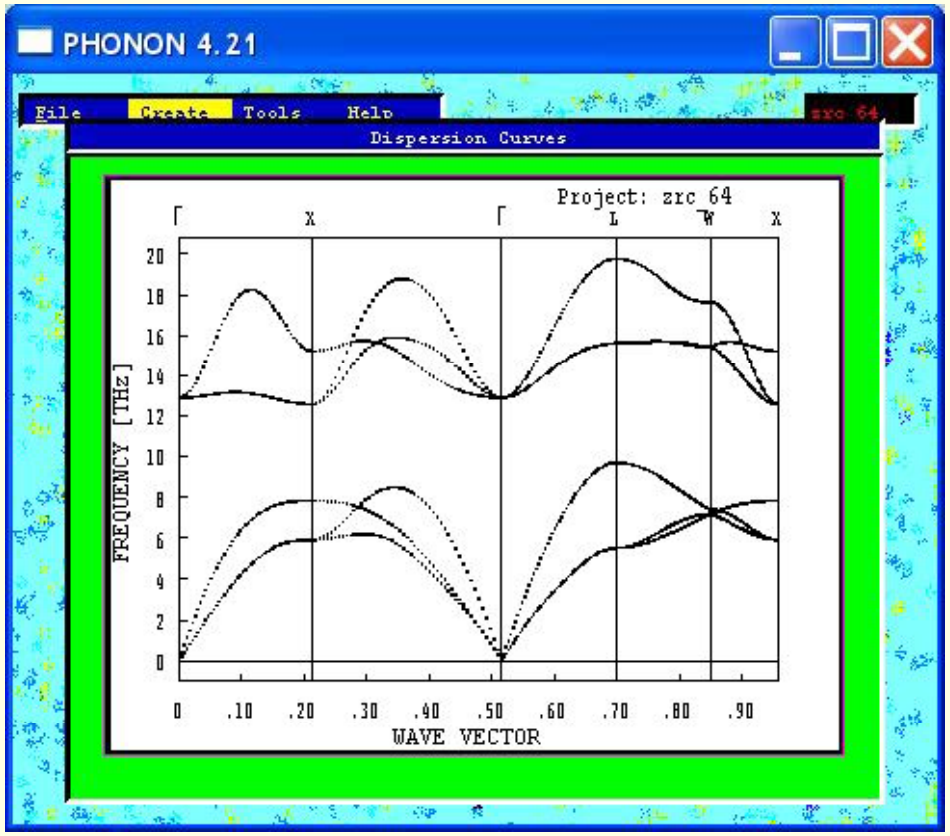
- Define an interaction range (supercell)
  - *create displacement file*
  - *transfer case.d45 to Unix*
- Calculate forces for all required displacements
  - *init_phonon_lapw*
    - for each displacement a case_XX.struct file is generated in an extra directory
    - runs nn and lets you define RMT values like:
      - 1.85 1-16



- init_lapw: either without symmetry (and then copies this setup to all case_XX)
  or with symmetry (must run init_lapw for all case_XX) (Do NOT use SGROUP)
- run_phonon: run_lapw –fc 0.1 –i 40 for each case_XX

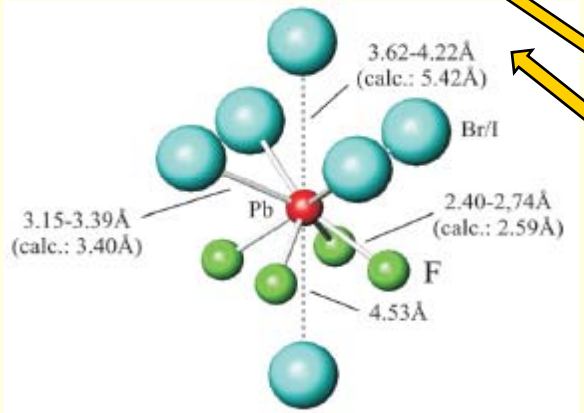
PHONON-III

- analyze_phonon_lapw
  - *reads the forces of the scf runs*
  - *generates „Hellman-Feynman" file case.dat and a „symmetrized HF-file case.dsy (when you have displacements in both directions)*
    - check quality of forces:
    - sum F_x should be small (0)
    - abs(F_x) should be similar for +/- displacements
- transfer case.dat (dsy) to Windows
- Import HF files to PHONON
- Calculate phonons

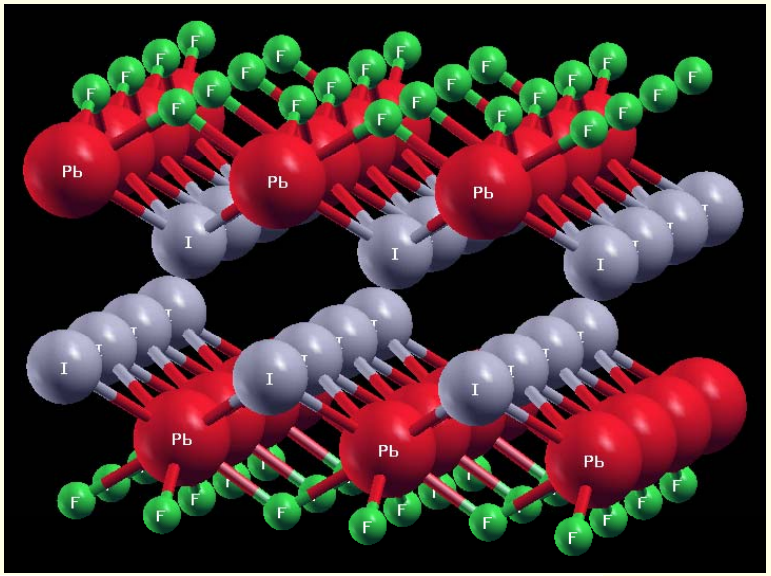


Γ - Phonons in matlockite PbFI

	a	c	c/a	z_I/c	z_{Pb}/c
Calc.	4.227	10.02	2.371	0.690 (0.659)	0.149 (0.167)
Expt	4.2374	8.800	2.077	0.663	0.164



I-I interaction



Symmetry	Atoms	Calc.[a]	Calc.[b]	Expt
$E_g(R)$	$Pb_1(x, y), Pb_2(-x, -y), I_1(-x, -y), I_2(x, y)$	36	41	36
$E_u(I)$	$Pb_1(-x, -y), Pb_2(-x, -y), F_1(x, y), F_2(x, y), I_1(x, y), I_2(x, y)$	35	47	50, 62 [16]
$E_g(R)$	$Pb_1(-x, -y), Pb_2(x, y), F_1(x, -y), F_2(-x, y), I_1(-x, -y), I_2(x, y)$	40	64	61
$A_{2u}(I)$	$Pb_1(-z), Pb_2(-z), I_1(z), I_2(z)$	79	71	
$A_{1g}(R)$	$Pb_1(z), Pb_2(-z), I_1(-z), I_2(z)$	61	73	67
$A_{1g}(R)$	$Pb_1(z), Pb_2(-z), I_1(z), I_2(-z)$	108	109	105
$E_u(I)$	$F_1(x, y), F_2(x, y)$	141	150	142, 154 [16]
$B_{1g}(R)$	$F_1(-z), F_2(z)$	194	207	206
$E_g(R)$	$F_1(-x, -y), F_2(x, y)$	212	217	
$A_{2u}(I)$	$F_1(z), F_2(z)$	274	259	318, 332 [16]

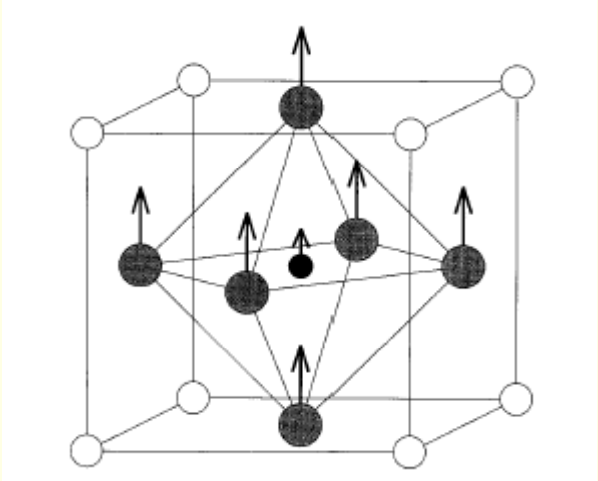
[a] Calculated at the theoretical lattice parameters (see table 4).
[b] Calculated at the experimental lattice parameters.

H. Hageman et al., J. Phys.: Cond. Mat. 19 (2007)

Ferroelectricity in Aurivillius phases

- ***Bilbao: J. Manuel Perez-Mato, M. Aroyo**
- **Universidad del País Vasco**
- ***Vienna: P. Blaha, K. Schwarz,**
- **J. Schweifer**
- ***Cracow: K. Parlinski**
- J.M. Perez-Mato et al. PRB, **70**, 214111

Ferroelectric Perovskites: PbTiO3



$PbTiO_3$

- Ferroelectric PT due to symmetry break at Tc:

  cubic ---- tetragonal

  Pm-3m ----- P4mm

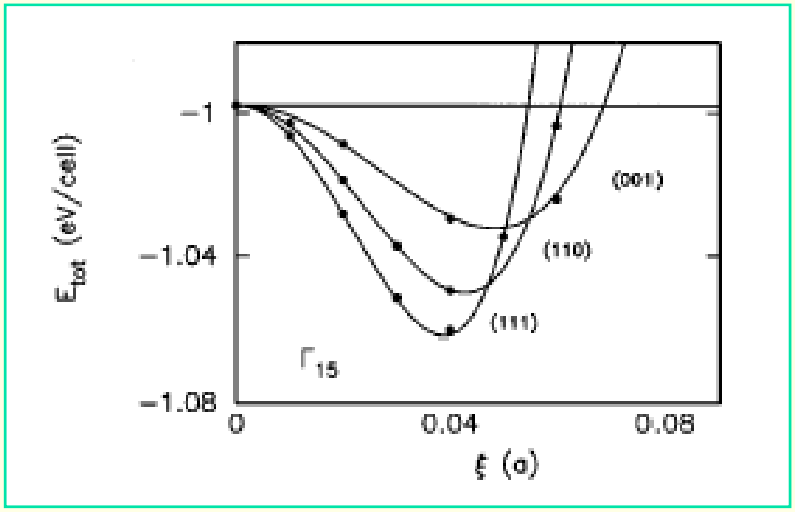
- A single (degenerate) *normal* mode is responsible for the PT

- Structure in Ferroelectric Phase:

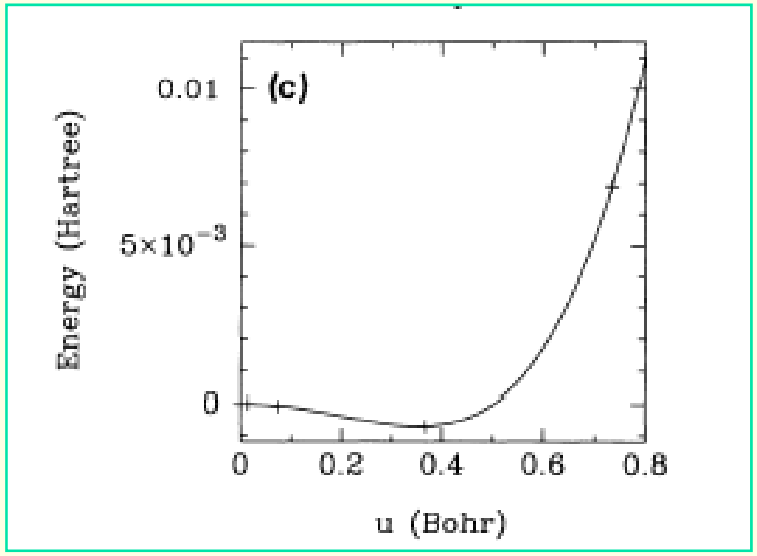
high-symmetry structure + frozen polar mode

Ab-initio “prediction” of the ferroelectric instability

$PbTiO_3$

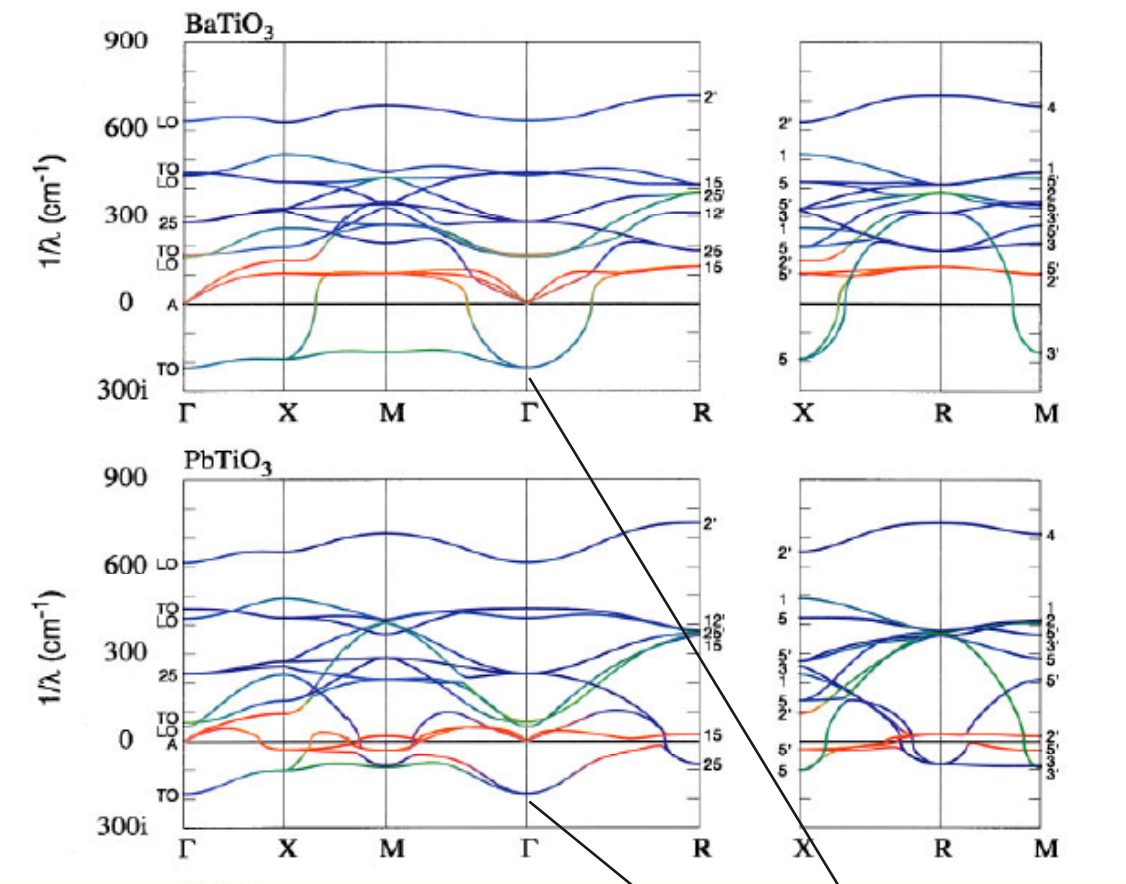


Waghmare&Rabe 1997



King-Smith&Vanderbilt 1994

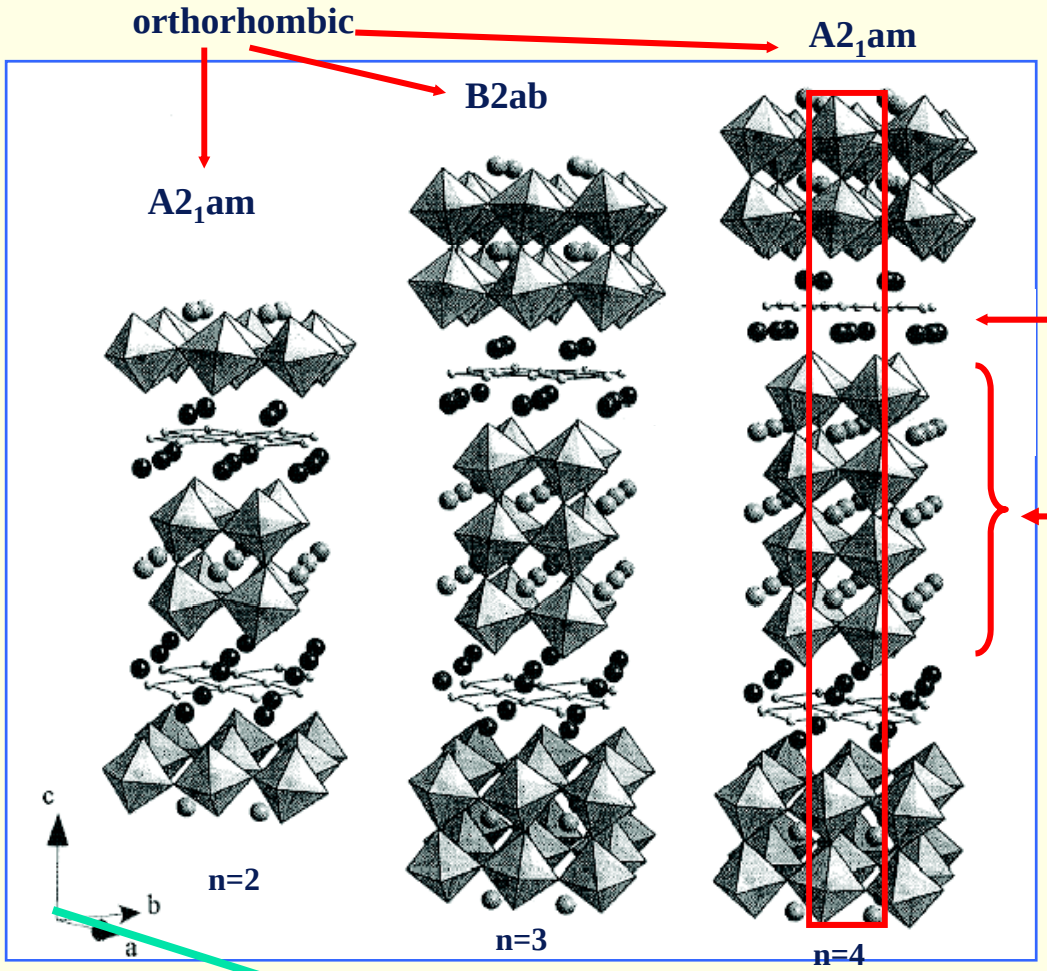
Ab-initio Phonon Branches



Ghosez et al. 1999

Polar unstable mode

The Aurivillius Compounds



$[Bi_2O_2]$-$[A_{n-1}B_nO_{3n+1}]$

Bi_2O_2

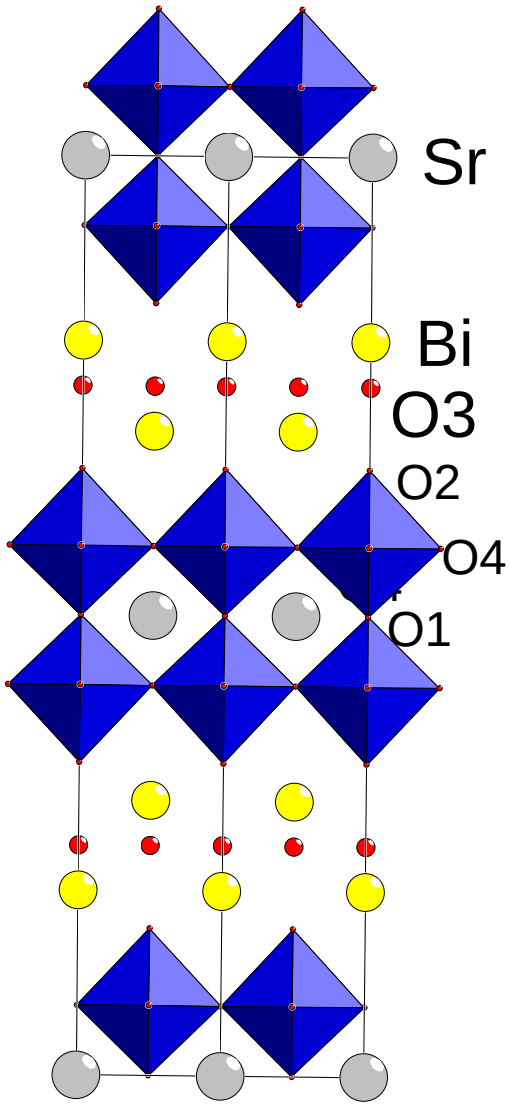
n-sized perovskite slab

cation deficient perovskites:

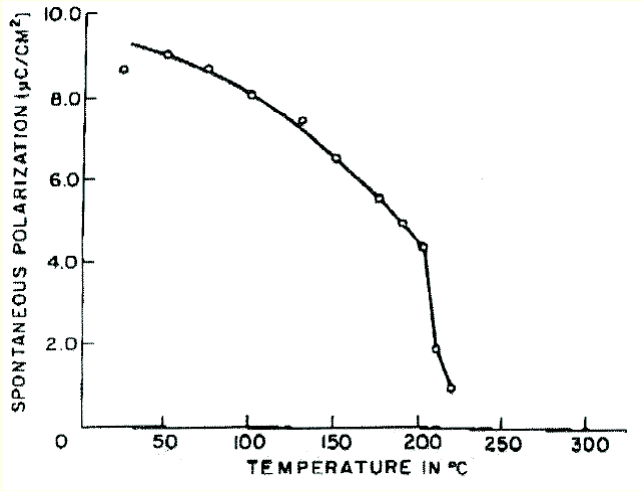
$[Bi,A]B_{1-x}O_3$

Dipl. Thesis -S. Borg 2001

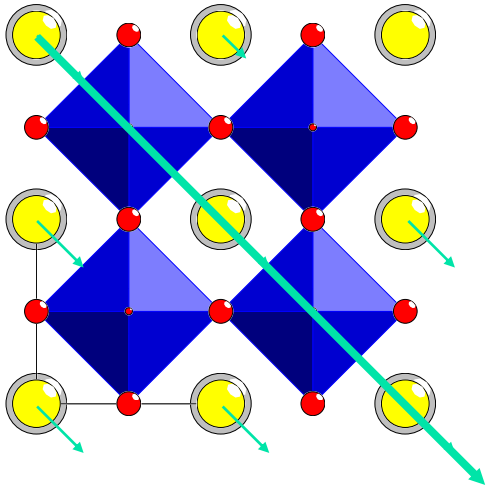
$Bi_2SrTa_2O_9$ - SBT



Spontaneous Polarization

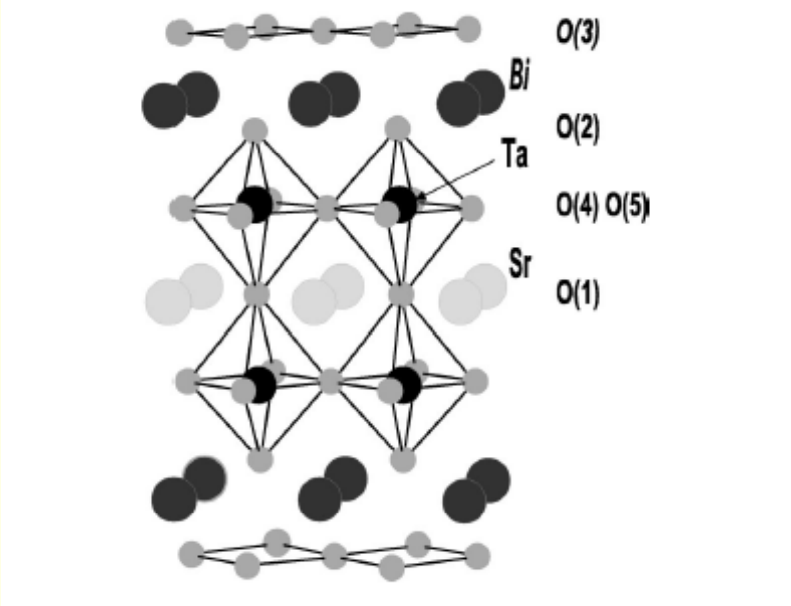


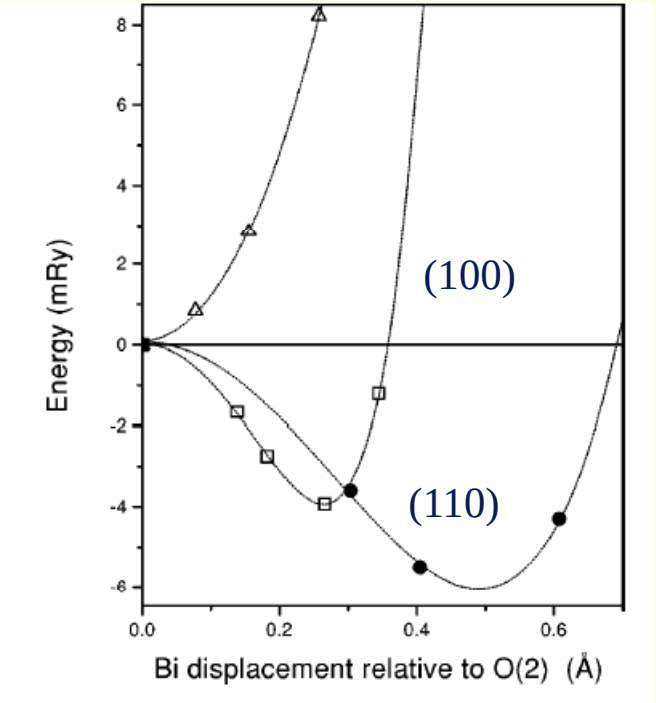
polar E_u mode (deg. 2)



Previous ab-initio calculations in SBT

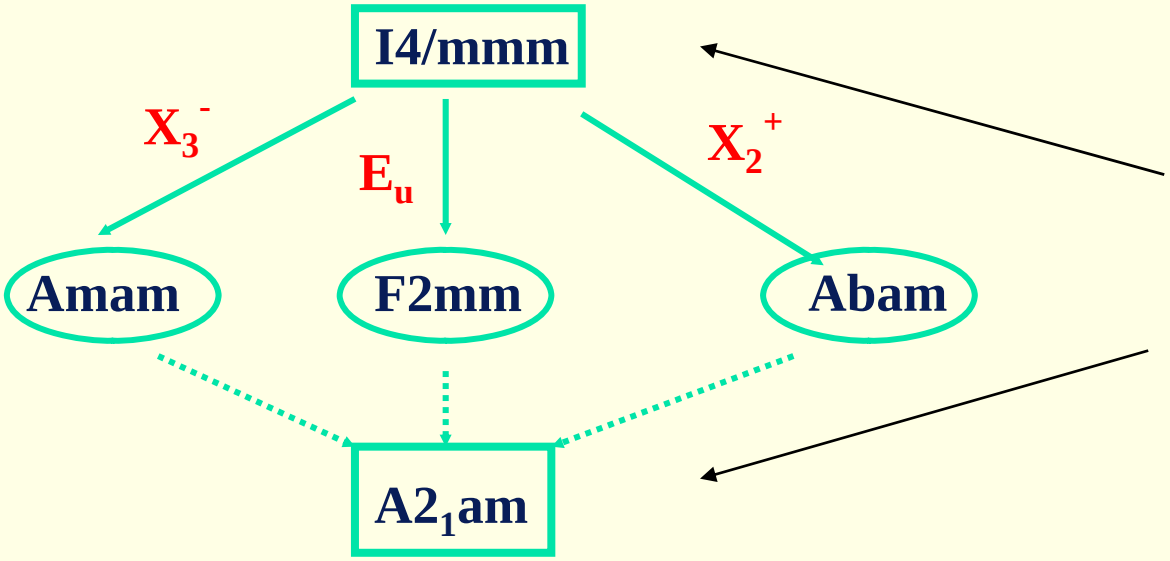
Stachiotti et al. 2000





- **Unstable E_u polar mode**
- **Strong contribution of Bi displacement : Bi-O(2) hybridization**

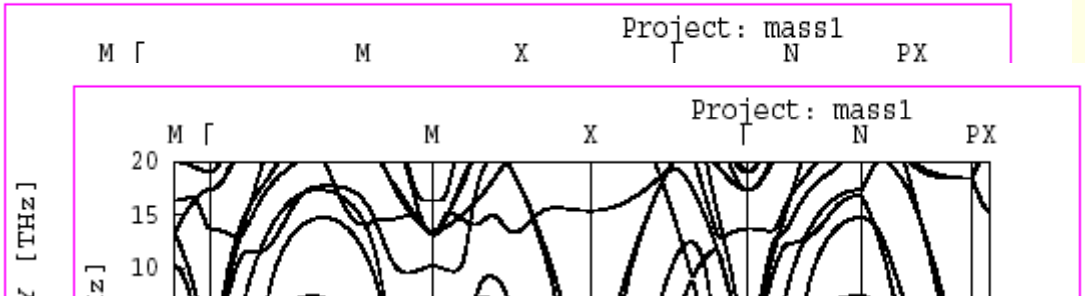
SBT – An Usual Ferroelectric? NO !

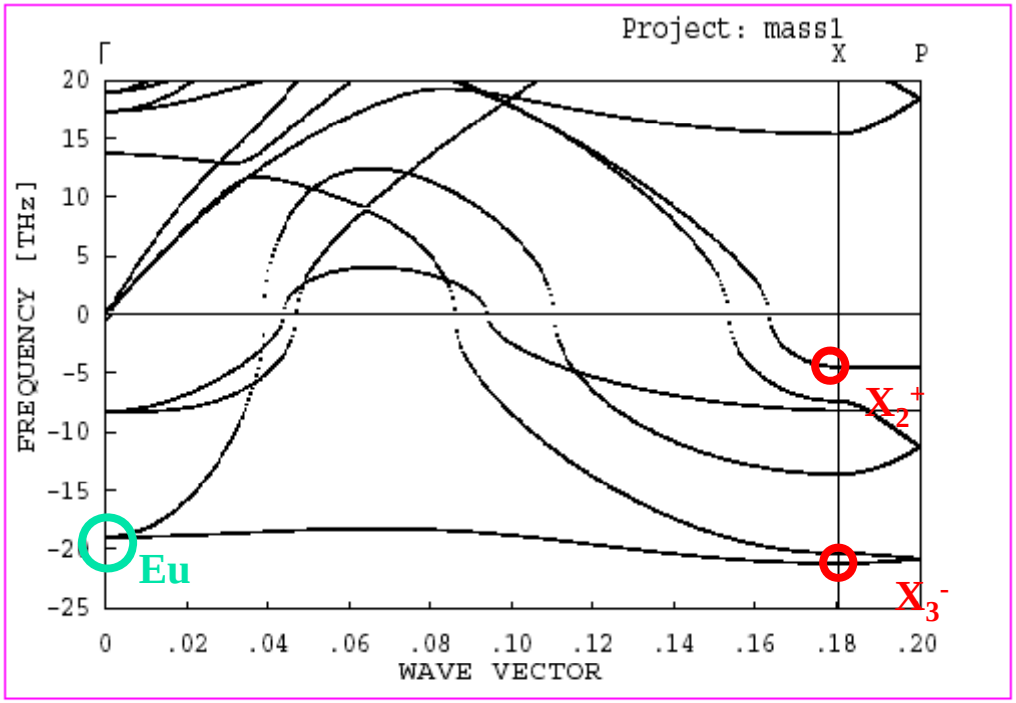


From symmetry analysis (group/ subgroup relations) the E_u mode alone cannot explain the complete phase transition

Ferroelectric Phase = E_u + X_3^- + X_2^+ mode

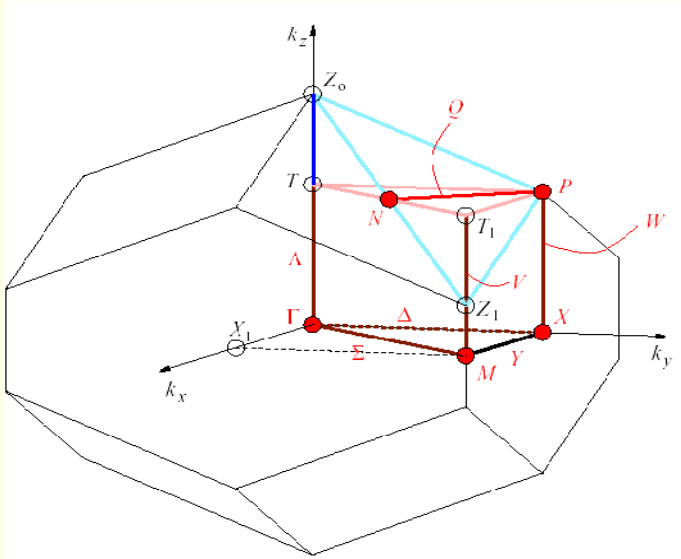
Phonons in SBT





SBT

CALCULATED "PHONON" BRANCHES



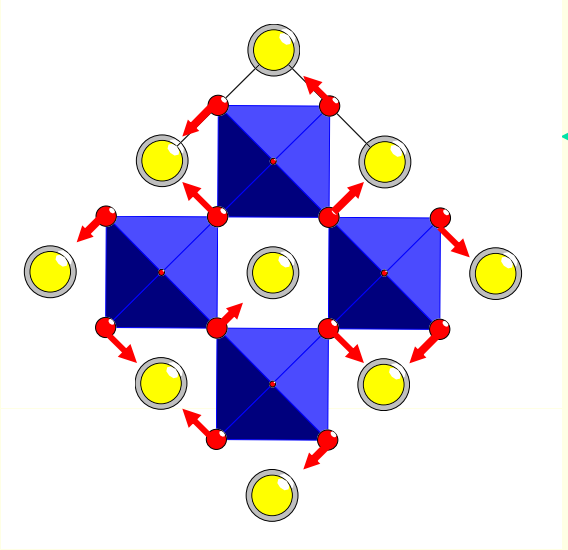
Comparing calculated and exp. soft-modes Eigenvectors:

Ferroelectric Phase = E_u + X_3^- + X_2^+ mode

Theoretical E_u and X_3- modes agree well with experimental modes

BUT ! …. The experimental frozen mode X_2^+ does not

Comparing exp. and calculated X_2^+ Modes

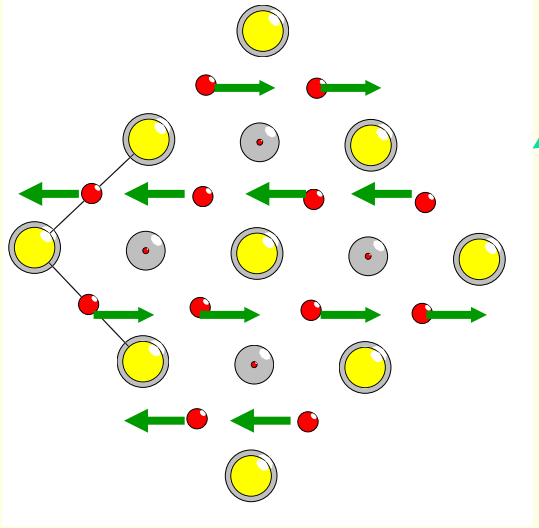


coincides approx. with calculated soft-mode X_2^+

"Part 1"

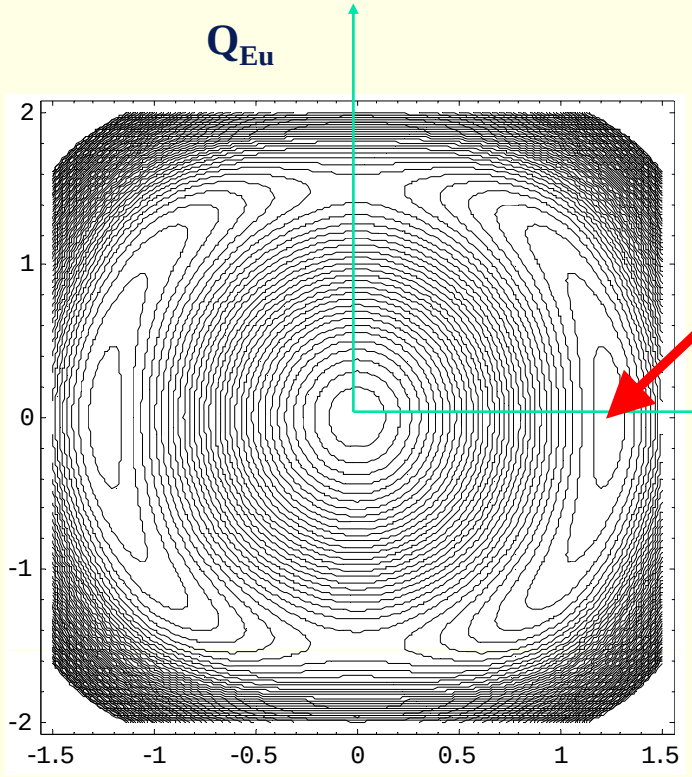
Two independent normal-modes

"Part 2"



coincides approx. with a second (hard) mode X_2^+

SBT – Energy Map: Coupling Eu –X_3^-



Predicted Ground State:

Only mode X_3^- frozen !

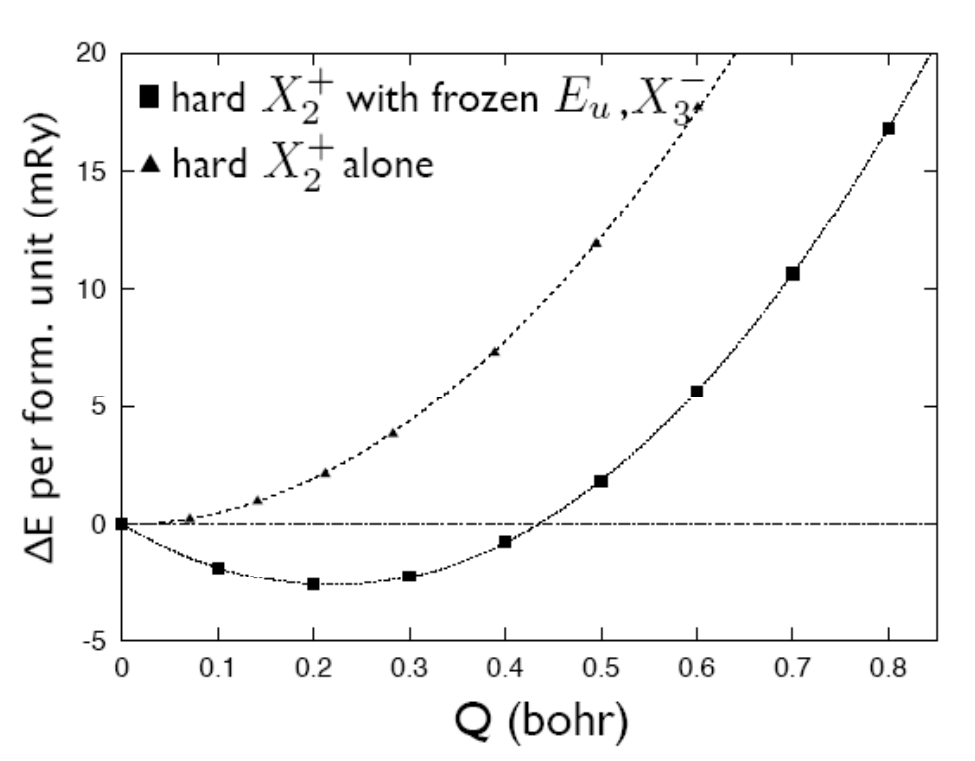
Space group Amam

Essential reason:
Strong biquadratic coupling penalizes "mixed" states

Something missing?
•coupling with X_2^+

Coupling with X_2^+

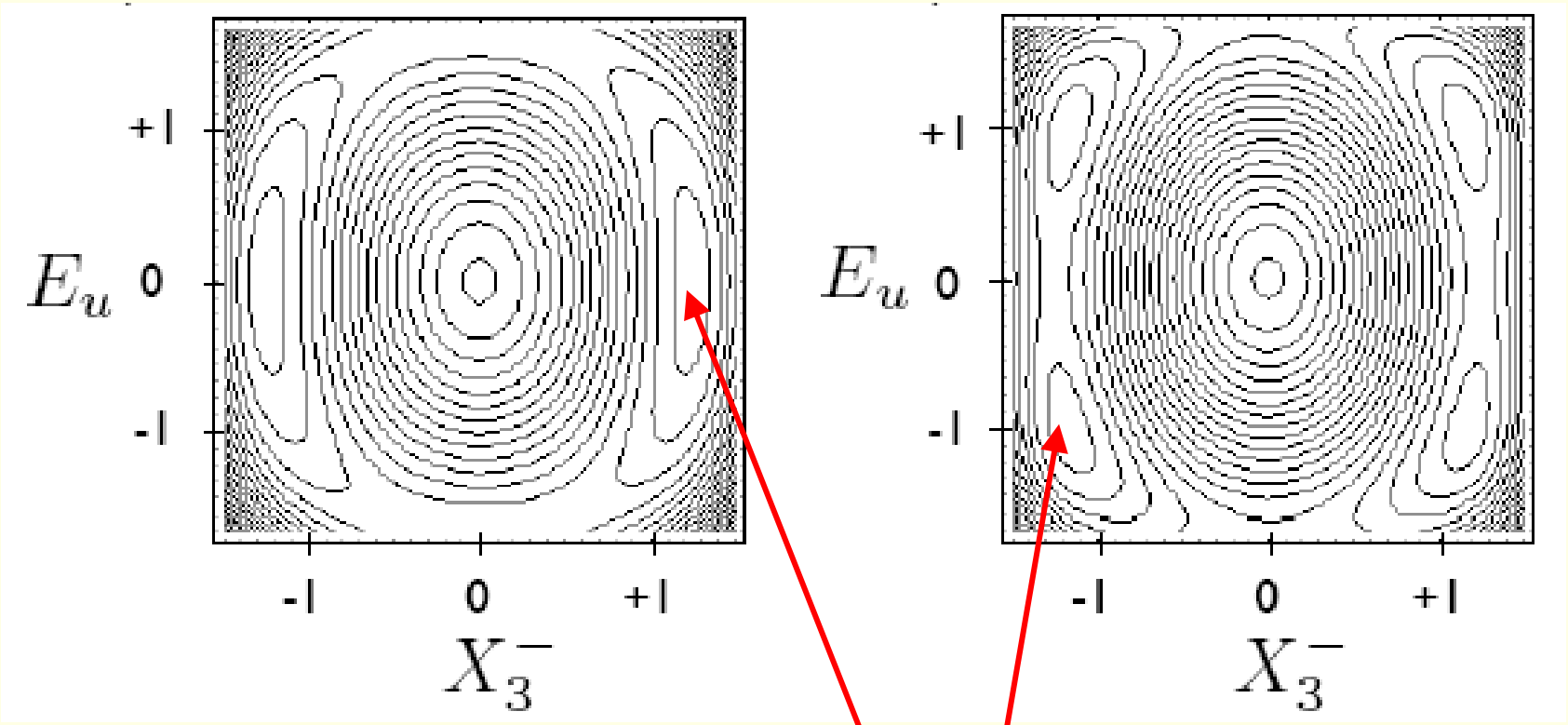
- Coupling with soft X_2^+ mode relatively weak !
- Strong renormalization of hard (second) X_2^+ mode



Energy landscape in SBT

including only soft X_2^+ mode

with additional hard X_2^+ mode

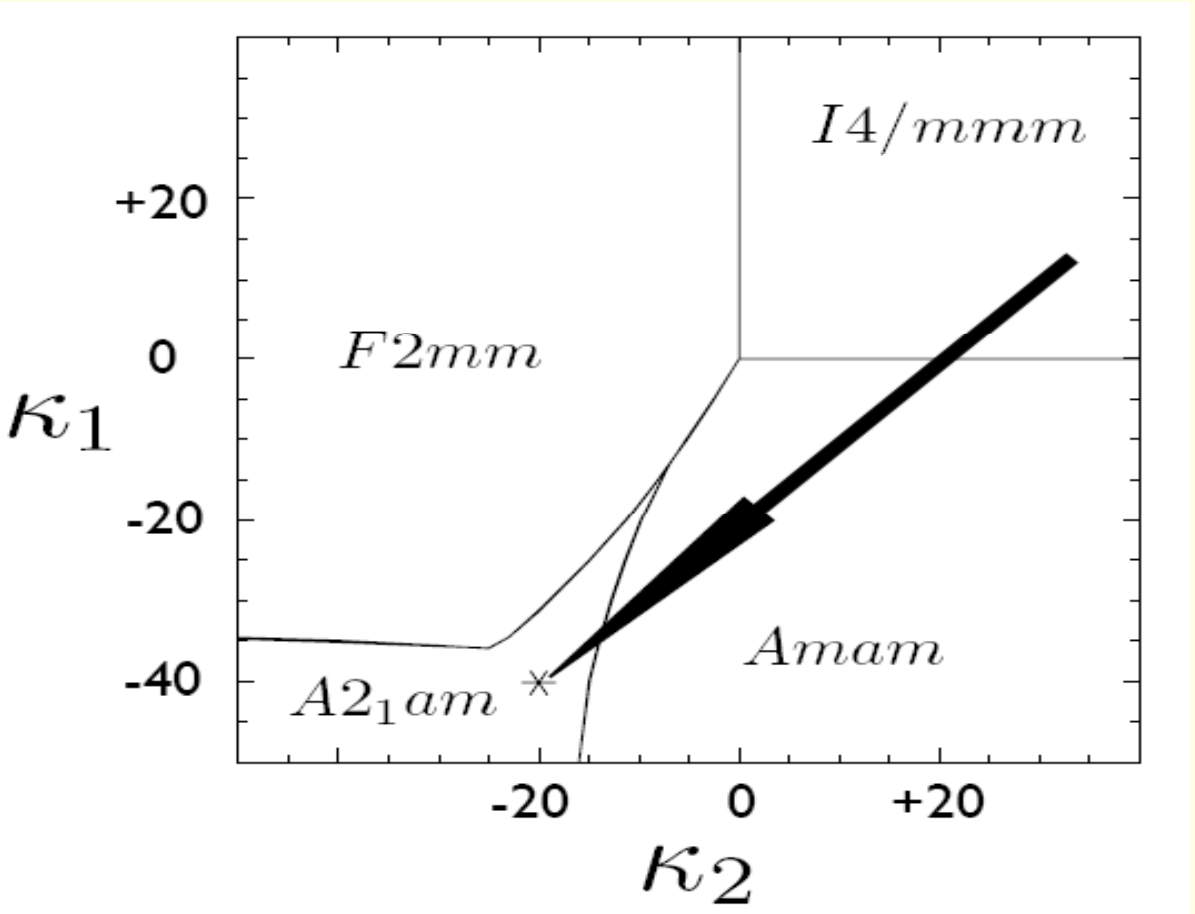


only with the additional hard X_2^+ mode the experimentally observed combination of 3 different modes can be established

Phase diagram for $Bi_2SrTa_2O_9$ - SBT

- Finite temperature renormalization of the T=0 energy map

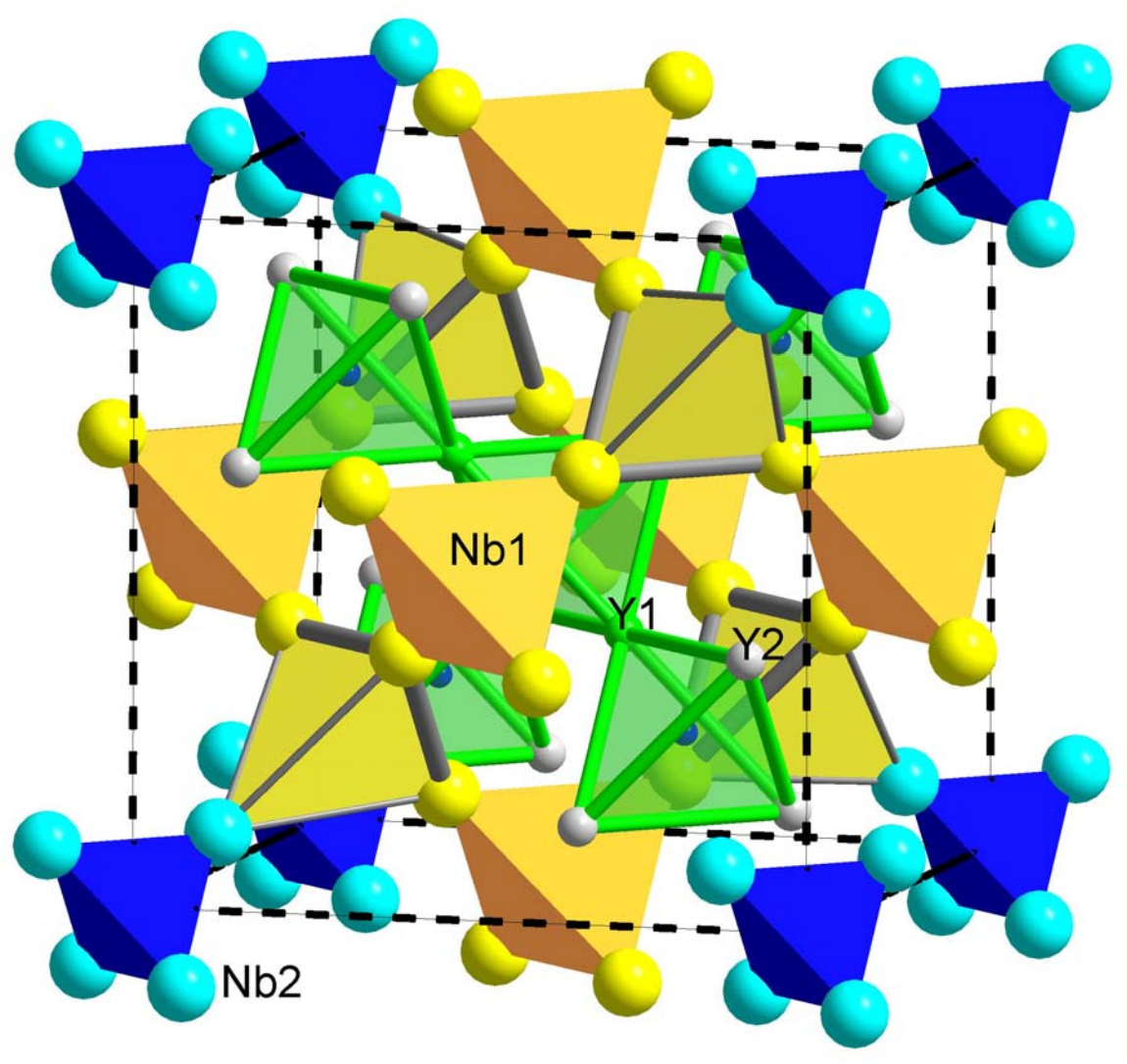
- Landau theory suggests linear T-variation of the quadratic stiffness coefficients κ_{Eu} and κ_{X3^-}

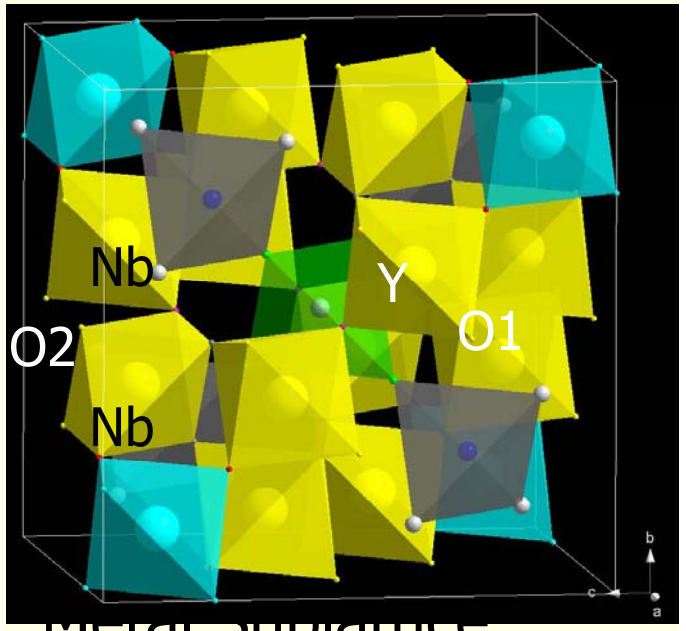


The topology of this phase diagram predicts **two second order** phase transitions and implies the existence of an intermediate phase of *Amam* symmetry. A **single first order** PT is impossible.

Pyrochlore $Y_2Nb_2O_7$

Insulating and non-magnetic **4d** TM-oxide





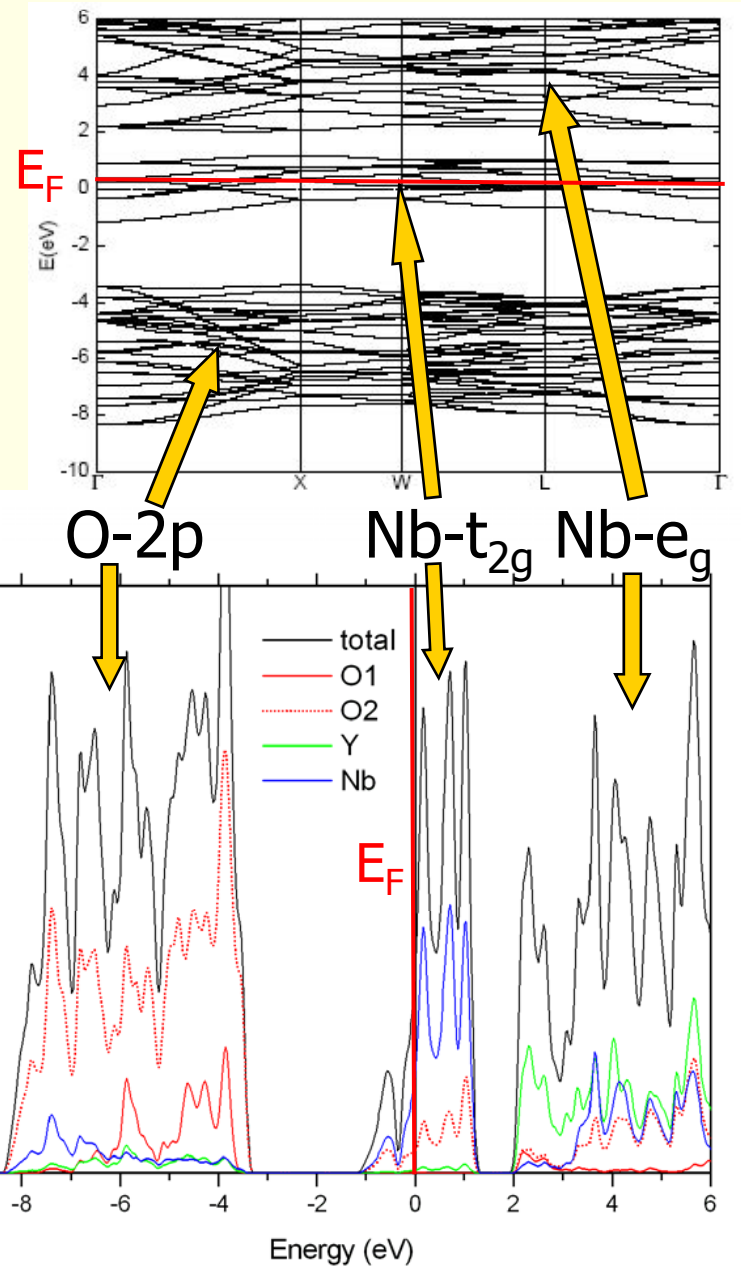
Metal Sublattice:
Corner-shared
tetrahedral network

P.Blaha, D.Singh, K.Schwarz,
PRL 93, 216403 (2004)

First theoretical results:

- Ionic model: $Y_2^{3+}Nb_2^{4+}O_7^{2-}$ Nb^{4+}: $4d^1$
- → metallic or localized system with spin ½ (neither one observed in exp.)
- LDA gives nonmagnetic metallic ground-state with conventional t_{2g}-e_g splitting due to the octahedral crystal field of the oxygen atoms.

"degenerate" t_{2g} states are only partly filled.

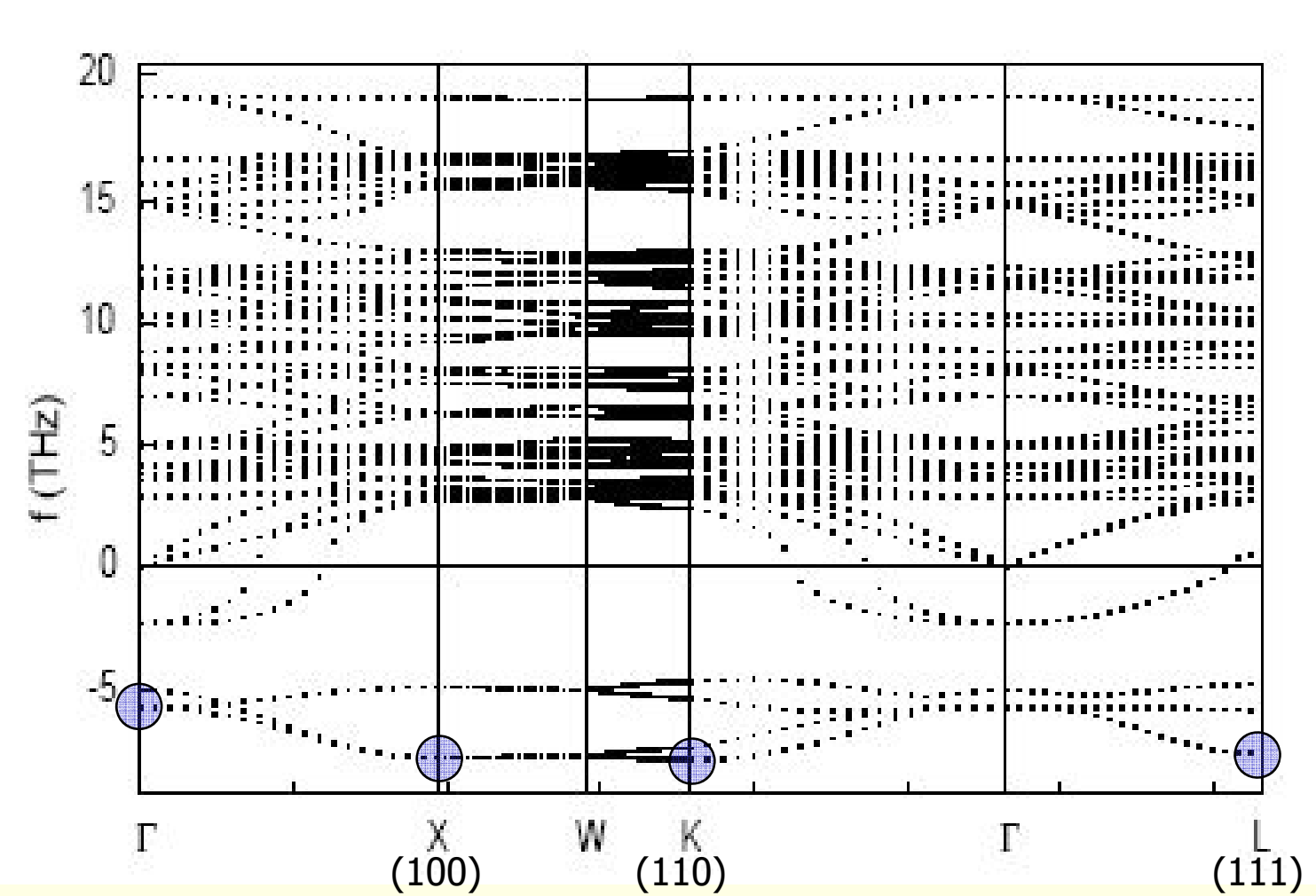


How could one obtain a non-magnetic insulator ?

- Antiferromagnetic s=1/2 solution
  - *(on geometrically frustrated lattice !?)*
- Localization, strong e^--e^- correlation:
  - ***4d*** *(not* ***3d*** *!) electrons,*
  - *thus correlation should be small (Hubbard-U ~ 2-3 eV)*
  - *LDA+U with U=6 eV gives insulator (FM ground state, no AFM)*
  - *bandwidth of t_{2g} bands: 2.5 eV (similar to U)*
- structural distortion, which breaks the dominant octahedral crystal field

- → Search for phonon-instabilities
  - *88 atom supercell, 46 symmetry adapted selected distortions from PHONON; resulting forces → back into PHONON*

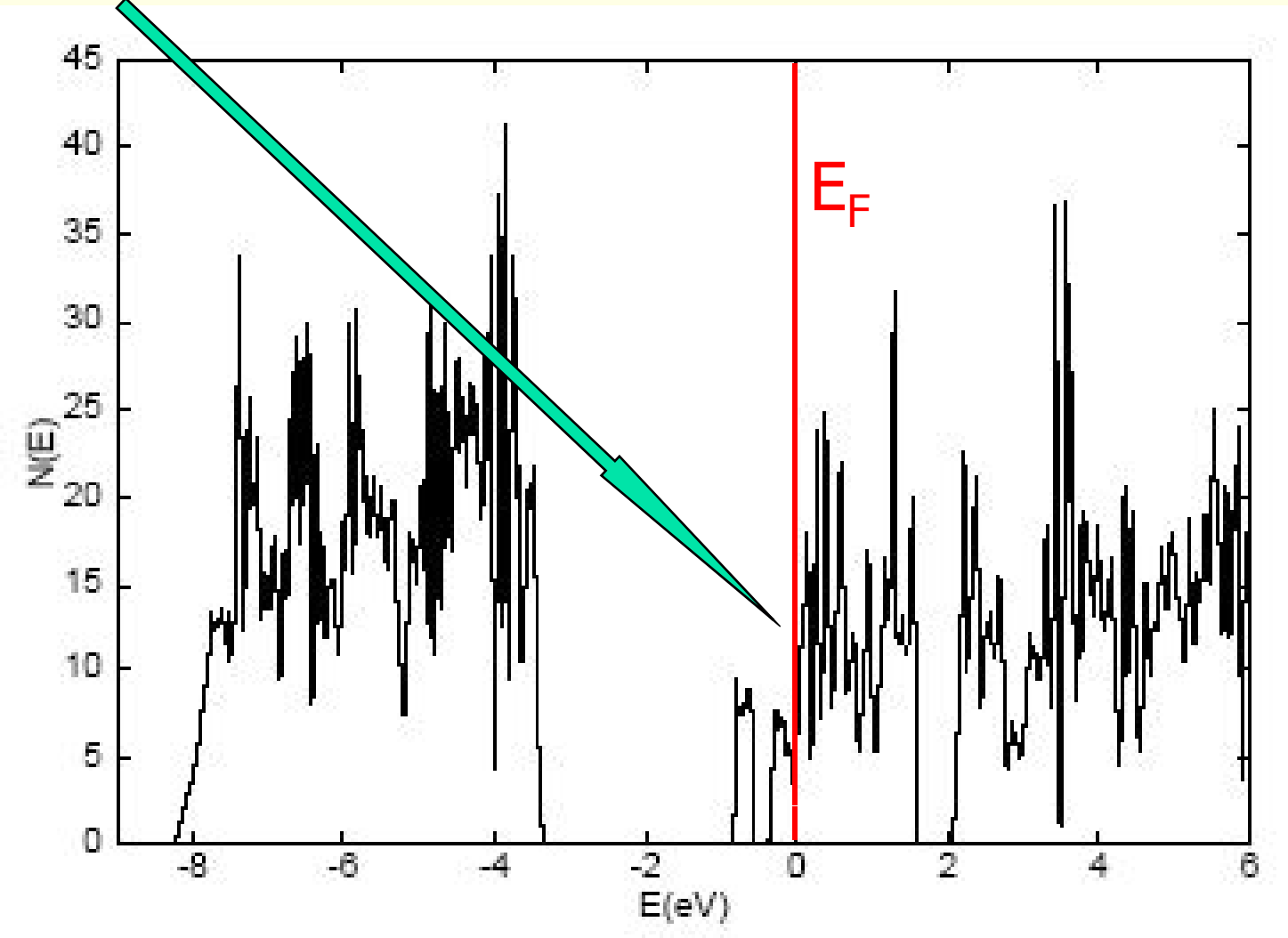
Phonon-bandstructure of $Y_2Nb_2O_7$



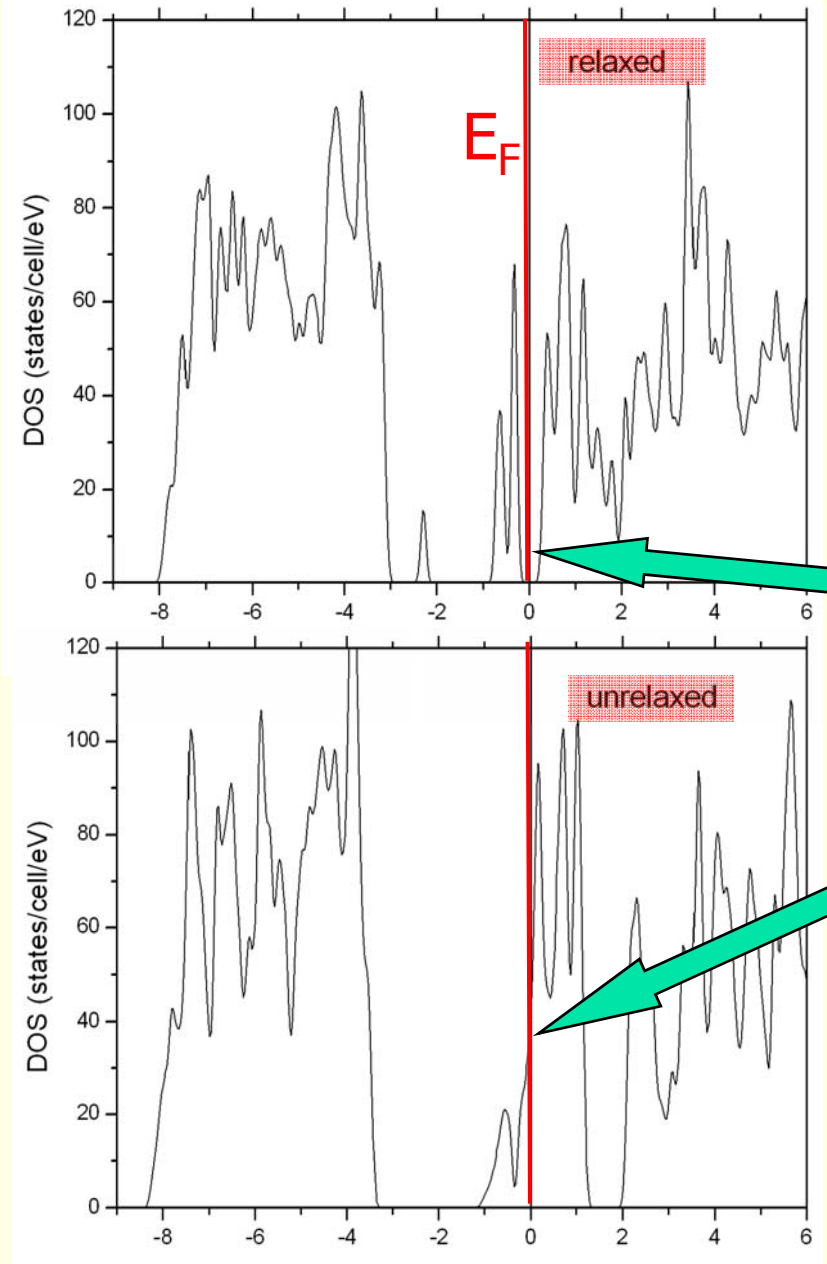
- strong Phonon-instabilities, lowest at X, K, L
- select a certain (unstable) phonon, freeze it into the structure with a certain amplitude and perform full structural optimization

Γ, X and K-point phonons:

- energy lower than in ideal pyrochlore structure, but still not insulating



L-point (111) phonon:



- Relaxed structure is an **Insulator**
- energy gain of 0.5 eV/FU

gap

metal

Relaxed structure:

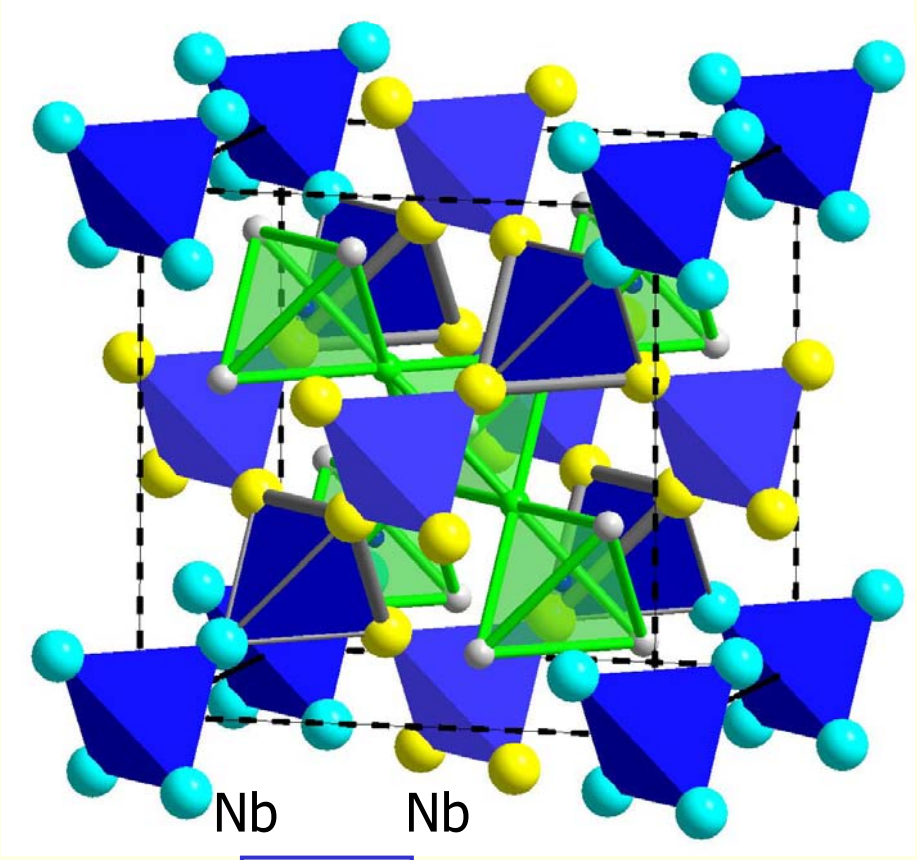
- Primitive supercell with 88 atoms
- all atoms inequivalent

  due to numerical optimization of the positions in P1
- Symmetrization using KPLOT (R.Hundt, J.C.Schön, A.Hannemann, M.Jansen: *Determination of symmetries and idealized cell parameters for simulated structures, J.Appl.Cryst. 32, 413-416* (1999))
  - *Tests possible symmetries with increasing tolerance*

- Space group ➔ P-43m, 88 atoms/cell,
  - *Inequivalent atoms:*
    - 2 Y
    - 2 Nb
    - 3 O1
    - 5 O2

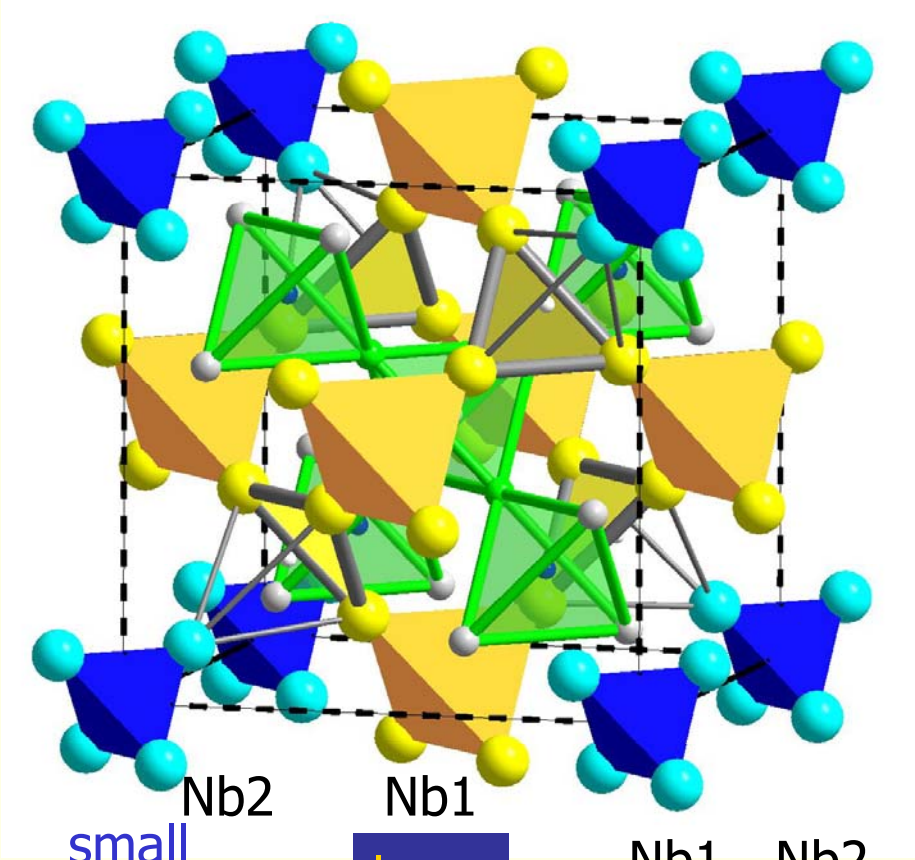
Main change in structural relaxation

Original pyrochlore



3.65 Å equal

Relaxed structure



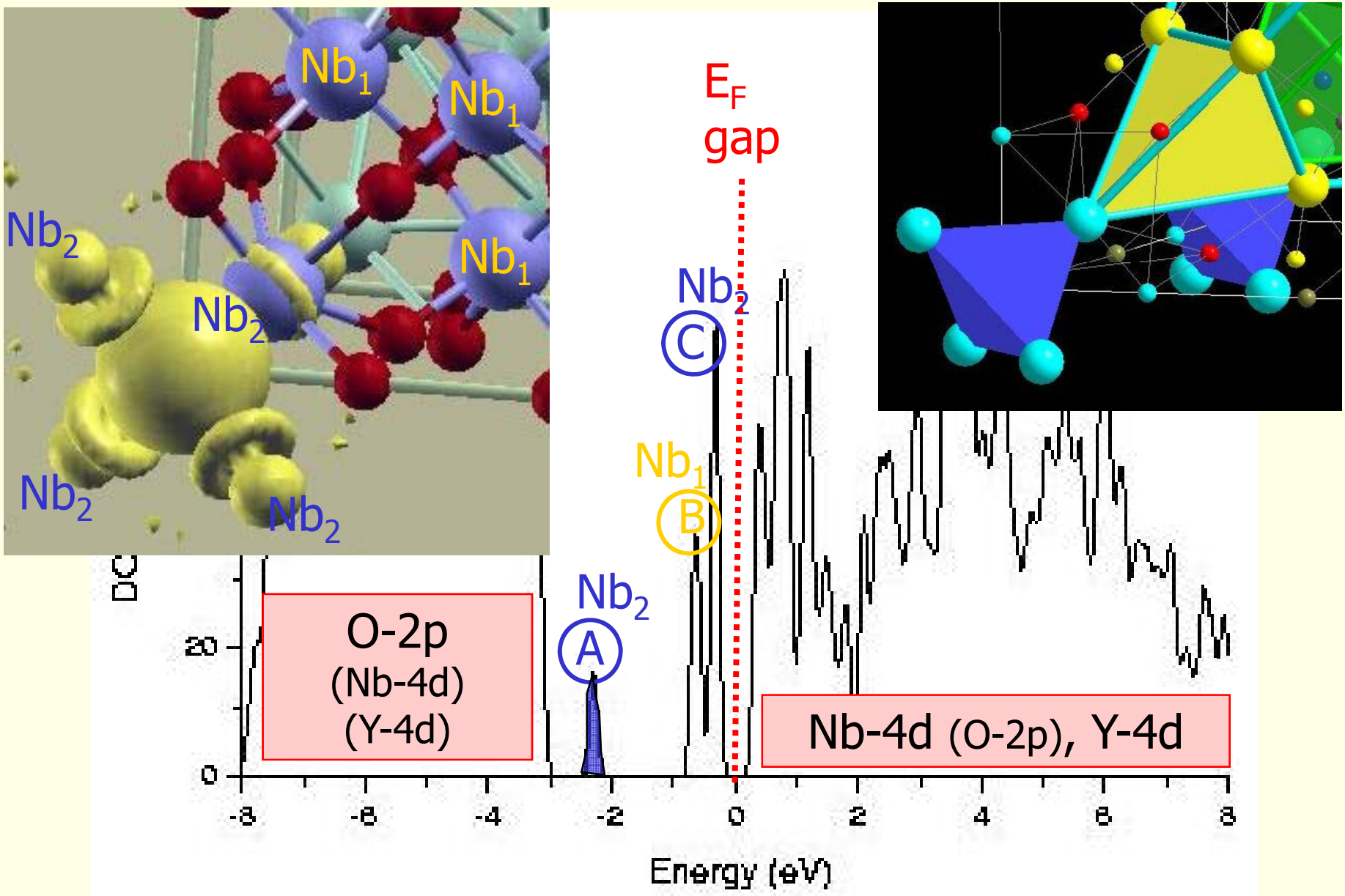
small
2.91 Å

large
3.90 Å

Nb1 - Nb2
3.89 Å

Nb1–triangle: 3.40 Å

Peak A (Nb_2) 4-center bond ($d\text{-}z^2$)



Conclusions

- WIEN2k is a powerful tool to understand solids
  - *electronic and geometric structure*
  - *interpretation of experiments (spectra)*
- Together with PHONON you can calculate phonons also in rather complicated structures
- Use "phonons" not only to match with experiment but to investigate interesting physics
  - *phase transitions*
  - *search for unknown structures*

Thank you for your attention !