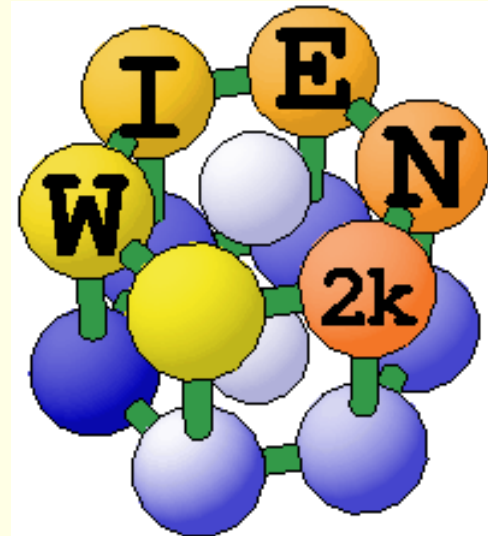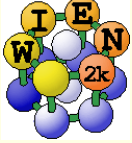# Electronic structure, atomic forces and structural relaxations by WIEN2k

Peter Blaha
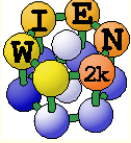
Institute of Materials Chemistry

TU Vienna, Austria

Outline:

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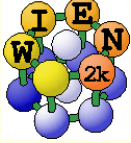 - *Structure of Pyrochlore $Y_2Nb_2O_7$*

APW based schemes

- **APW (J.C.Slater 1937)**
  - *Non-linear eigenvalue problem*
  - *Computationally very demanding*
- **LAPW (O.K.Anderssen 1975)**
  - *Generalized eigenvalue problem*
  - *Full-potential total-energies (A.Freeman etal.)*
- **Local orbitals (D.J.Singh 1991)**
  - *treatment of semi-core states (avoids ghostbands)*
- **APW+lo (E.Sjöstedt, L.Nordstörm, D.J.Singh 2000)**
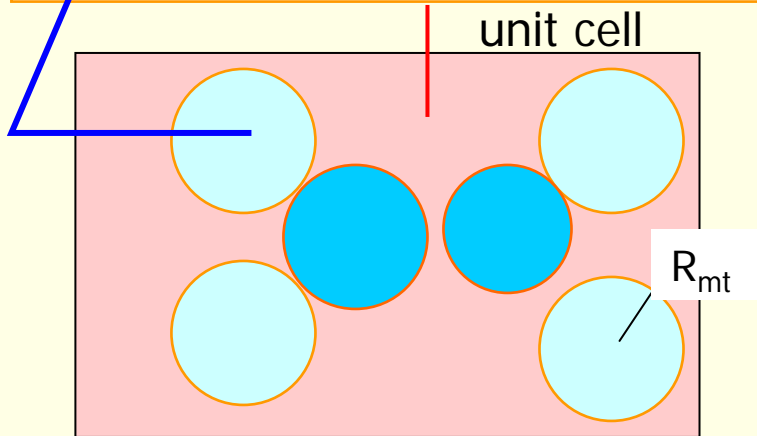 - *Efficience of APW + convenience of LAPW*
  - *Basis for*
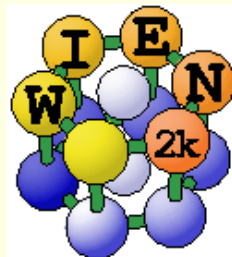
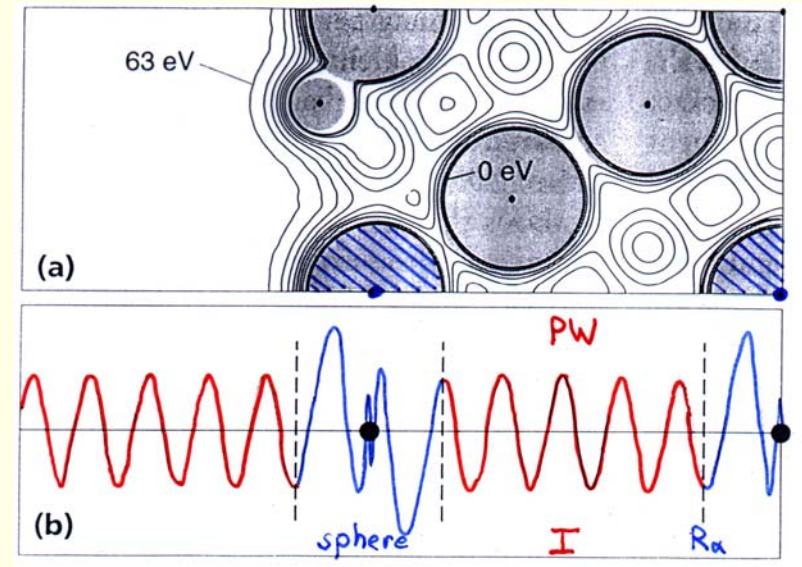K.Schwarz, P.Blaha, G.K.H.Madsen,
Comp.Phys.Commun.**147**, 71-76 (2002)

The unit cell is partitioned into:
  atomic spheres
  Interstitial region

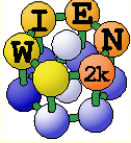Bloch wave function:
  atomic partial waves
  Plane Waves (PWs)

unit cell

R_{mt}

63 eV

0 eV

(a)

PW

(b) sphere   I R_α

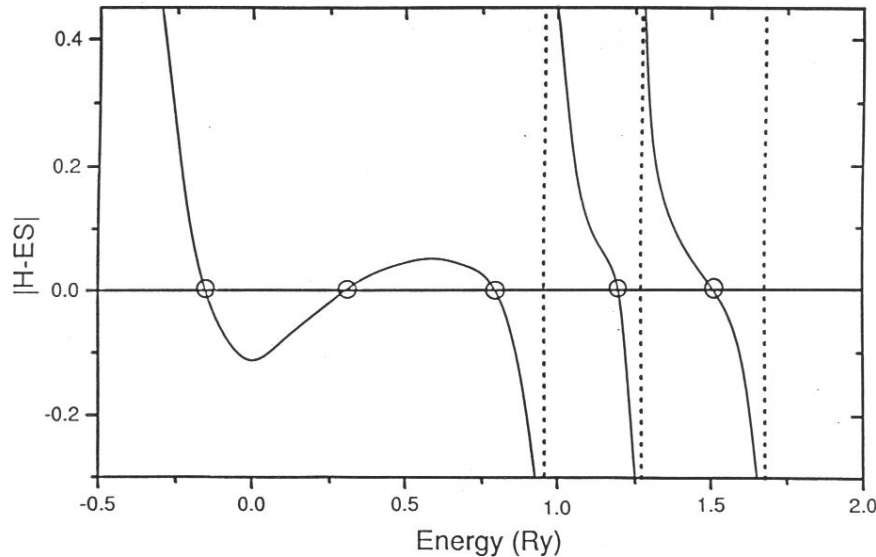PW: $e^{i(\vec{k}+\vec{K}).\vec{r}}$ ── join ── Atomic partial waves
$$\sum_{\ell m} a_{\ell m}^{K} u_{\ell}(r', \varepsilon) Y_{\ell m}(\hat{r}')$$

matching coefficient, radial function, spherical harmonics

Atomic partial waves

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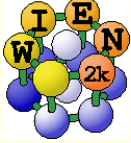
Energy dependent

Radial basis functions lead to

H Hamiltonian
S Overlap matrix

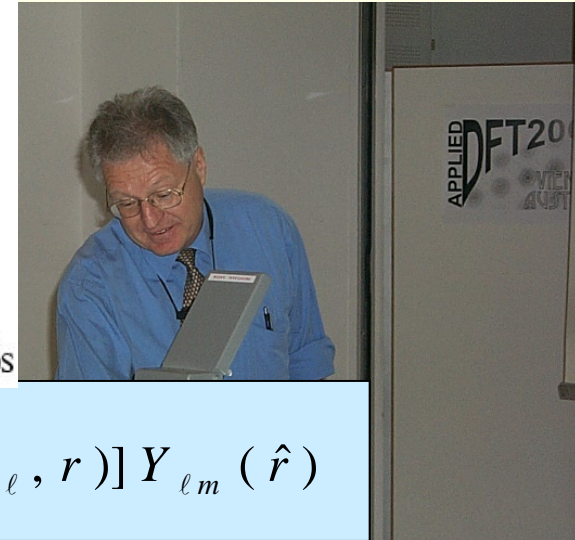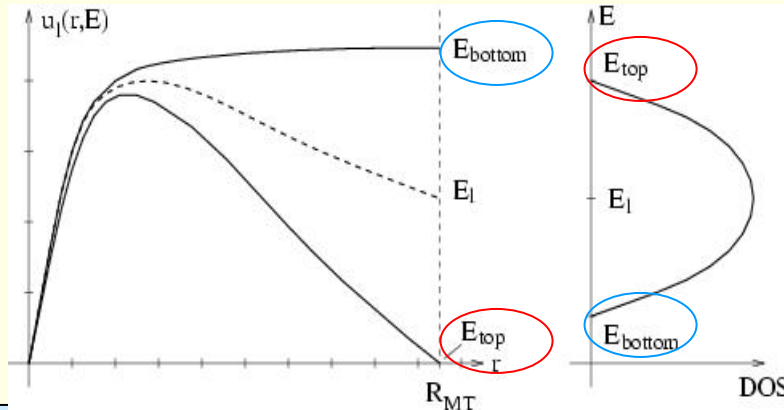**Non-linear eigenvalue problem**

Computationally very demanding

One had to numerically search for the energy, for which the det|H-ES| vanishes.

Linearization of energy dependence

LAPW suggested by

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

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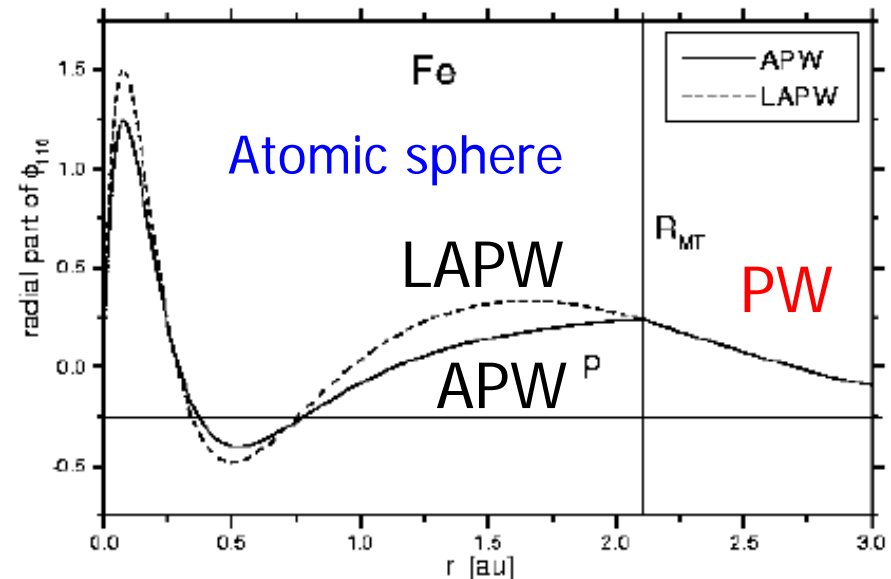
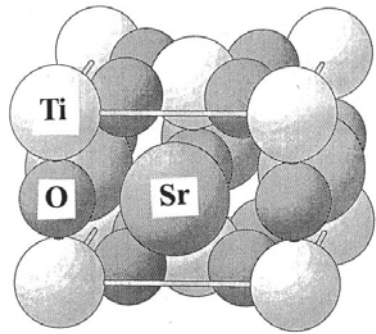$$\dot{u}_l = \partial u_l / \partial \varepsilon$$

join PWs in value and slope

u_l expanded at E_l („energy parameter")
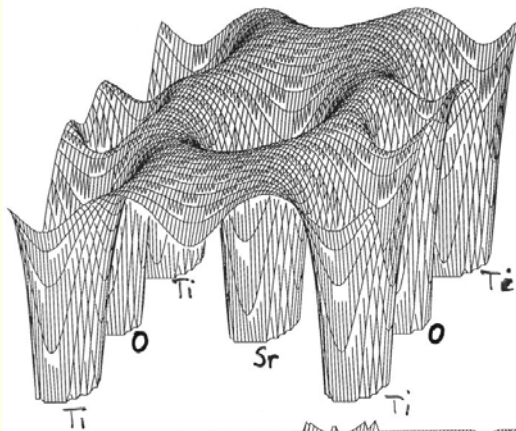
→additional constraint requires more PWs than APW
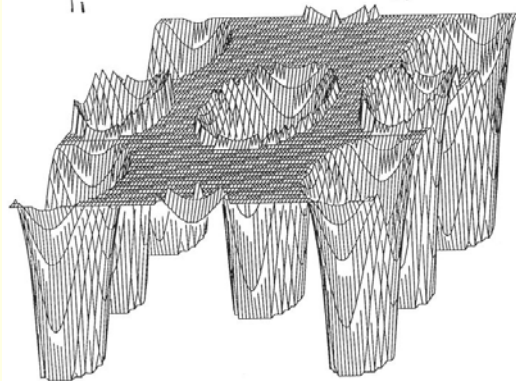
basis flexible enough for single diagonalization

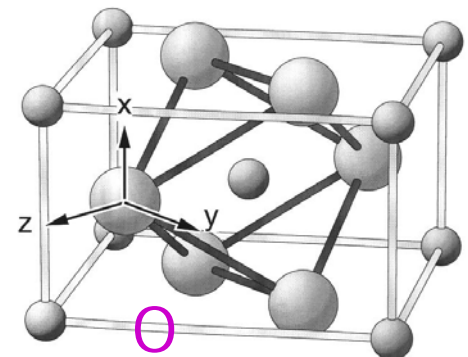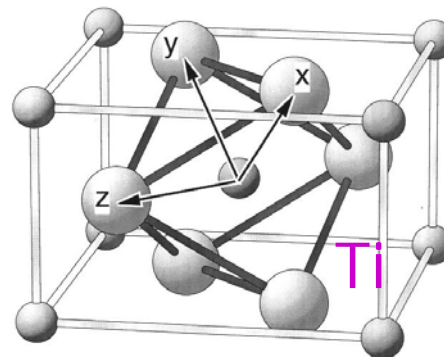# Full-potential total-energy (A.Freeman etal.)

SrTiO$_3$

Full potential

Muffin tin approximation
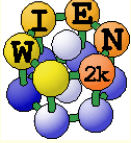
TiO$_2$ rutile

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

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

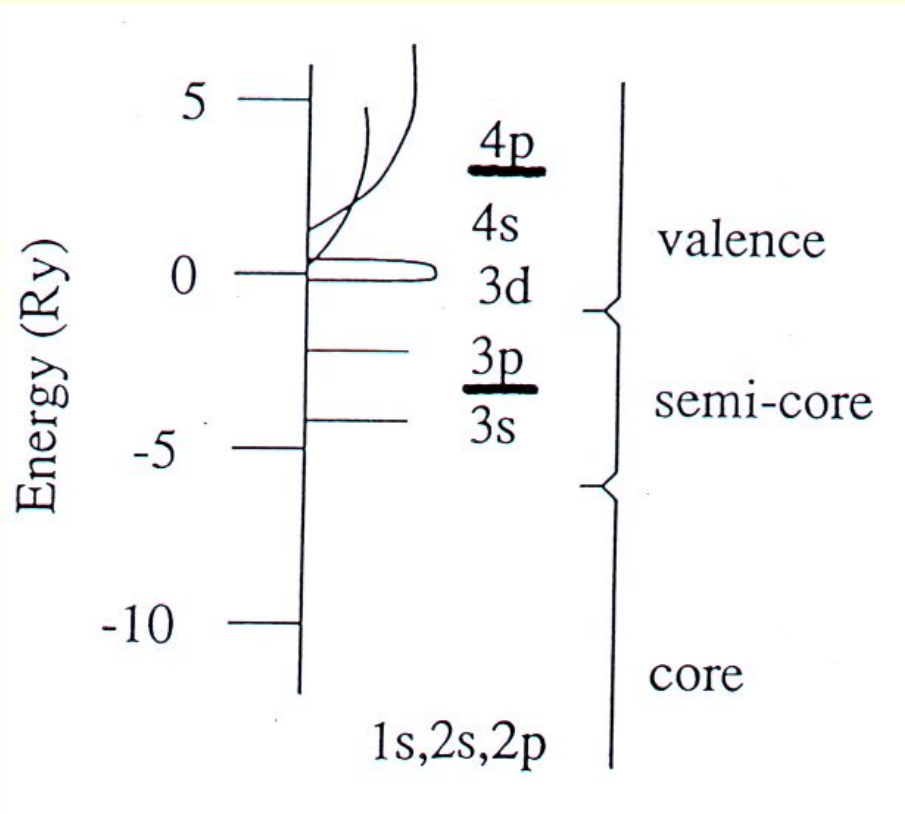- Inside each atomic sphere a local coordinate system is used
  (defining LM)

Ti

O

For example: Ti

- **Valences states**
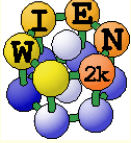 - *High in energy*
  - *Delocalized wavefunctions*
- **Semi-core states**
  - *Medium energy*
  - *Principal QN one less than valence (e.g.in Ti 3p and 4p)*
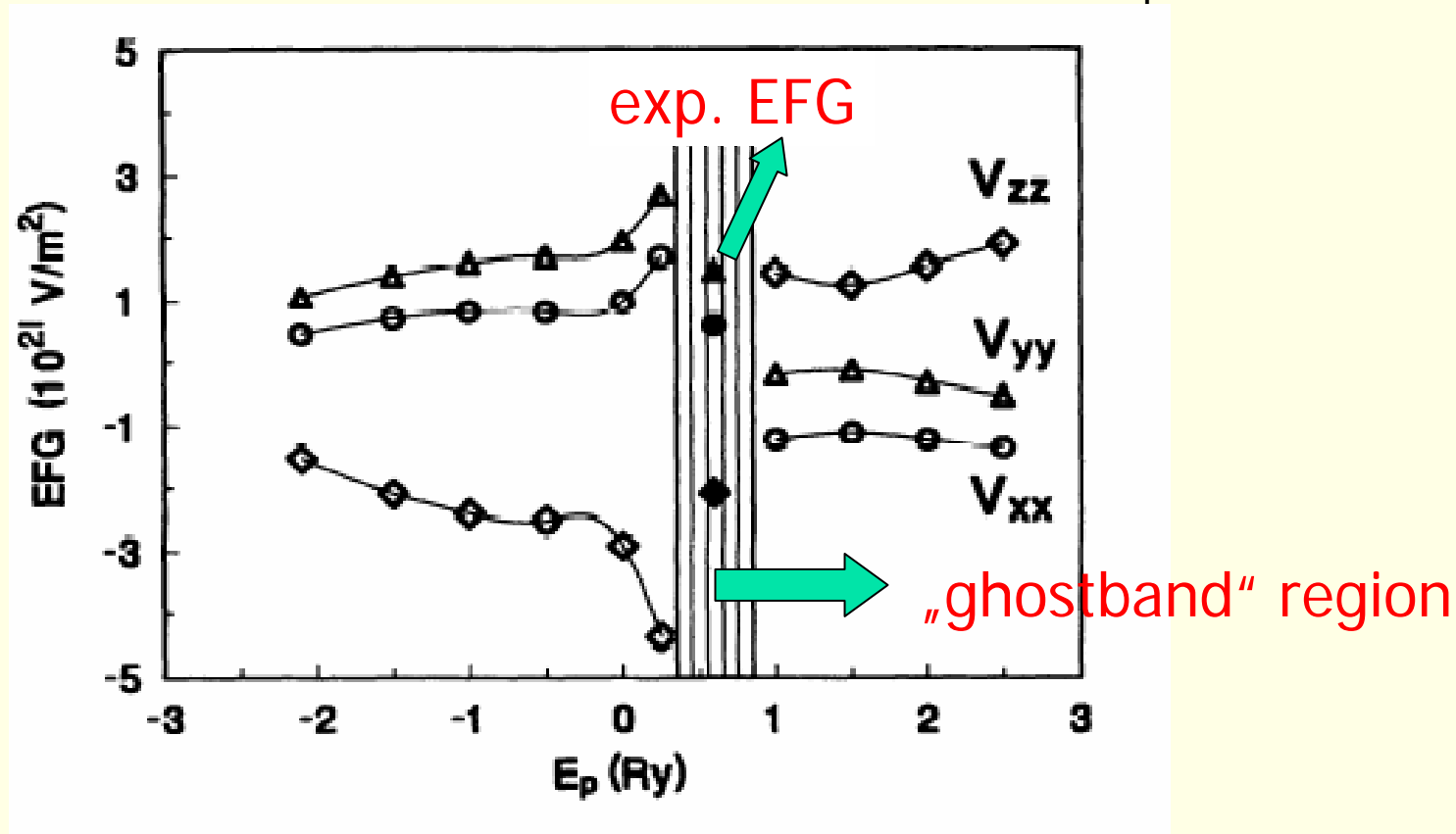 - *not completely confined inside sphere*
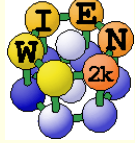- **Core states**
  - *Low in energy*
  - *Reside inside sphere*

Problems of the LAPW method:

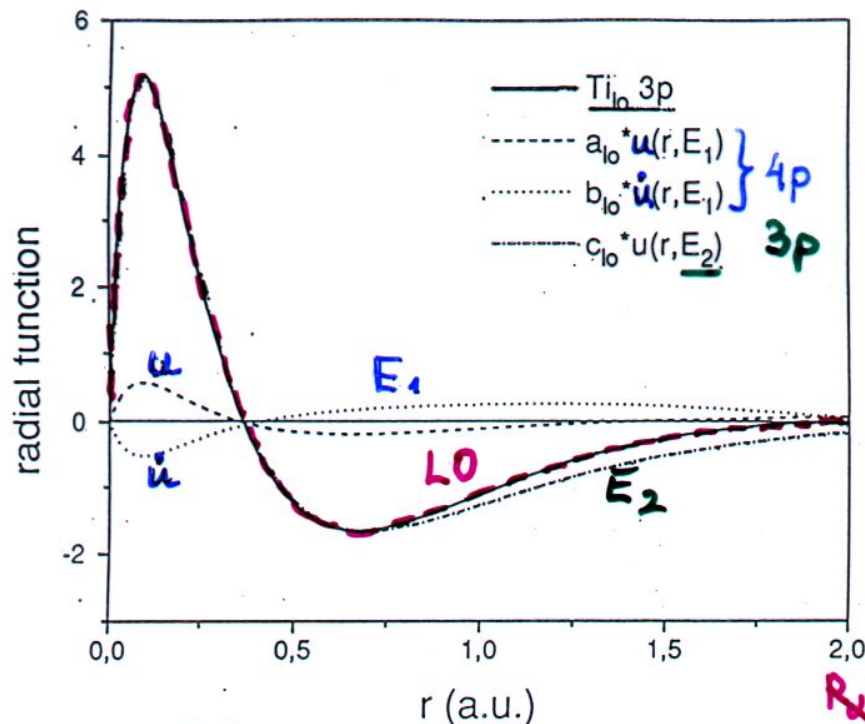## EFG Calculation for Rutile TiO_2 as a function of the Ti-p linearization energy E_p

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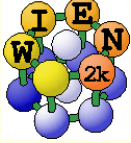Phys. Rev. B **46**, 1321 (1992).

Problems with semi-core states

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

- LO ⬆4p ⬆3p

  - *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)

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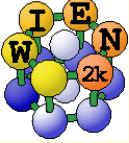Solid State Commun. 114, 15 (2000)

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

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

$$\Phi_{lo} = [A_{\ell m} u_\ell^{E_1} + B_{\ell m} \dot{u}_\ell^{E_1}] Y_{\ell m}(\hat{r})$$
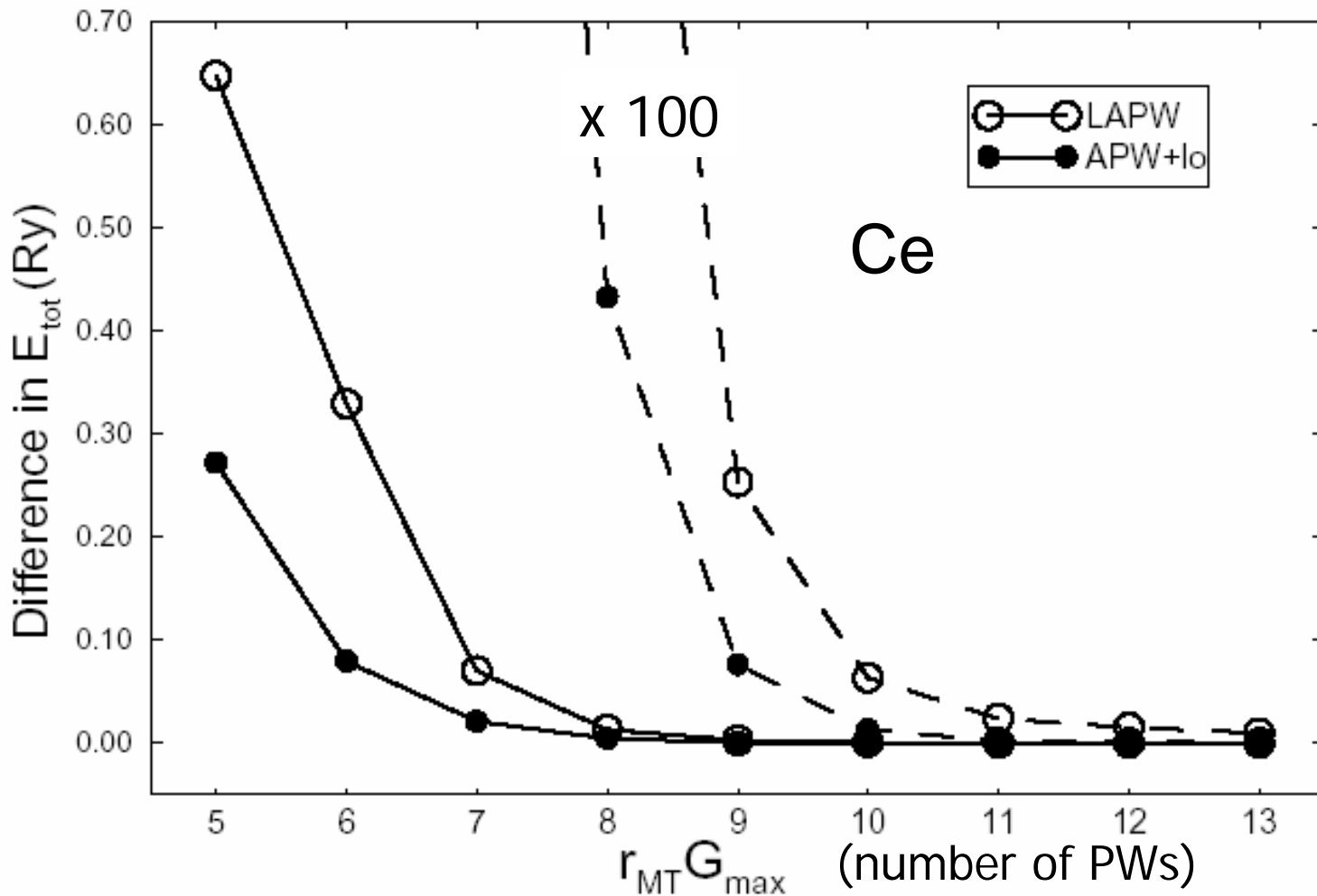
optimal solution: mixed basis (K.Schwarz, P.Blaha, G.K.H.Madsen,
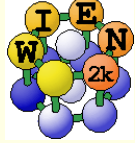Comp.Phys.Commun.**147**, 71-76 (2002))

- 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 angular momenta

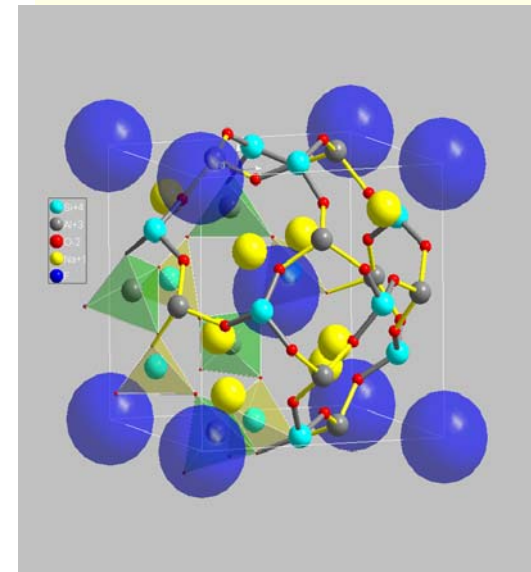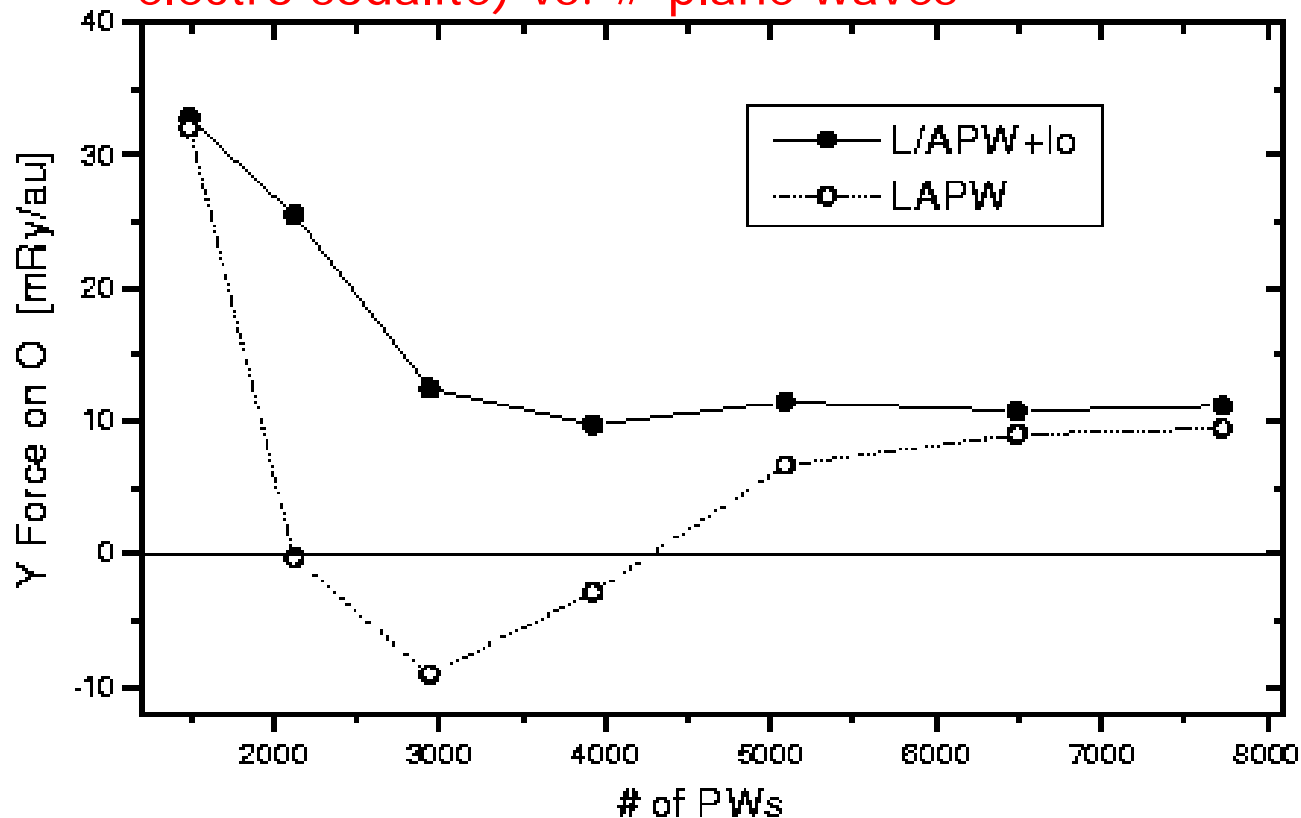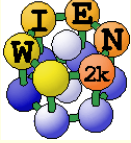E. Sjostedt, L. Nordstrom and D.J. Singh, Solid State Commun. **114**, 15 (2000).

Improved convergence of APW+lo

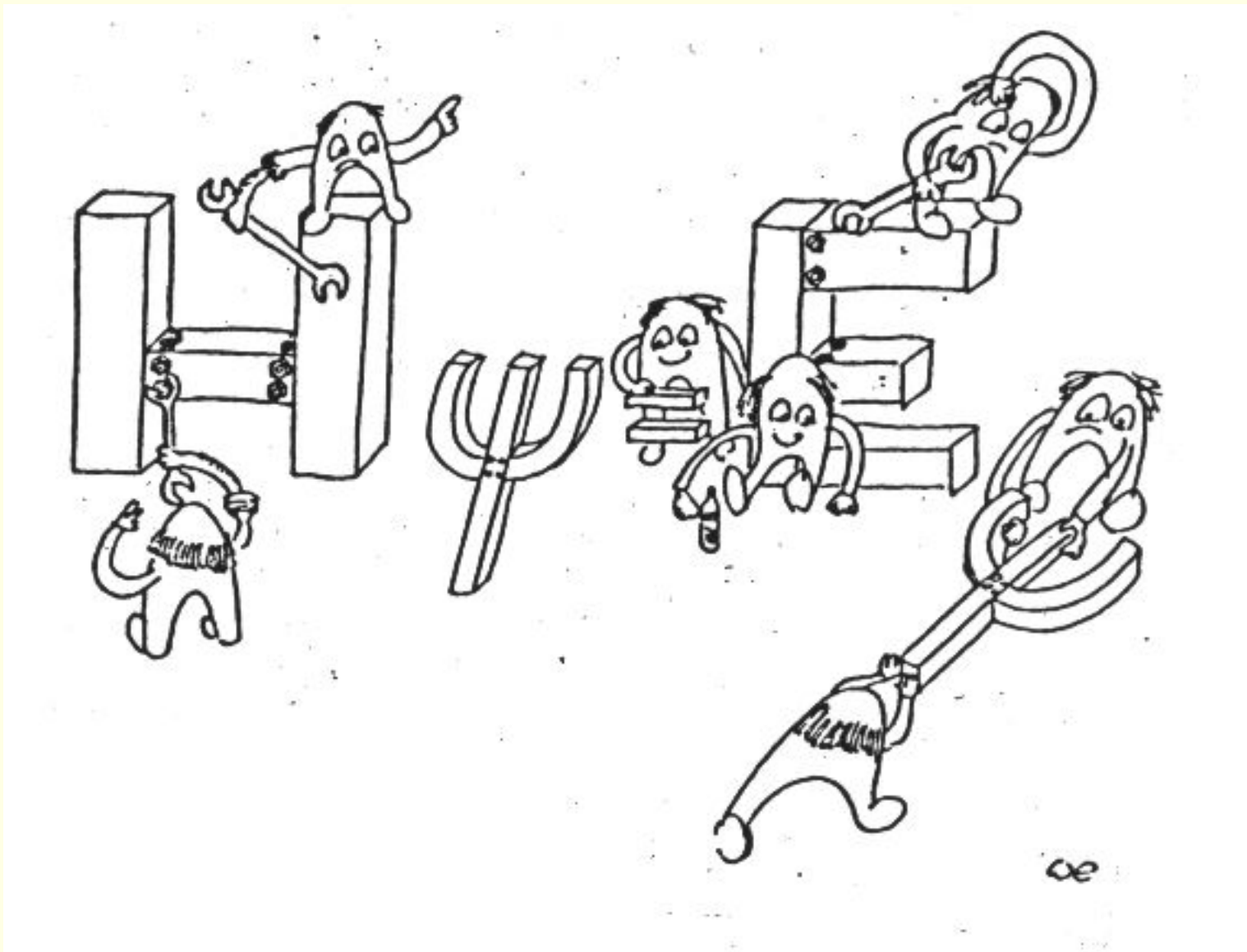K.Schwarz, P.Blaha, G.K.H.Madsen,
Comp.Phys.Commun.**147**, 71-76 (2002)

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

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

WIEN2k software package

**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
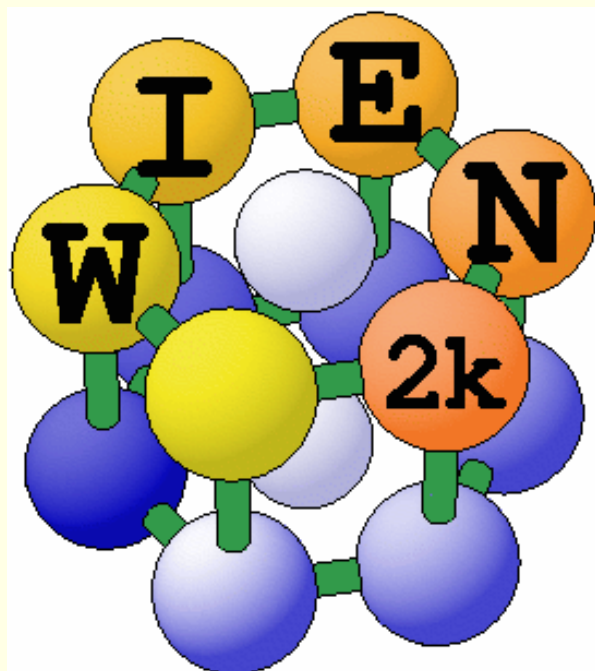
WIEN97: ~500 users
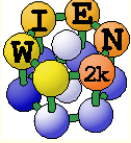WIEN2k: ~730 users

Development of WIEN2k

- **Authors of WIEN2k**

  P. Blaha, K. Schwarz, D. Kvasnicka, G. Madsen and J. Luitz

- **Other contributions to WIEN2k**

  - *C. Ambrosch-Draxl (Univ. Graz, Austria), optics*
  - *U. Birkenheuer (Dresden), wave function plotting*
  - *T. Charpin (Paris), elastic constants*
  - *R. Dohmen und J. Pichlmeier (RZG, Garching), parallelization*
  - *R. Laskowski (Vienna), non-collinear magnetism*
  - *P. Novák and J. Kunes (Prague), LDA+U, SO*
  - *B. Olejnik (Vienna), non-linear optics*
  - *C. Persson (Uppsala), irreducible representations*
  - *M. Scheffler (Fritz Haber Inst., Berlin), forces*
  - *D.J.Singh (NRL, Washington D.C.), local oribtals (LO), APW+lo*
  - *E. Sjöstedt and L Nordström (Uppsala, Sweden), APW+lo*
  - *J. Sofo and J. Fuhr (Barriloche), Bader analysis*
  - *B. Yanchitsky and A. Timoshevskii (Kiev), spacegroup*
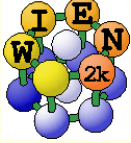
- **and many others ....**

- **More than 700 user groups worldwide**
  - *40 industries (Canon, Eastman, Exxon, Fuji, A.D.Little, Mitsubishi, Motorola, NEC, Norsk Hydro, Osram, Panasonic, Samsung, Sony, Sumitomo).*
  - *Europe: (EHT Zürich, MPI Stuttgart, Dresden, FHI Berlin, DESY, TH Aachen, ESRF, Prague, Paris, Chalmers, Cambridge, Oxford)*
  - *America: ARG, BZ, CDN, MX, USA (MIT, NIST, Berkeley, Princeton, Harvard, Argonne NL, Los Alamos Nat.Lab., Penn State, Georgia Tech, Lehigh, Chicago, SUNY, UC St.Barbara, Toronto)*
  - *far east: AUS, China, India, JPN, Korea, Pakistan, Singapore,Taiwan (Beijing, Tokyo, Osaka, Sendai, Tsukuba, Hong Kong)*
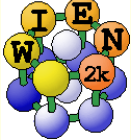- **Registration at www.wien2k.at**
  - *400/4000 Euro for Universites/Industries*
  - *code download via www (with password), updates, bug fixes, news*
  - *usersguide, faq-page, mailing-list with help-requests*

WIEN2k- hardware/software
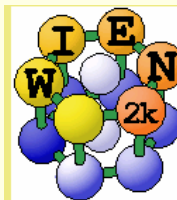
- WIEN2k runs on any Unix/Linux platform from PCs, workstations, clusters to supercomputers

- Fortran90 (dynamical allocation)

- many individual modules, linked together with C-shell or perl-scripts

- f90 compiler, BLAS-library (mkl, Atlas), perl5, ghostview, gnuplot, Tcl/Tk (Xcrysden), www-browser

- web-based GUI – w2web
- real/complex version (inversion)
- 10 atom cells on 128Mb PC
- 100 atom cells require 1-2 Gb RAM
- k-point parallel on clusters with common NFS (slow network)
- MPI/Scalapack parallelization for big cases (>50 atoms) and fast network
- installation support for many platforms

Session: **TiC** User: **pblaha**
/susi/pblaha/lapw/TiC

Thu Nov 29 13:22:25 2001
STATUS: idle
refresh   norefresh

w2web, the fully web-enabled interface to WIEN2k
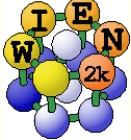
Execution >>
  StructGen™
  initialize calc.
  run SCF
  single program
  command line

Utils. >>

Tasks >>

Files >>
  struct file(s)
  input files
  output files
  SCF files

Session Mgmt. >>
  change session
  change directory
  change info

Configuration >>

Usersguide
  html–Version
  pdf–Version

Session Name:	TiC
Session ID:	599582
Directory:	/susi/pblaha/lapw/TiC
Last changed:	Wed Nov 21 10:12:17 2001
Comments:	

☐ spin polarized calculation
☐ AFM calculation
☐ complex calculation (no inversion)
☐ parallel calculation

Change session information

w2web @ luitz.at

2web

Idea and realization by *luitz.at* © 2001

- **Based on www**
  - *WIEN2k can be managed remotely via w2web*
  - *Secure (Password)*
- **Important steps:**
  - *start w2web on all your hosts*
  - *use your favorite browser and connect to the master host:port*
  - *define a session on the desired host*

Welcome to *w2web*
the fully web–enabled interface to WIEN2k

Select stored session:

show only selection

Fccni
TiC
TiO2
bccw
fcccu_ldau
fcccu
fccyb_sp
fccyb
he_surf_0
nibnn
si_goessl
test
tic_goessl
tic_puls
tio_puls

Select

Create new session:

Session_name

Create

on host–node

master node
http://jupiter:10000
http://homer:10000
http://pauli:10000
http://fp98.zserv:10000
http://hal.zserv:10000

edit hosts

w2web © luitz.at

W2web

GUI (Graphical user interface)

- **Structure generator**
  - *cif-file converter*
  - *spacegroup selection*
- **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*
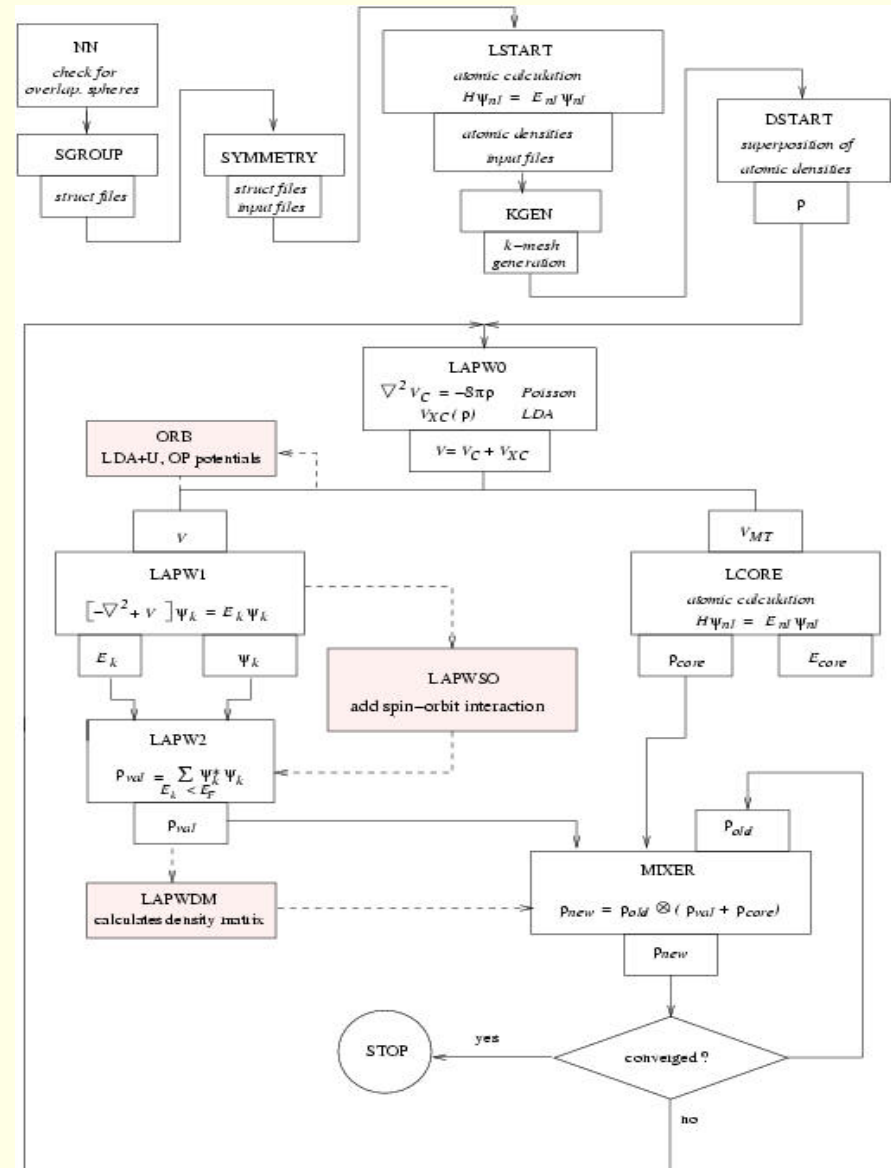 - *Electron density*
  - *X-ray spectra*
  - *Optics*

Session: **TiC** User: **pblaha**
/susi/pblaha/lapw/TiC

Thu Nov 29 13 23 11 2001
STATUS: idle
refresh   norefresh

StructEdit /susi/pblaha/lapw/TiC

StructGen™

You have to click "Save Structure" for changes to take effect!

Save Structure

Execution >>
StructGen™
initialize calc.
run SCF
single program
command line

Utils. >>

Tasks >>

Files >>
struct file(s)
input files
output files
SCF files

Session Mgmt. >>
change session
change directory
change info

Configuration >>

Usersguide
html-Version
pdf-Version

Title: TiC

Treatment of core: relativistic

Lattice:
Type: F

P
F
B

inequivalent Atoms: **2**

Lattice parameters in   Å

a= 4.46770858   b= 4.46770858   c= 4.46770858

a= 90.000000   b= 90.000000   g= 90.000000

Atom 1: Ti   I   Z= 22.0   remove atom

NPT= 781   RMT= 2.000   RO= 0.00005   Non-cubic

Pos 1: x= 0.00000000   y= 0.00000000   z= 0.00000000   remove
add position

Atom 2: C   I   Z= 6.0   remove atom

NPT= 781   RMT= 1.900   RO= 0.00010   Non-cubic

Pos 1: x= 0.50000000   y= 0.50000000   z= 0.50000000   remove
add position

add an atom

Number of symmetry operations: 48

Idea and realization by *lwitz.at* ©2001

Program structure of WIEN2k

- **init_lapw**
  - *initialization*
  - *symmetry detection (F, I, C-centering, inversion)*
  - *input generation with recommended defaults*
  - *quality (and computing time) depends on k-mesh and R.Kmax (determines #PW)*

- **run_lapw**
  - *scf-cycle*
  - *optional with SO and/or LDA+U*
  - *different convergence criteria (energy, charge, forces)*

Task for electron density plot

- **A task consists of**
  - *a series of steps*
  - *that must be executed*
  - *to generate a plot*
- **For electron density plot**
  - *select states (e.g. valence e⁻)*
  - *select plane for plot*
  - *generate 3D or contour plot with gnuplot or Xcrysden*

- **Energy bands**
  - *classification of irreducible representations*
  - *´character-plot´ (emphasize a certain band-character)*
- **Density of states**
  - *including partial DOS with l and m- character (eg. p_x , p_y , p_z)*
- **Electron density, potential**
  - *total-, valence-, difference-, spin-densities, ρ of selected states*
  - *1-D, 2D- and 3D-plots (Xcrysden)*
  - *X-ray structure factors*
  - *Bader´s atom-in-molecule analysis, critical-points, atomic basins and charges ($\nabla \rho . \vec{n} = 0$)*
  - *spin+orbital magnetic moments (spin-orbit / LDA+U)*
- **Hyperfine parameters**
  - *hyperfine fields (contact + dipolar + orbital contribution)*
  - *Isomer shift*
  - *Electric field gradients*

- **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 transititons (momentum transfer)
  - *optical properties (dielectric function, JDOS including momentum matrix elements and Kramers-Kronig)*
  - *fermi surface (2D, 3D)*
- **Total energy and forces**
  - *optimization of internal coordinates, (MD, BROYDEN)*
  - *cell parameter only via E_{tot} (no stress tensor)*
  - *elastic constants for cubic cells*
  - *Phonons via supercells*
    - interface to PHONON (K.Parlinski) – bands, DOS, thermodynamics, neutrons

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

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

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

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

- **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*
- *Pulay corrections*
  - Core
  - Valence

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

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

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

$$F_{val}^\alpha = \int_\alpha V_{eff}(r)\nabla_\alpha \rho_{val}(r)\ d\vec{r} + \sum_{k,i} n_i \sum_{K,K'} c_i^*(K')c_i(K) \times$$
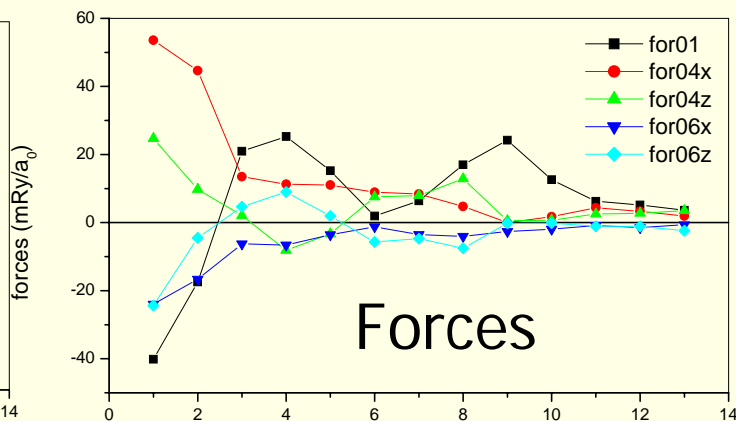
$$\left[(K^2 - \varepsilon_i)\oint \phi_{K'}^*(r)\phi_K(r)\ dS_\alpha - i(K - K')\langle\phi_{K'}|H - \varepsilon_i|\phi_K\rangle_\alpha\right]$$
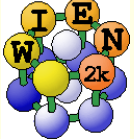
- damped Newton scheme
(not user friendly, input adjustment by hand)
- new quite efficient Broyden scheme

W impurity in Bi (2x2x2 cell: $Bi_{15}W$)
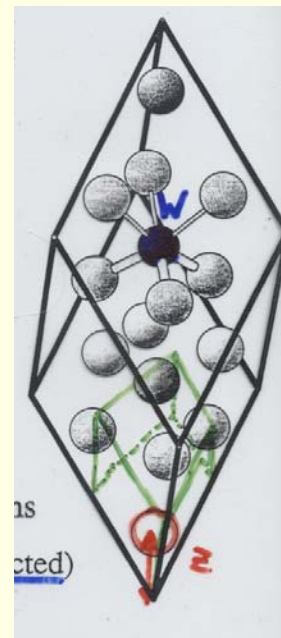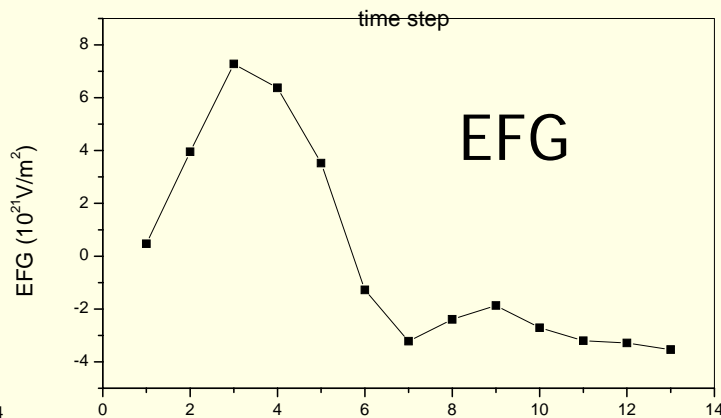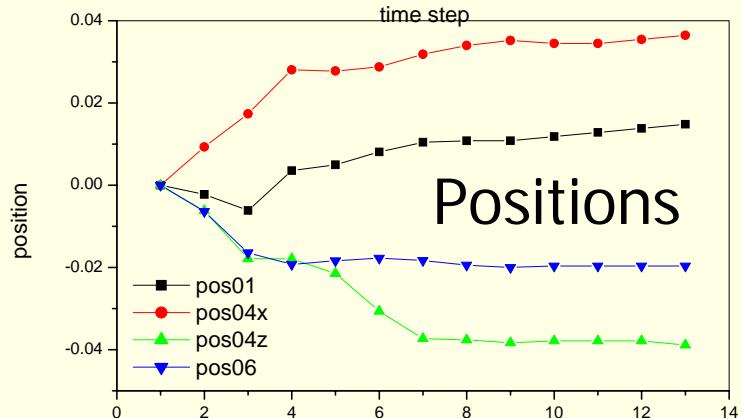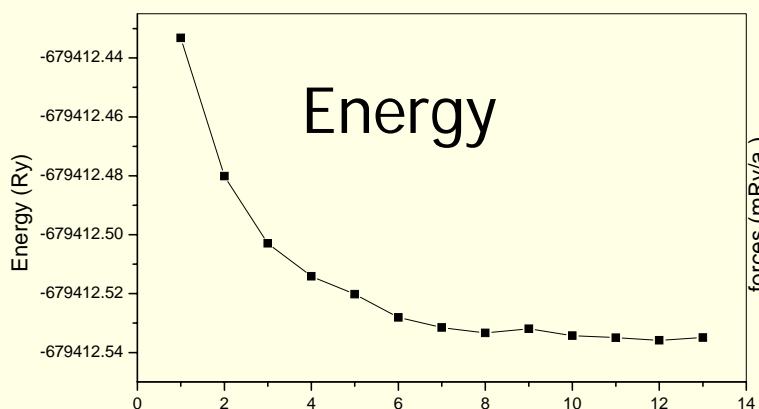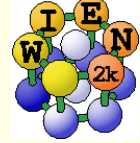
- **PHONON**
  - *by K.Parlinski (Crakow)*
  - *runs under MS-windows*
  - *uses a „direct" method to calculate Force-constants with the help of an ab initio program*
  - *with these Force-constants phonons at arbitrary k-points can be obtained*

- **Define your spacegroup**
- **Define all atoms at previously optimized positions**
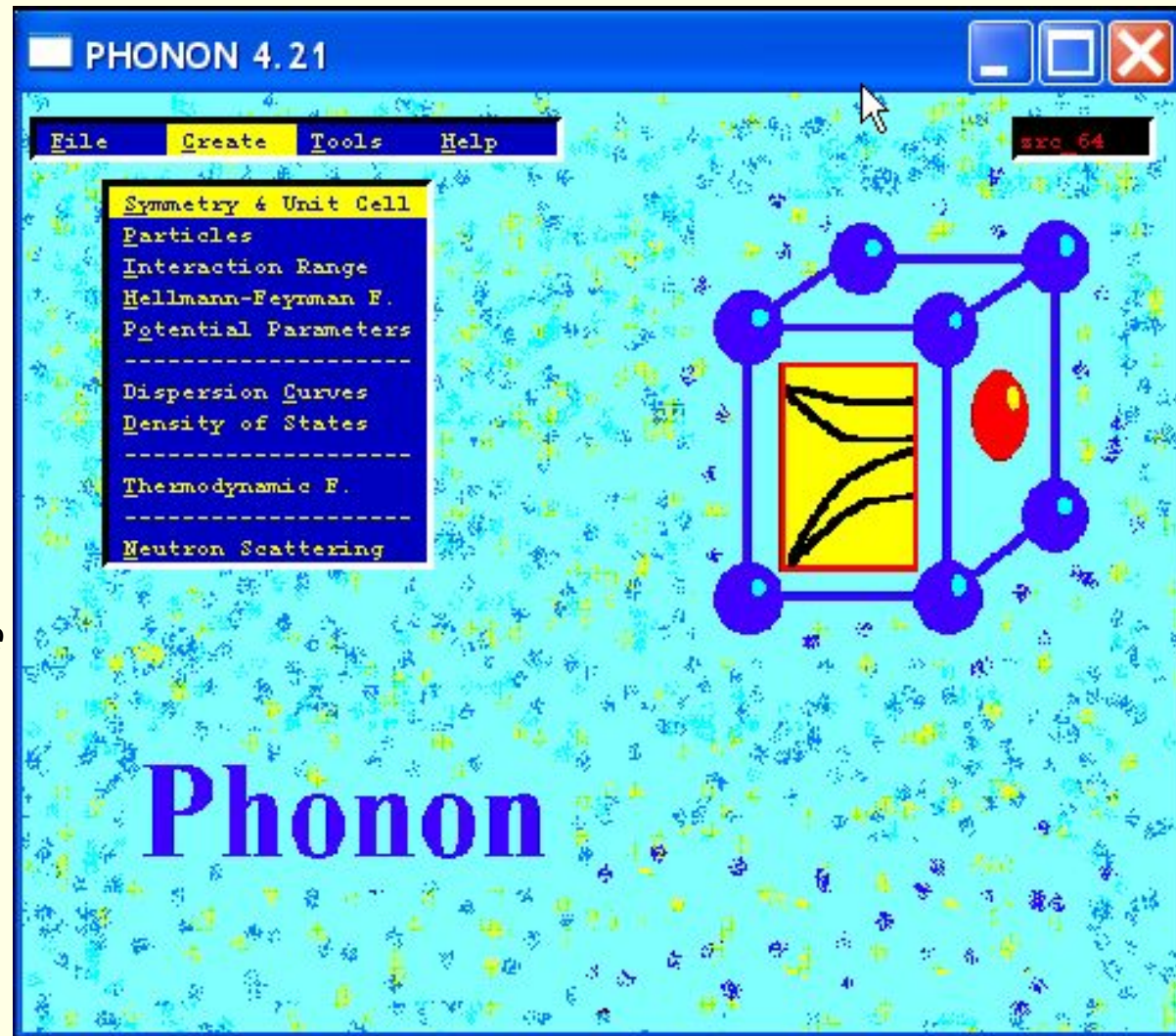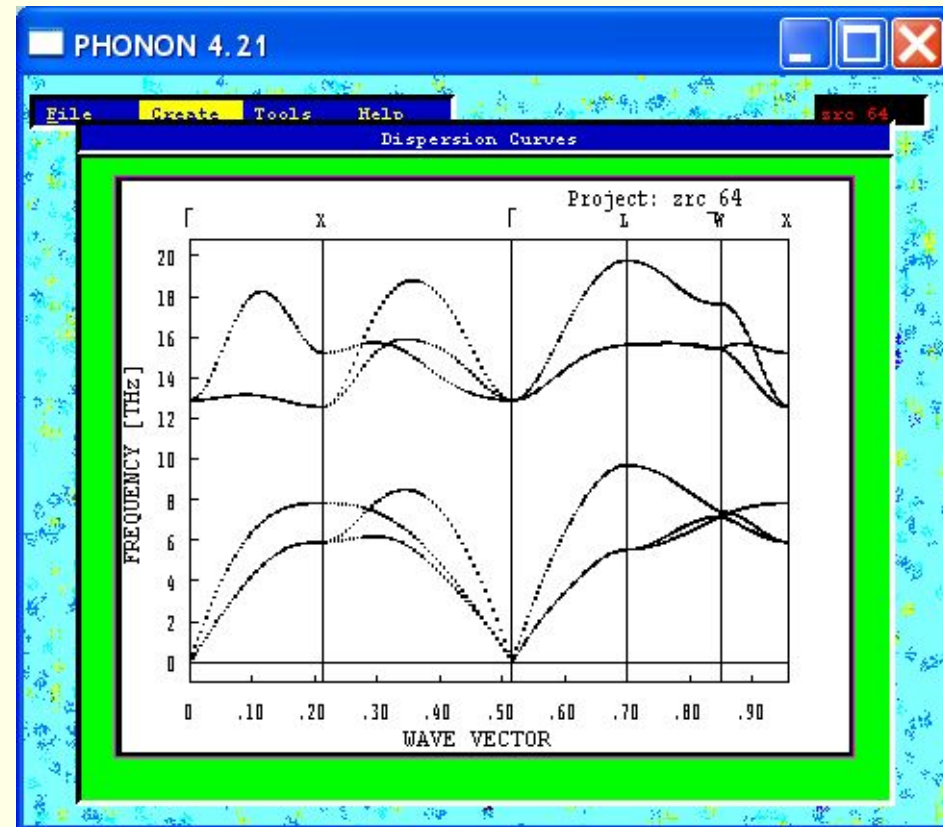
PHONON-II

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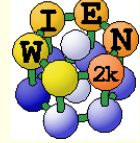
- **analyze_phonon_lapw**
  - *reads the forces of the scf runs*
  - *generates „Hellman-Feynman" file case.dat and a „symmetrized HF-file case.dsy (when you have displacements in both directions)*
    - check quality of forces:
    - sum F_x should be small (0)
    - abs(F_x) should be similar for +/-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

PHONON 4.21

File   Create   Tools   Help   zrc 64

Dispersion Curves

Project: zrc 64

- ***Bilbao: J. Manuel Perez-Mato, M. Aroyo**
- **Universidad del País Vasco**
- ***Vienna: P. Blaha, K. Schwarz,**
- **J. Schweifer**
- ***Cracow: K. Parlinski**
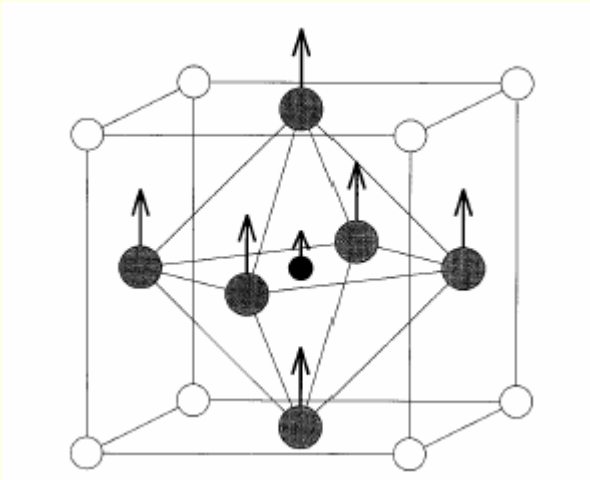
Classical Example of a Ferroelectric

PbTiO$_3$

(perovskite distorted structure)

Features:

• spontaneous polarization- frozen polar mode
• phase transition:

$$\text{paraelectric} \xrightarrow{\text{Tc}} \text{ferroelectric}$$

$PbTiO_3$
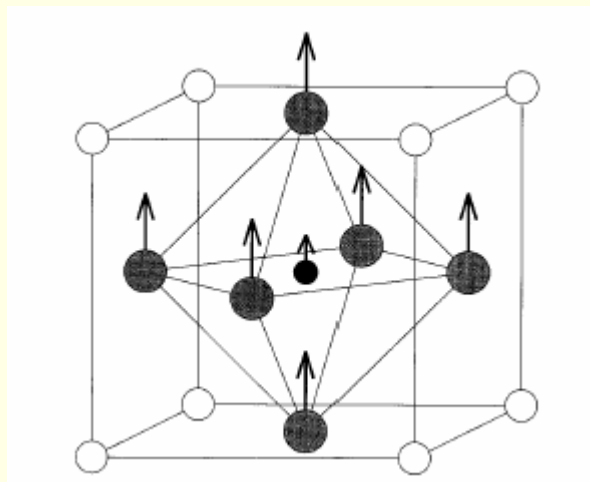
- **Symmetry break at Tc:**

    cubic   ---- tetragonal

    Pm-3m ----- P4mm
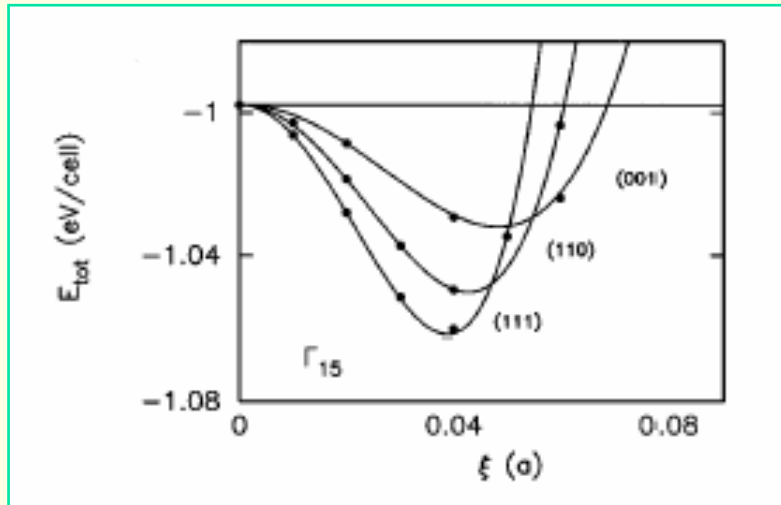
- **A single (degenerate) *normal* mode responsible for the transition**

- **Structure in Ferroelectric Phase:**

    high-symmetry structure + frozen polar mode

- **Strain: spontaneous strain $\Delta\varepsilon \approx 10^{-2}$**
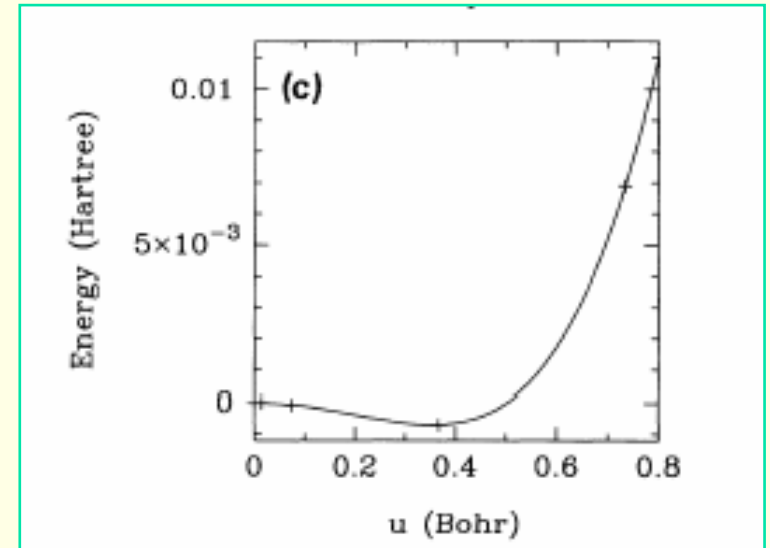
PbTiO$_3$

Waghmare&Rabe 1997

King-Smith&Vanderbilt 1994
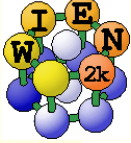
Ab-initio
Phonon Branches
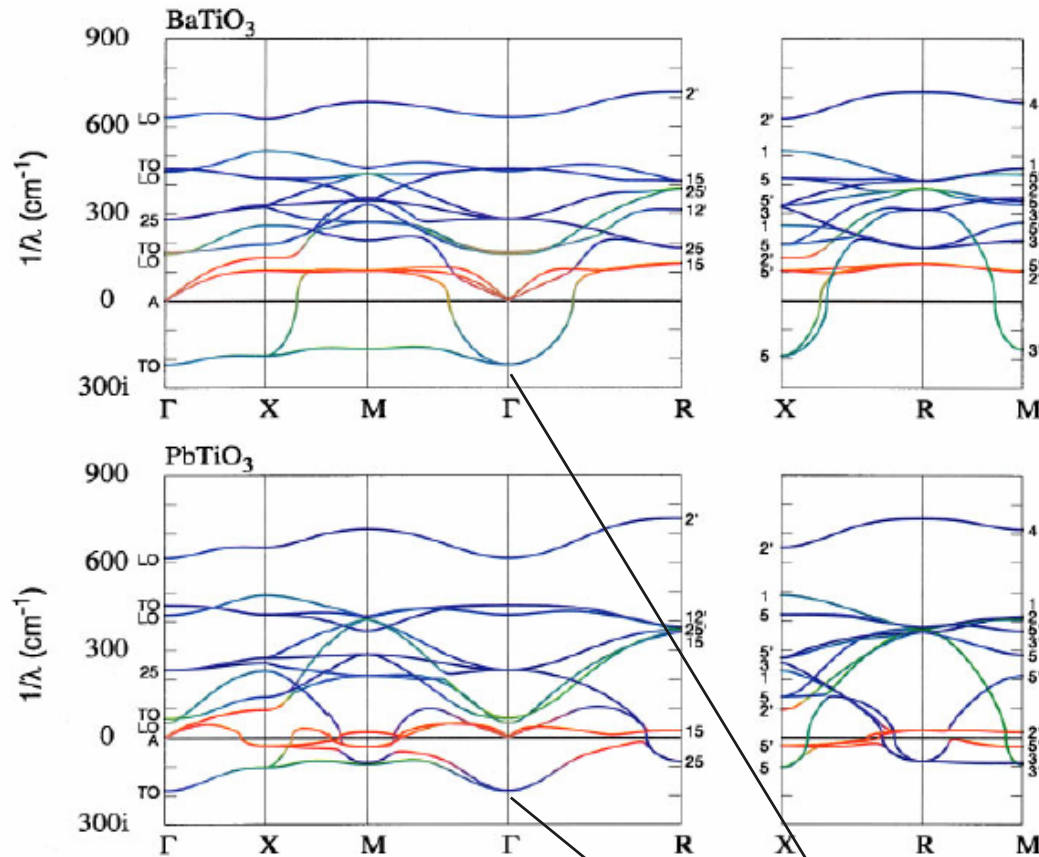
Ghosez et al. 1999

Polar unstable mode

The Aurivillius Compounds

orthorhombic $\rightarrow$ A2$_1$am

B2ab

A2$_1$am

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

Bi$_2$O$_2$

n-sized perovskite slab

cation deficient perovskites:

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

n=2

n=3

n=4

Ps

Dipl. Thesis -S. Borg 2001

Bi$_2$SrTa$_2$O$_9$ -   SBT

Sr

Bi

O3

O2

O4

O1
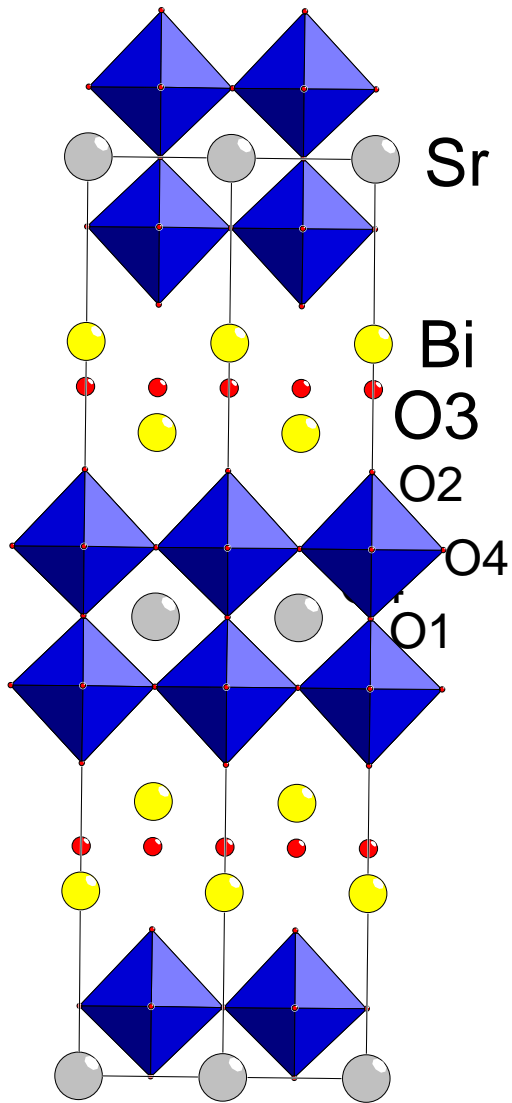
Spontaneous Polarization
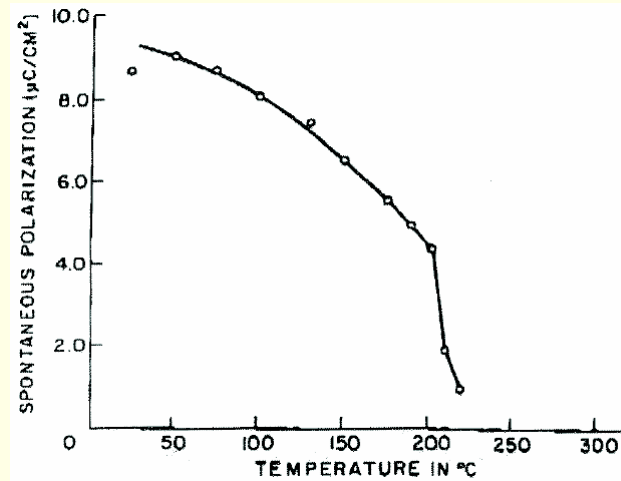
polar mode Eu (deg. 2)
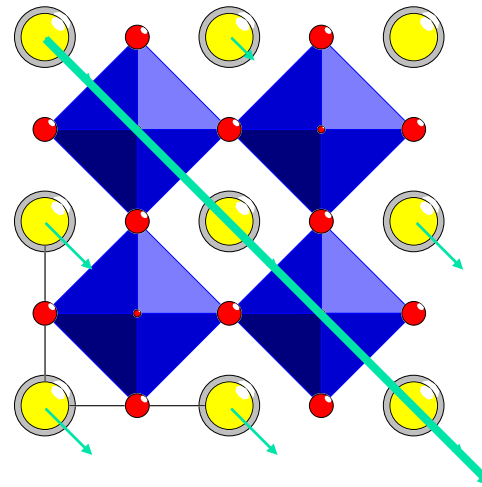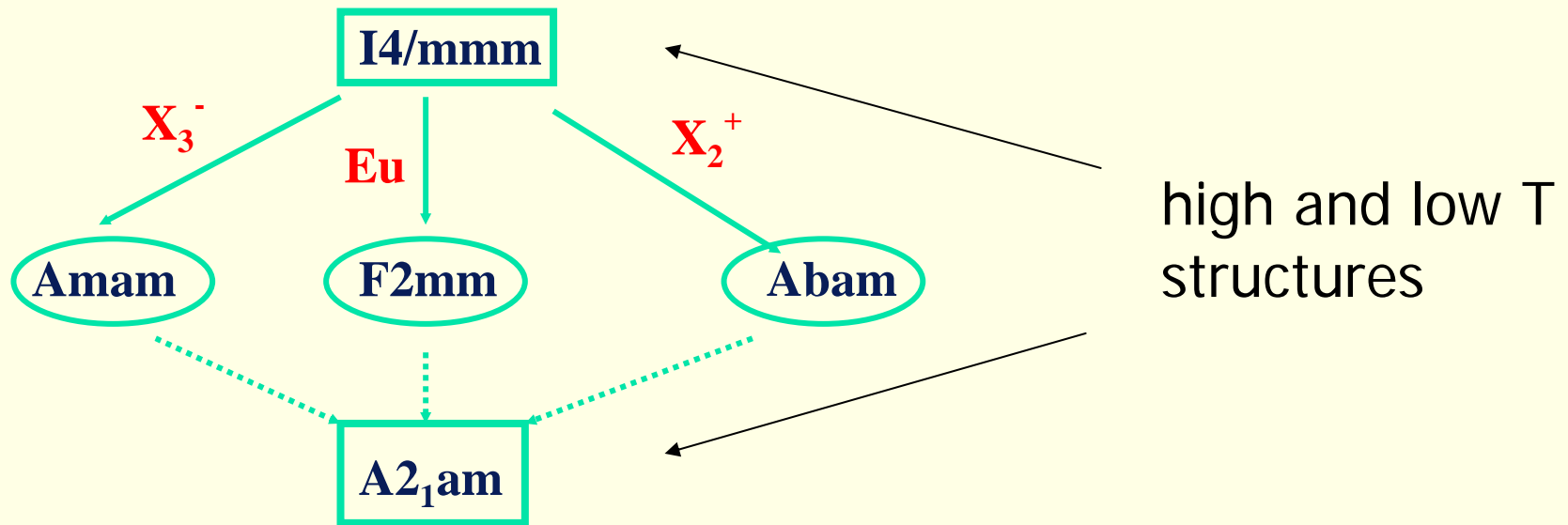
Stachiotti et al. 2000
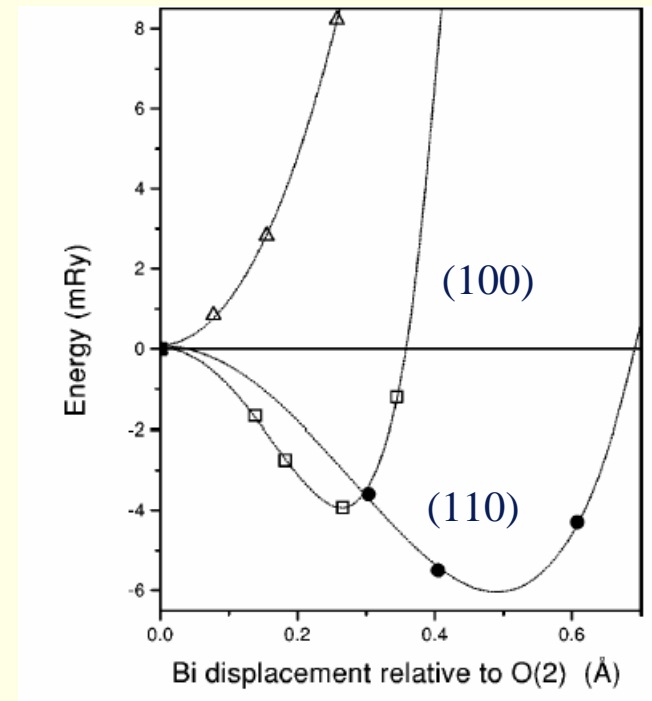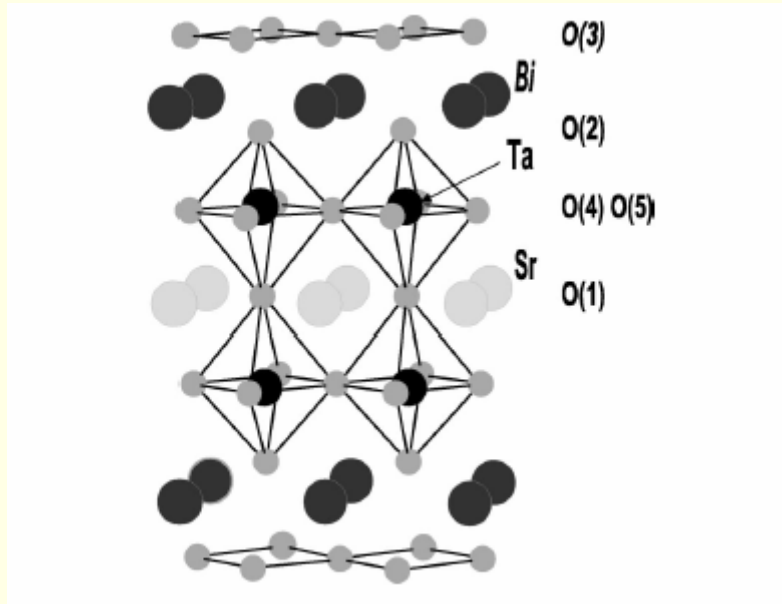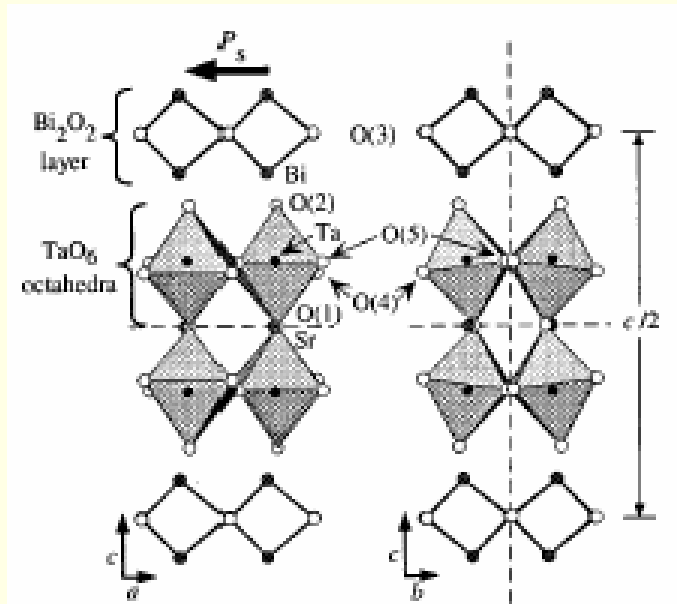
- **Unstable Eu polar mode**
- **Strong contribution of Bi displacement :**
  Bi-O(2) hybridization

X_3^-

Eu

X_2^+

$$I4/mmm$$

Amam   F2mm   Abam

$A2_1am$

high and low T structures

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

Ferroelectric Phase = mode Eu + mode X3- + mode X2+

Frozen distortions in SBT
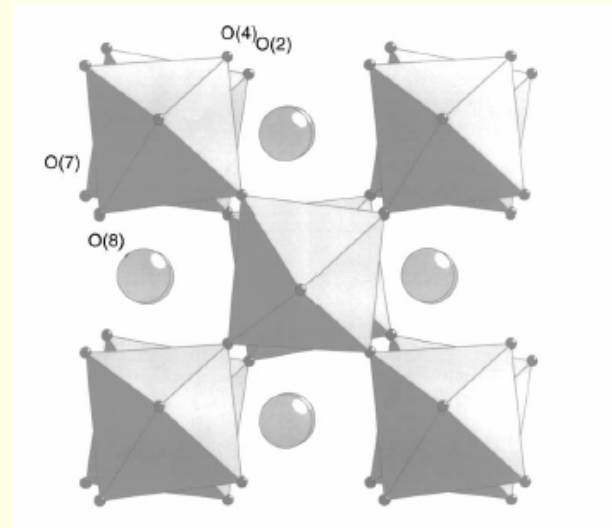
mode X_3^-

mode X_2^+

Shimakawa et al. 1999

Hervoches et al. 2002

Ferroelectric Phase = mode Eu + mode X3- + mode X2+
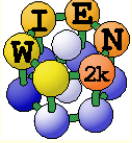
Eigenvectors:	e_{Eu}	e_{X3}	e_{X2}
Mode Amplitudes (bohrs) :	**QEu = 0.82**	**QX3= -1.20**	**QX2= -0.35**

Prototype tetragonal paraelectric phase
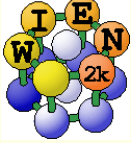
Not possible through the freezing
of a polar mode!

Ferroelectric orthorhombic phase
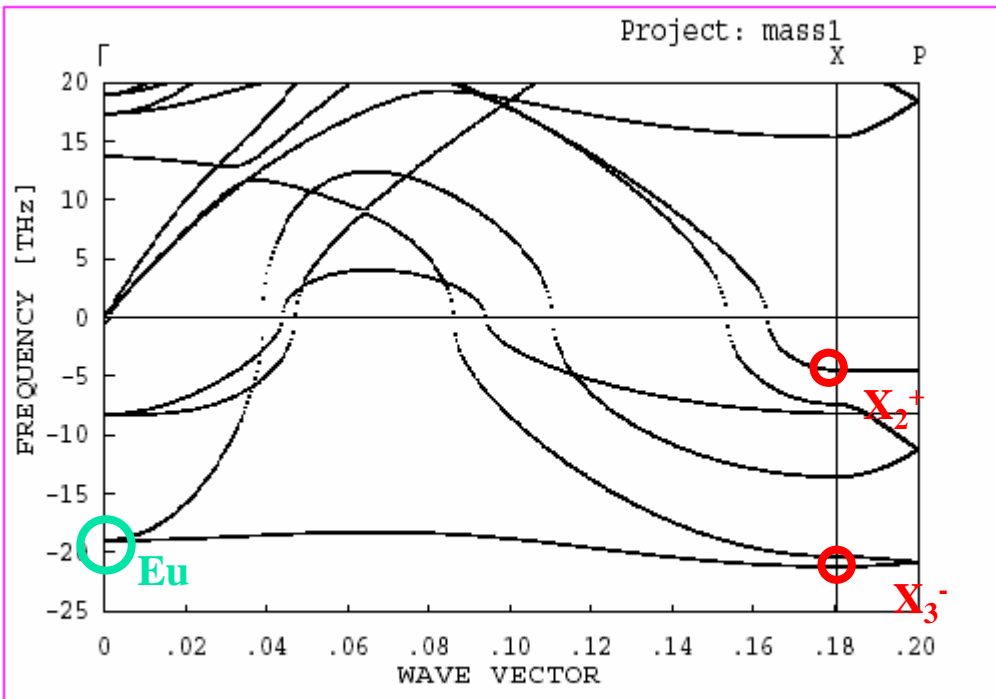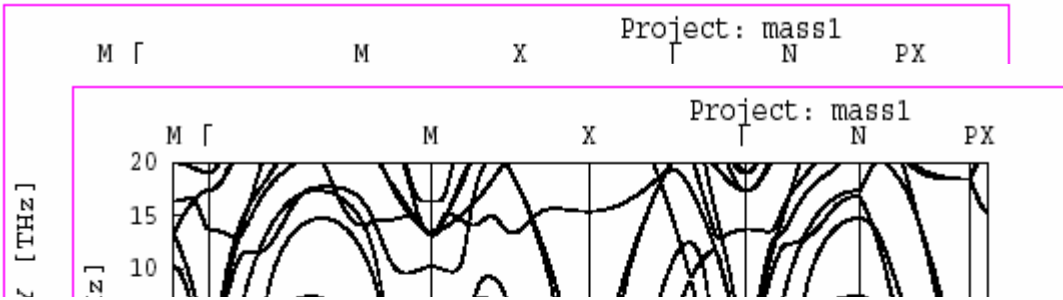
•**A single order parameter can not produce this transition.**

According to Landau theory:

•**Either discontinuous transition or intermediate phases**
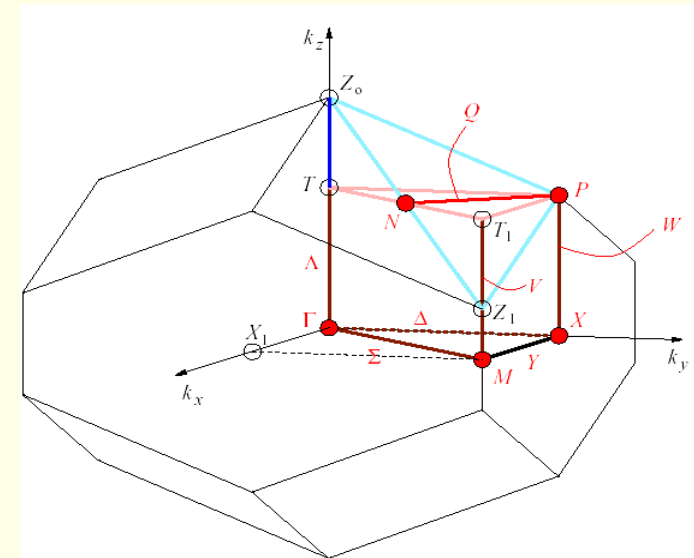
SBT

CALCULATED "PHONON" BRANCHES

Ferroelectric Phase = mode Eu + mode X3- + mode X2+

In general, good agreement with experimental frozen modes

Except !…. The experimental frozen mode X_2^+
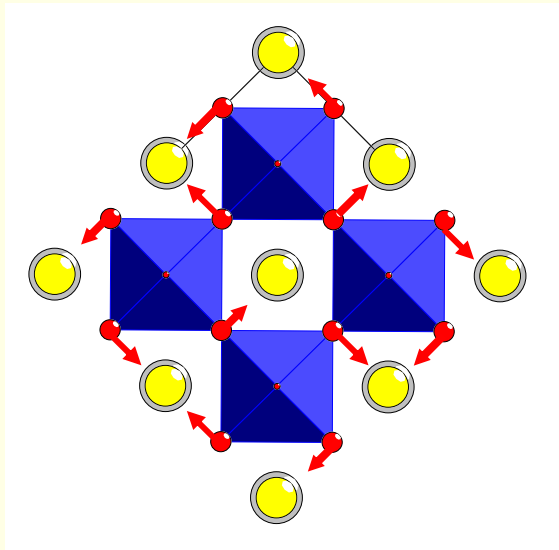
coincides approx. with calculated **soft-mode** X_2^+

"Part 1"

Two independent normal-modes
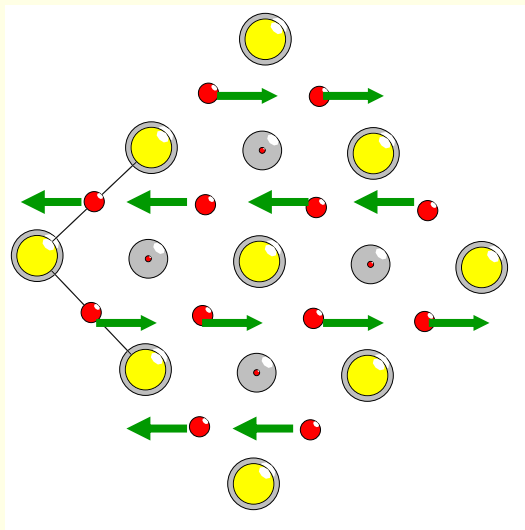
"Part 2"

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

ground state

Q_{X2}

Q_{Eu}

Q_{X3}

Tc1

Tc2

Q_{Eu}

Tc1

Tc2

Q_{X3}
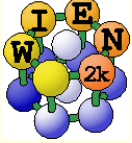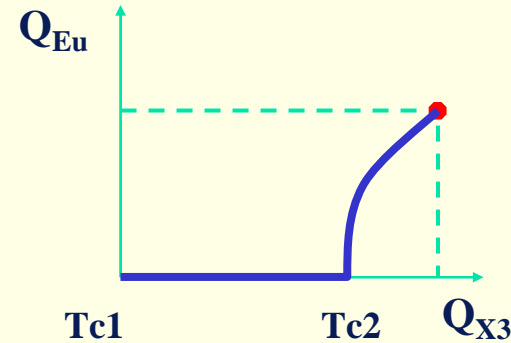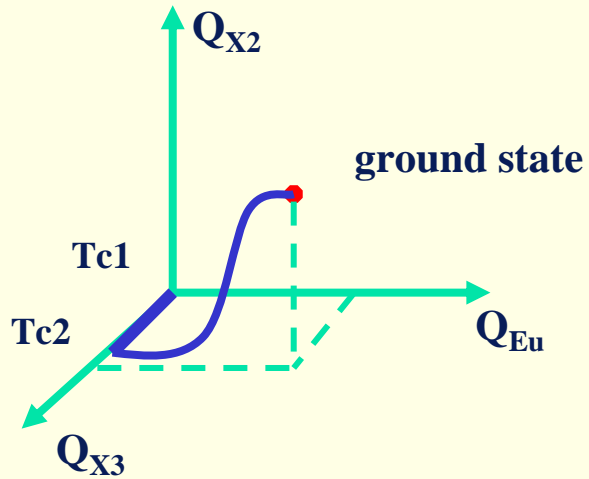
$$\text{Energy} = \text{Eo} + \tfrac{1}{2}\,\kappa_{Eu}\,Q_{Eu}^2 + \tfrac{1}{2}\,\kappa_{X3}\,Q_{X3}^2 + \tfrac{1}{2}\,\kappa_{X2}\,Q_{X2}^2 + \ldots\ldots$$

$$\kappa_{Eu} < 0,\quad \kappa_{X3} < 0$$

Transition Sequence:

$$\text{Thermal Free Energy} = \text{Fo} + \tfrac{1}{2}\,\alpha_{Eu}(T)Q_{Eu}^2 + \tfrac{1}{2}\,\alpha_{X3}(T)Q_{X3}^2 + \tfrac{1}{2}\,\alpha_{X2}\,Q_{X2}^2 + \ldots\ldots$$
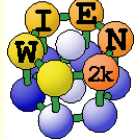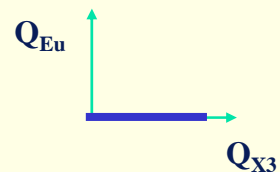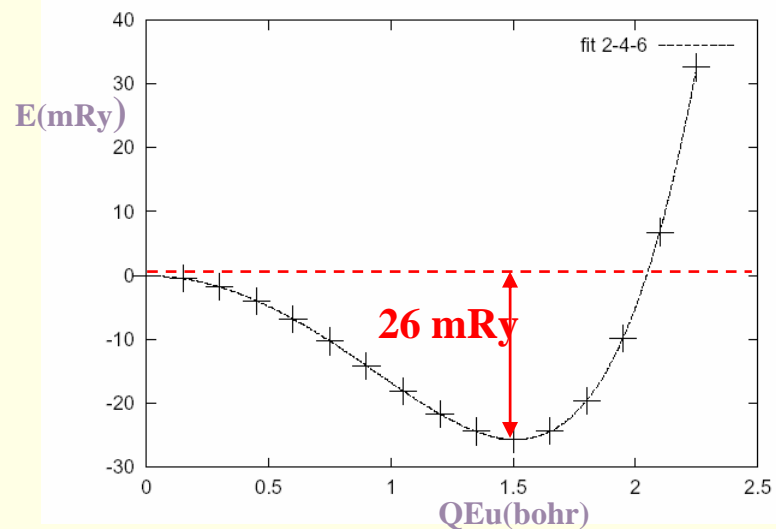
Space Group Amam

$$E_{X3} = -40.2\, Q_{X3}^2 + 10.9\, Q_{X3}^4 + 0.87\, Q_{X3}^6$$

33 mRy
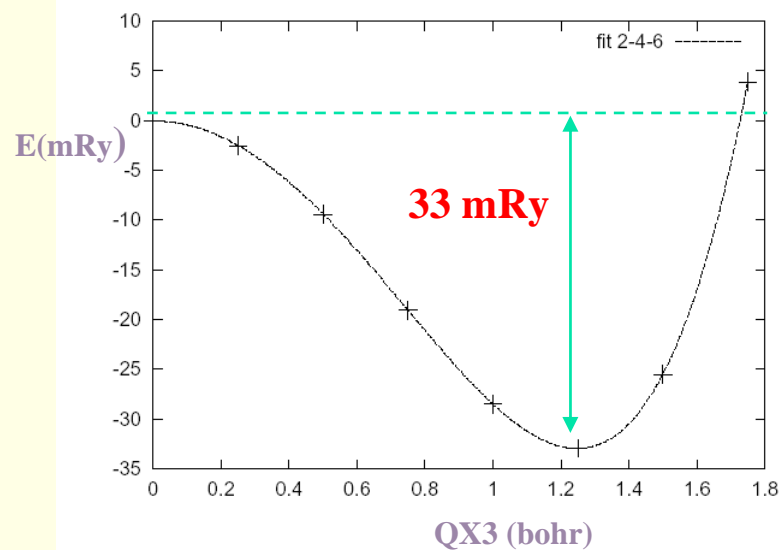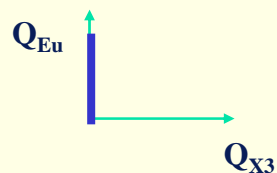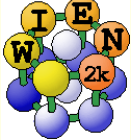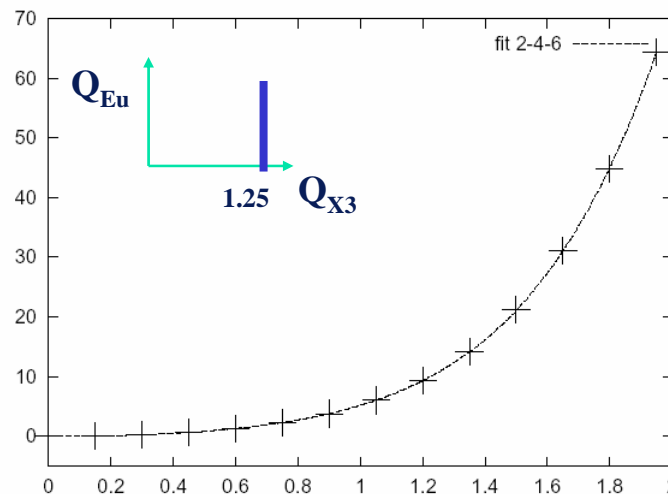
Space Group F2mm

$$E_{Eu} = -19.9\, Q_{Eu}^2 + 2.6\, Q_{Eu}^4 + 0.52\, Q_{Eu}^6$$

26 mRy
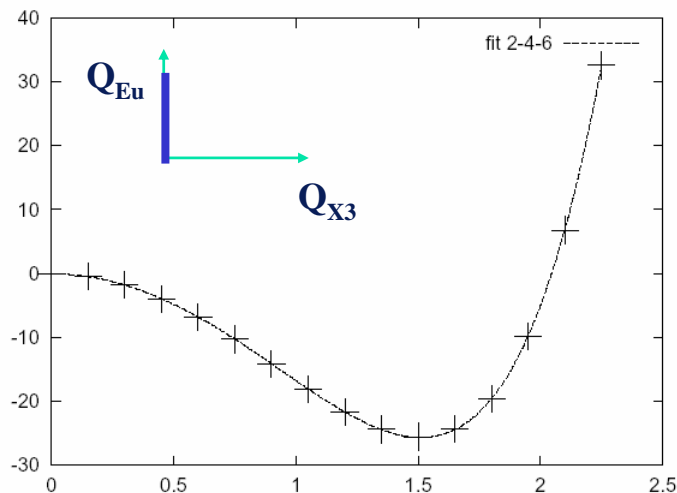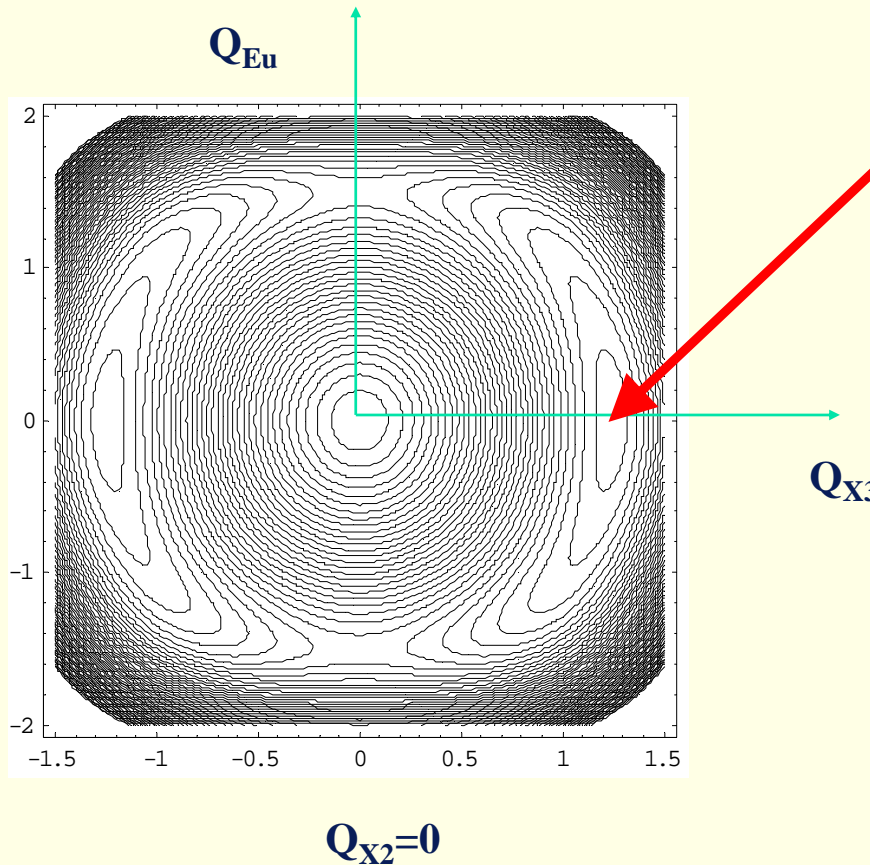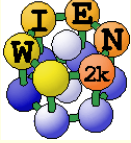
$$E_{Eu} = -19.9\, Q_{Eu}^2 + 2.6\, Q_{Eu}^4 + 0.51\, Q_{Eu}^6$$

$$E_{Eu} = +3.1\, Q_{Eu}^2 + 1.6\, Q_{Eu}^4 + 0.53\, Q_{Eu}^6$$

$$+14.7\, Q_{Eu}^2\, Q_{X3}^2 - 0.63\, Q_{Eu}^4\, Q_{X3}^2$$

Strong biquadratic coupling Eu –X$_3^-$

Q_{Eu}

Q_{X3}

$Q_{X2}=0$

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 soft X_2^+ mode relatively weak !

- Strong renormalization of hard (second) X_2^+ mode
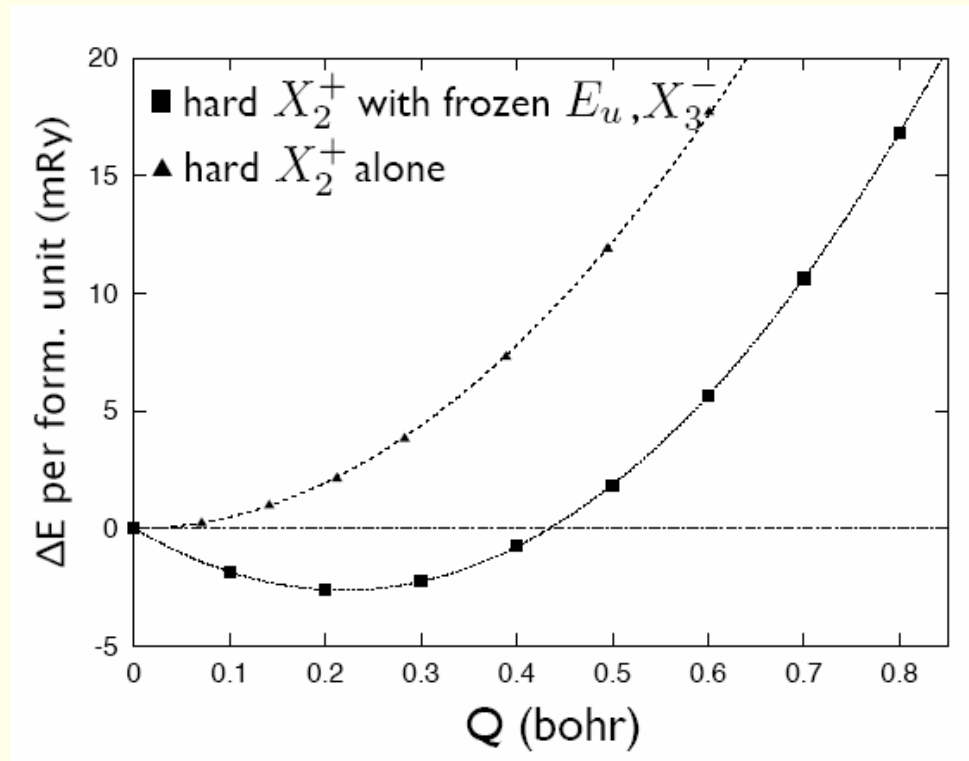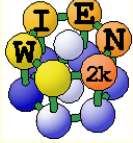
including only soft X_2^+ mode   with additional hard X_2^+ mode
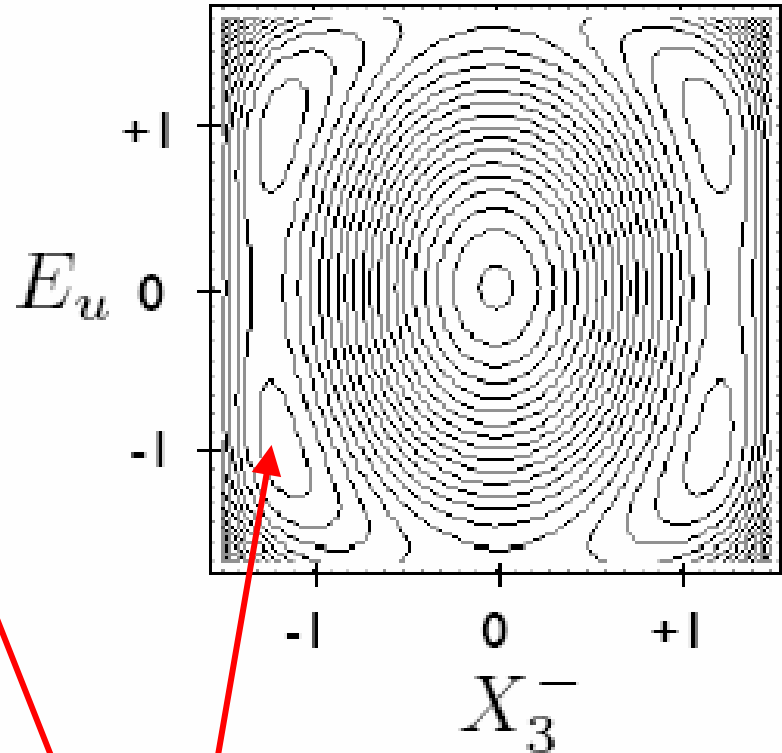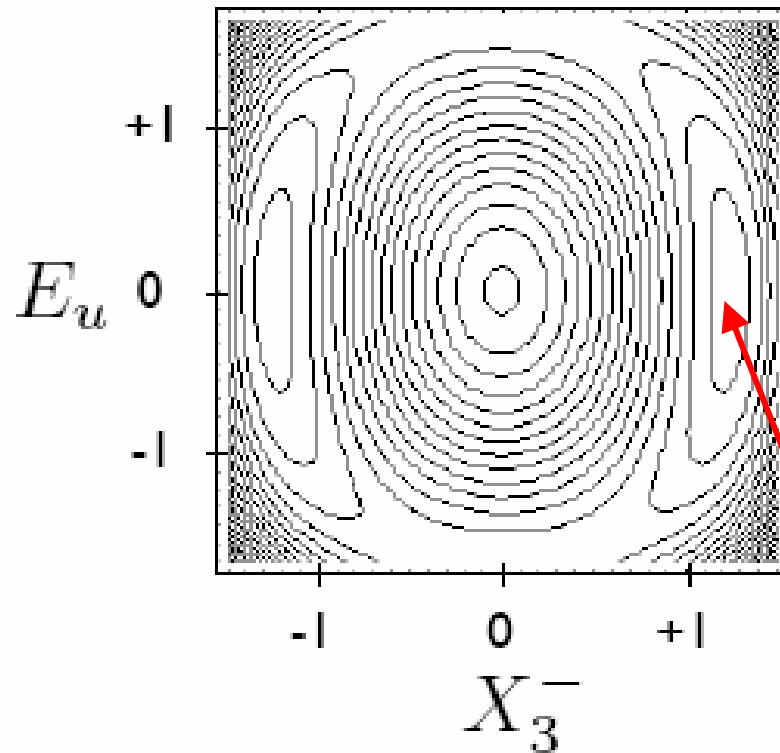
only with the additional hard X_2^+ mode the experimentally observed combination of 3 different modes can be established
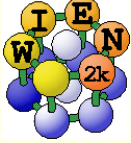
• Finite temperature renormalization of the T=0 energy map

• Landau theory suggests linear T-variation of the quadratic stiffness coefficients κ_{Eu} and κ_{X3^-}
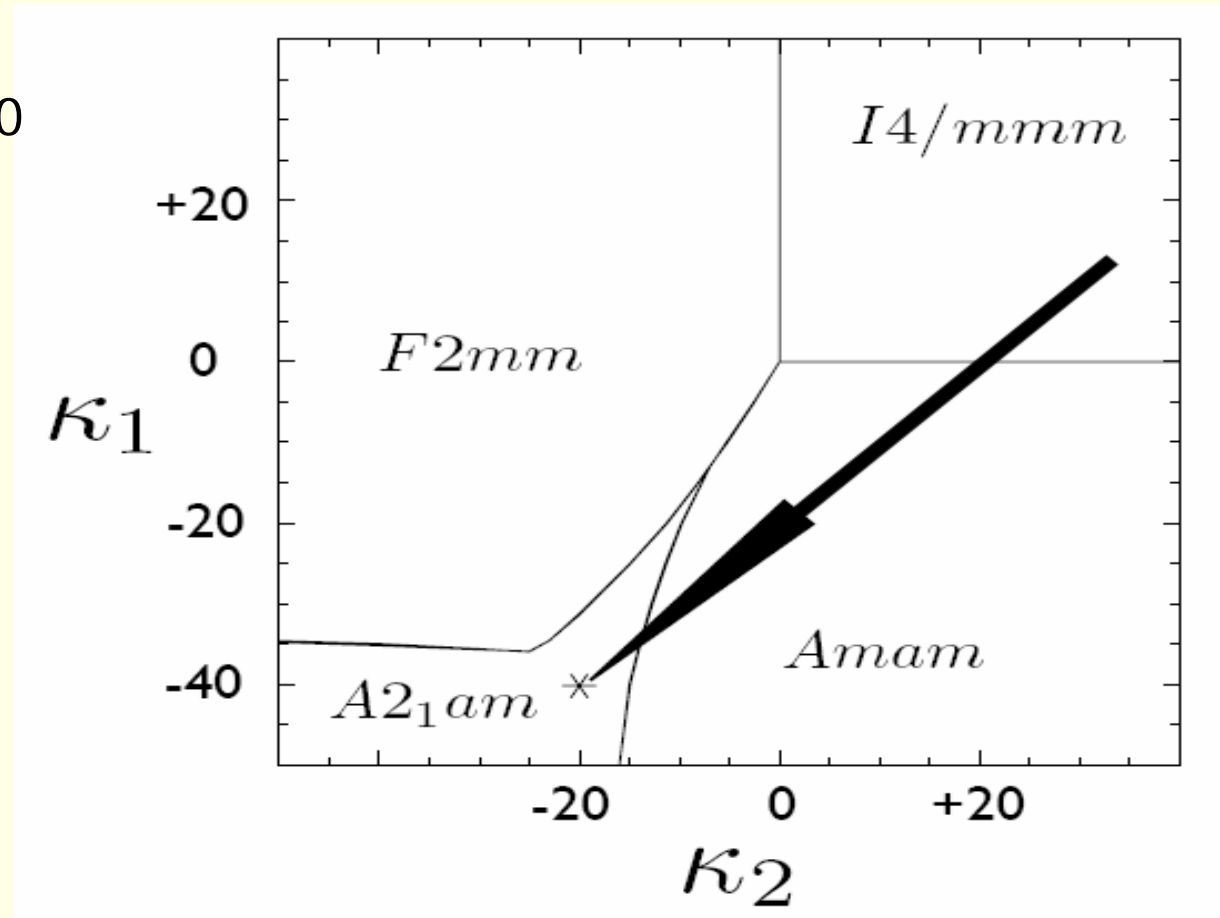
The topolgy of this phase diagram predicts **two second order** phase transitions and implies the existence of an intermediate phase of Amam symmetry. A **single first order** PT is impossible.

Insulating and non-magnetic **4d** TM-oxide
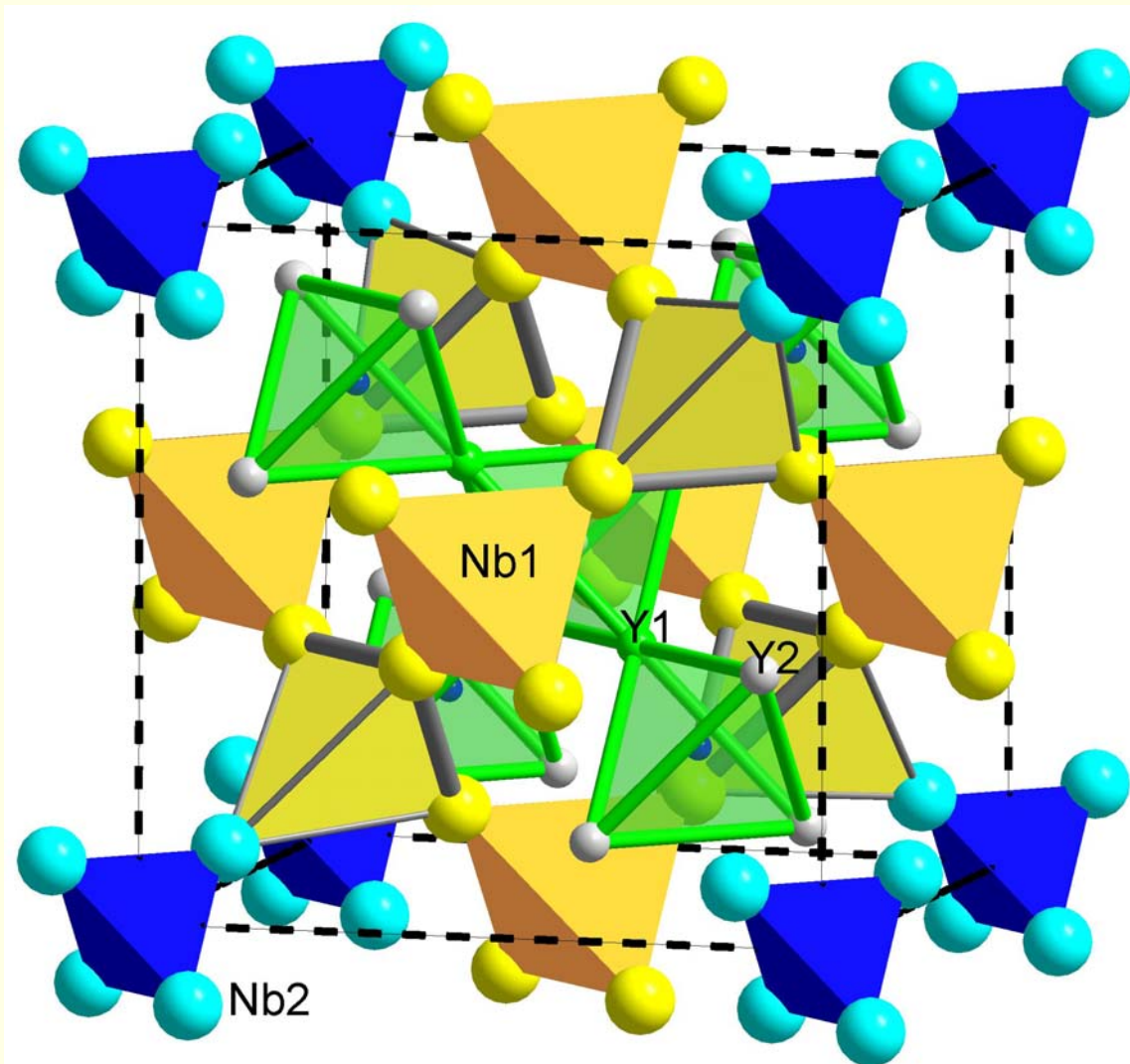
P.Blaha, D.Singh, K.Schwarz, PRL in print (2004)

Metal Sublattice: Corner-shared tetrahedral network
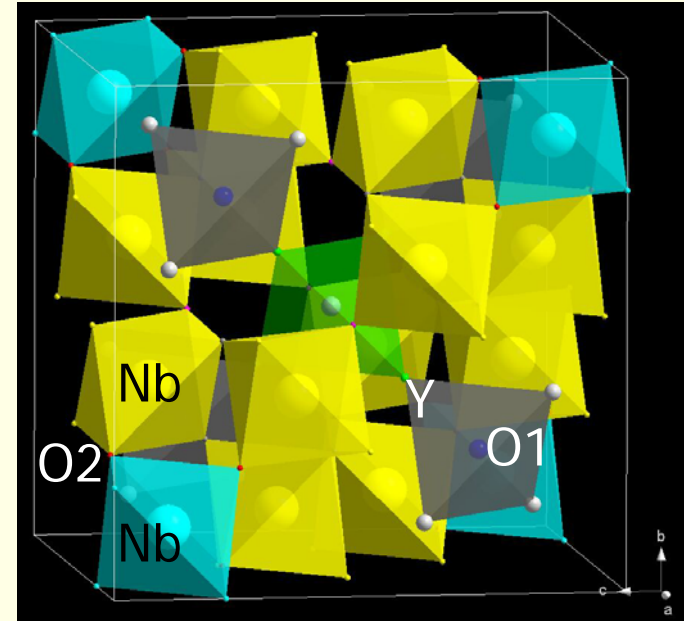
Pyrochlore structure of $Y_2Nb_2O_7$:

- **Experimental structure** from powder diffraction (Fukazawa,Maeno):

  > Y.Maeno et al, Nature 372, 532 (1994)
  > H.Fukazawa, Y.Maeno, Phys.Rev. B 67, 054410 (2003)

  - *Pyrochlore structure: Fd-3m, a_0=10.33 Å*
  - *22 atoms (2 FU/cell)*
  - *One free parameter for O2: (0.344,1/8,1/8)*
- **Corner shared Nb - O octahedra**
- **Corner shared O1 - Y tetrahedra**
- **Y surrounded by 8 oxygens (~ cube)**

- **Metal sublattices**
  - *Nb-tetrahedra (empty)*
  - *Y-tetrahedra (around O)*

- Insulator
- Nonmagnetic
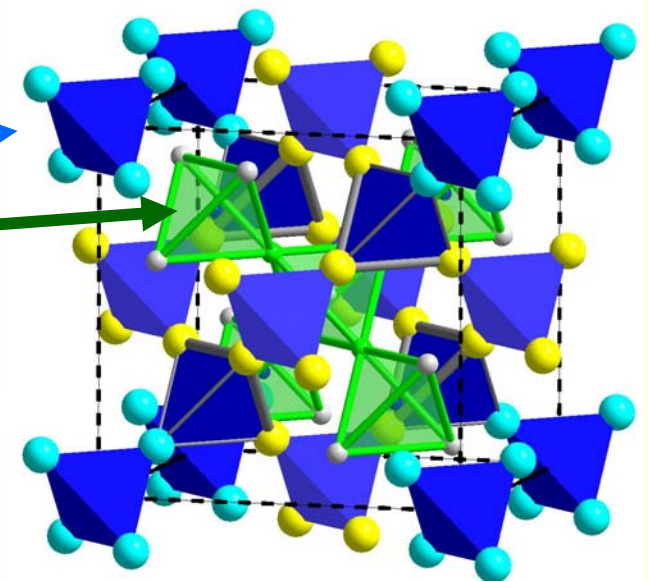
- Ionic model: $Y_2^{3+}Nb_2^{4+}O_7^{2-}$ $Nb^{4+}: 4d^1$

- → 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.

E_F

O-2p   Nb-t_{2g} Nb-e_g

E_F

DOS (states/eV)

- total
- O1
- O2
- Y
- Nb

Energy (eV)
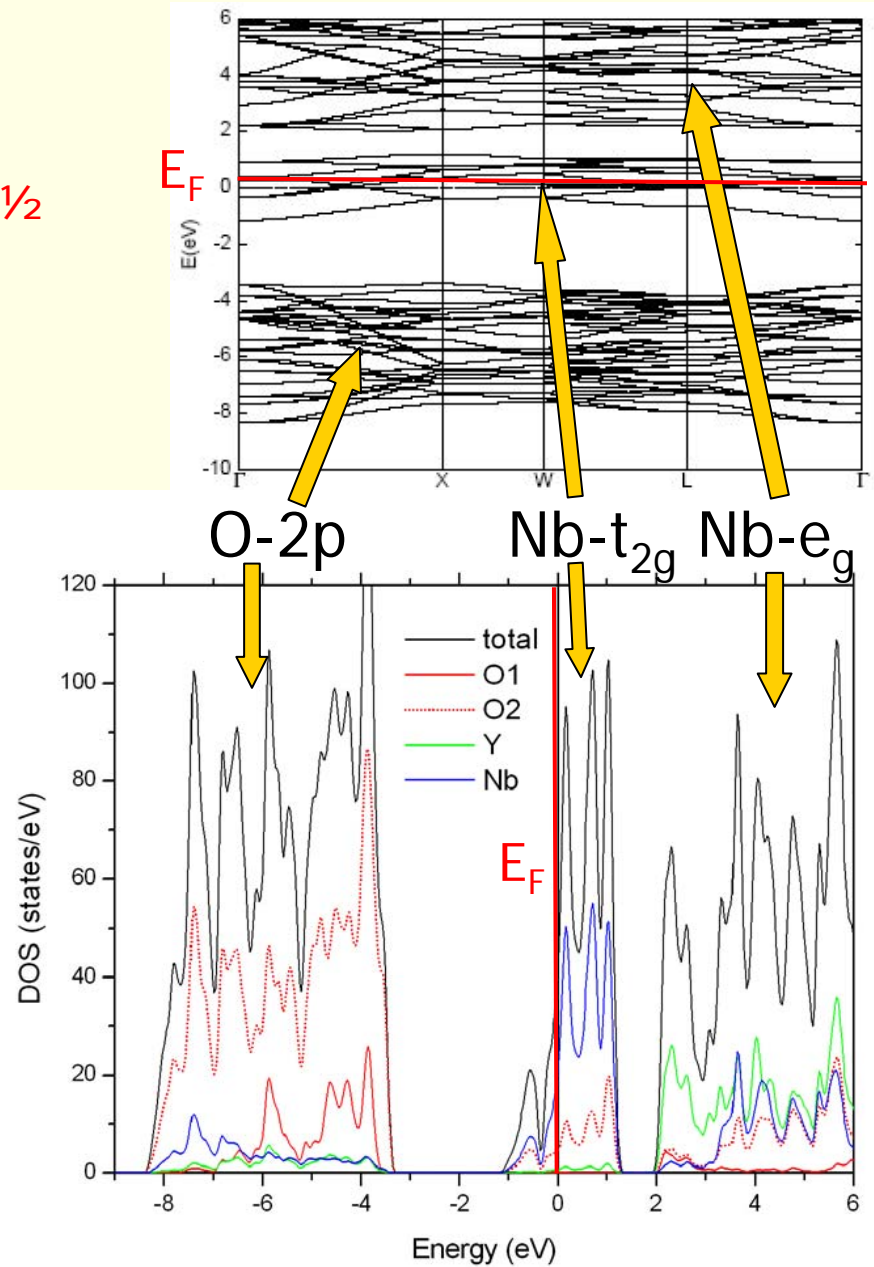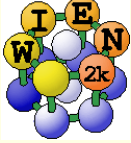
- **Antiferromagnetic s=1/2 solution**
  - *(on geometrically frustrated lattice !?)*
- **Localization, strong e⁻-e⁻ correlation:**
  - *$4d$ (not $3d$!) electrons,*
  - *thus correlation should be small (Hubbard-U ~ 2-3 eV)*
  - *LDA+U with U=6 eV gives insulator (FM ground state, no AFM)*
  - *bandwidth 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*
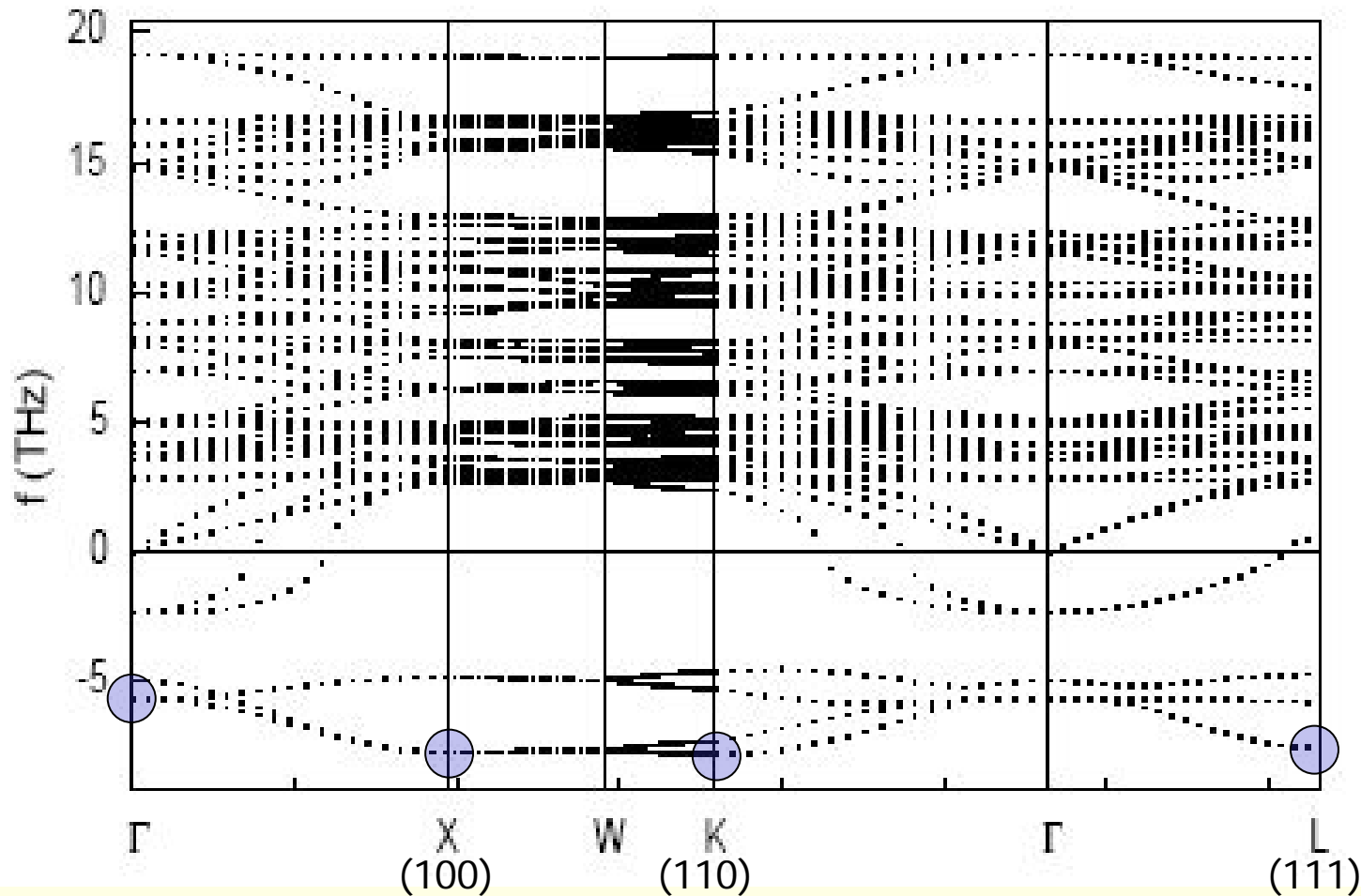
- strong Phonon-instabilities, lowest at X, K, L
- select a certain (unstable) phonon, freeze it with certain amplitude into the structure and perform full structural optimization

- energy lower than in ideal pyrochlore structure, but still not insulating
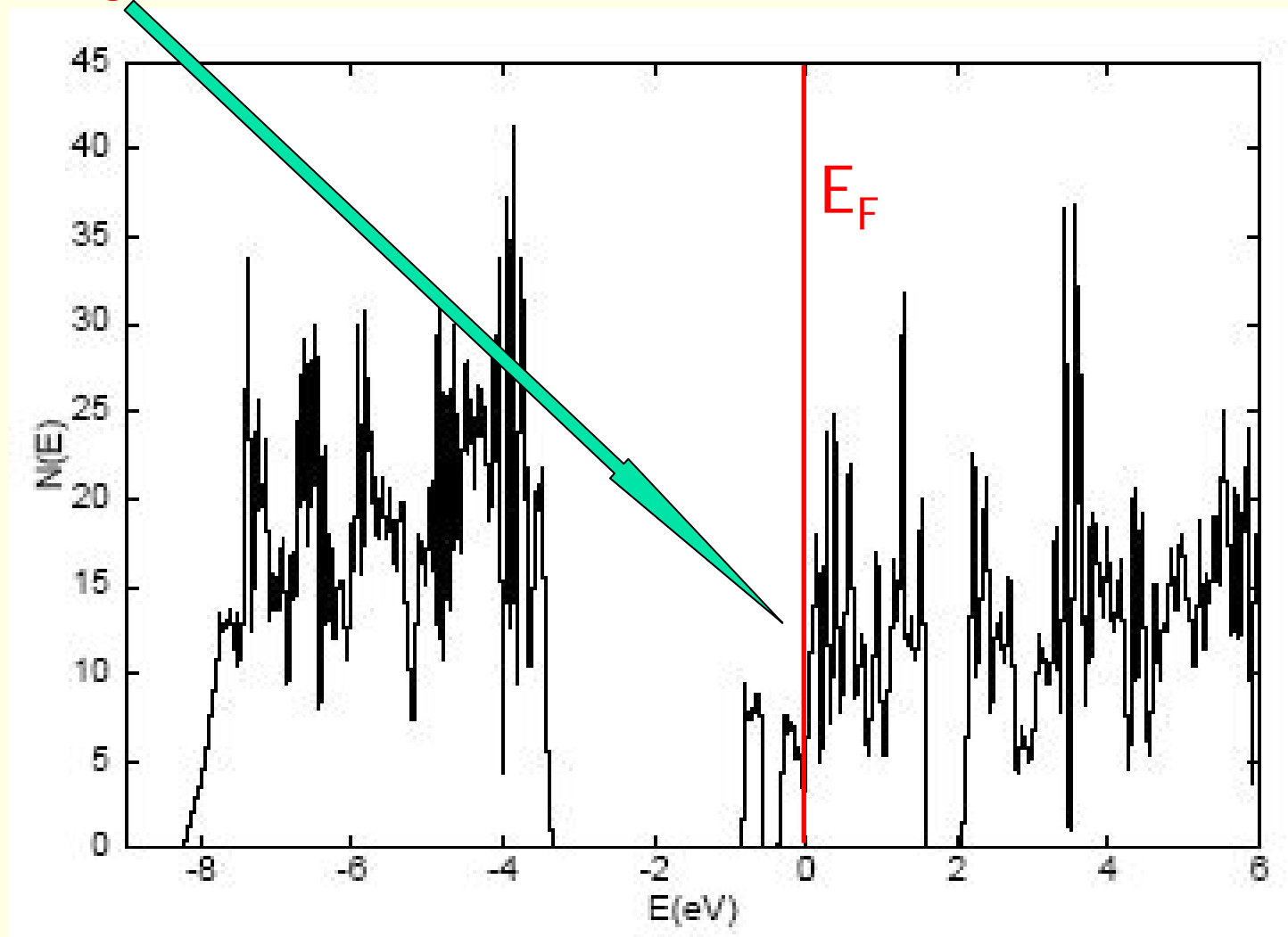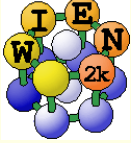
L-point (111) phonon:
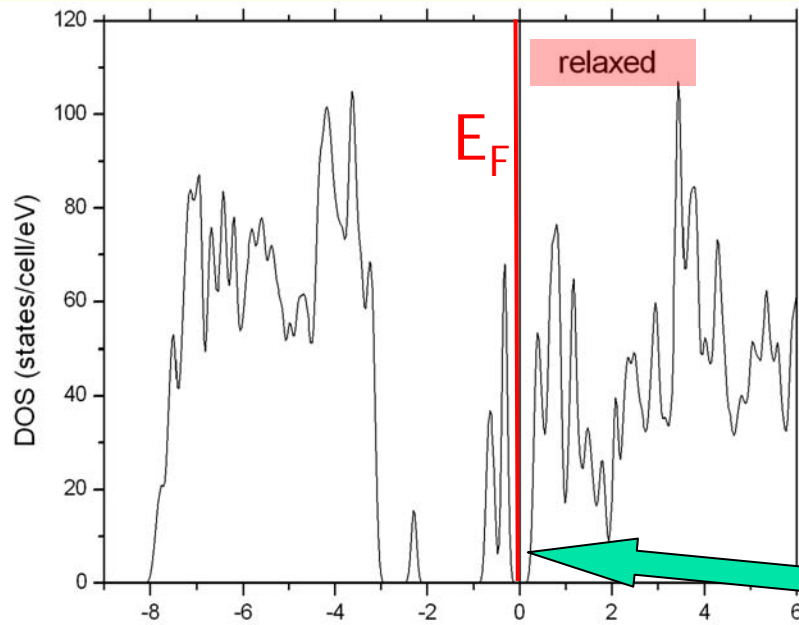
- **Relaxed structure is an Insulator**
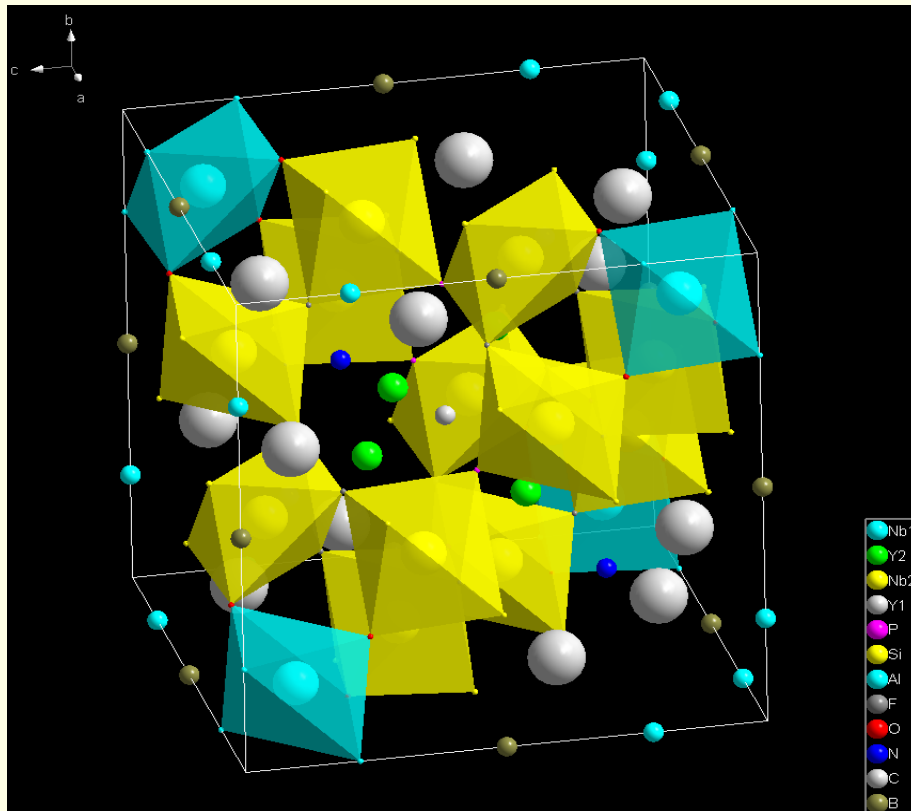- energy gain of 0.5 eV/FU
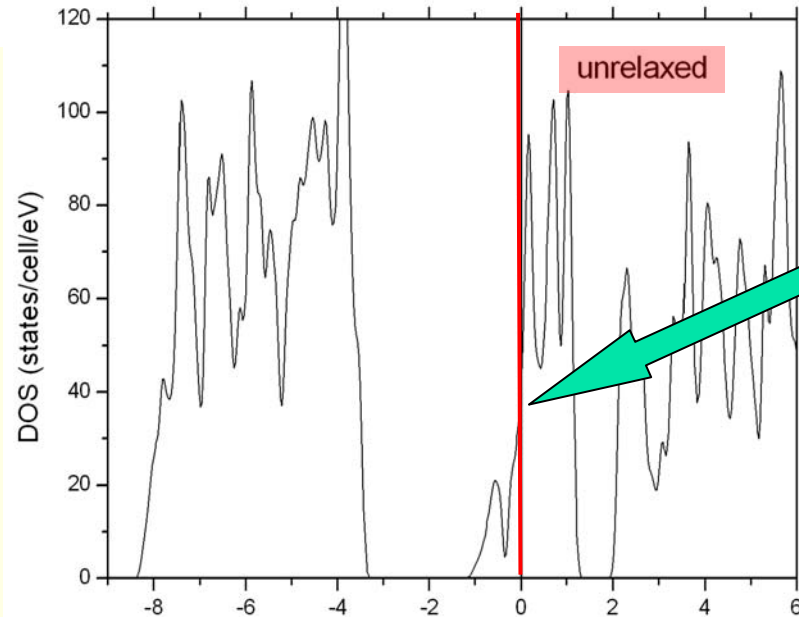
gap

metal
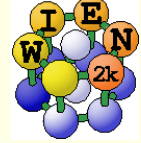
Relaxed structure:

- **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

Experimental (ideal)
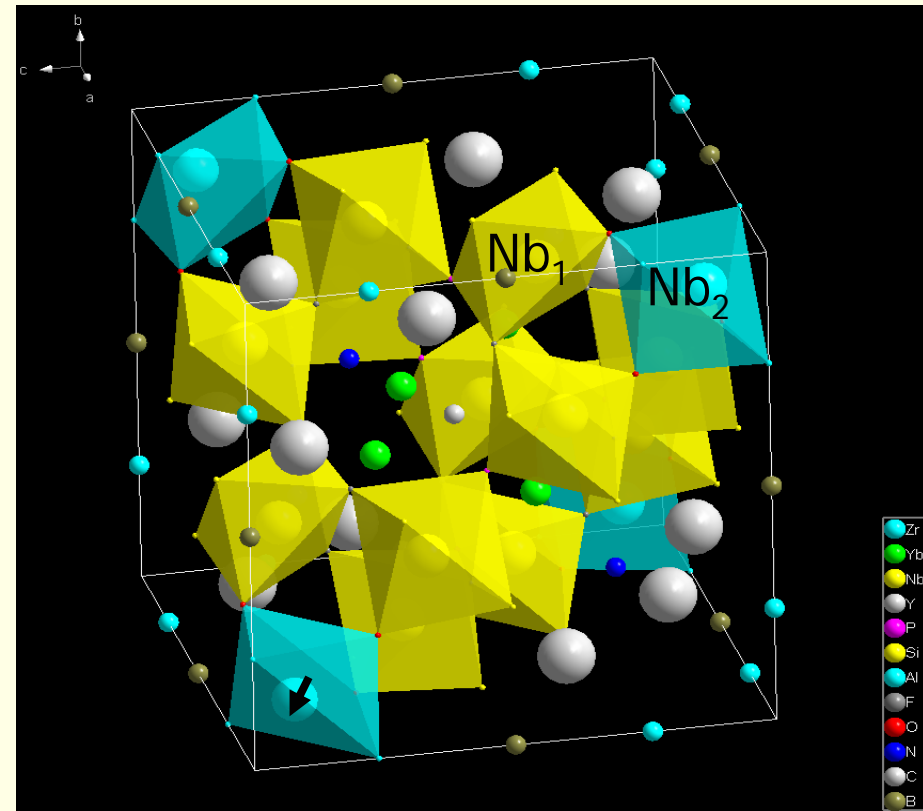
relaxed:
Nb_2 moves „off-center", O octahedra changes little, Nb_2-Nb_2 bonds ?

Original pyrochlore

Relaxed structure

Nb   Nb

3.65 Å equal

Nb2   Nb1

small   large   Nb1 - Nb2
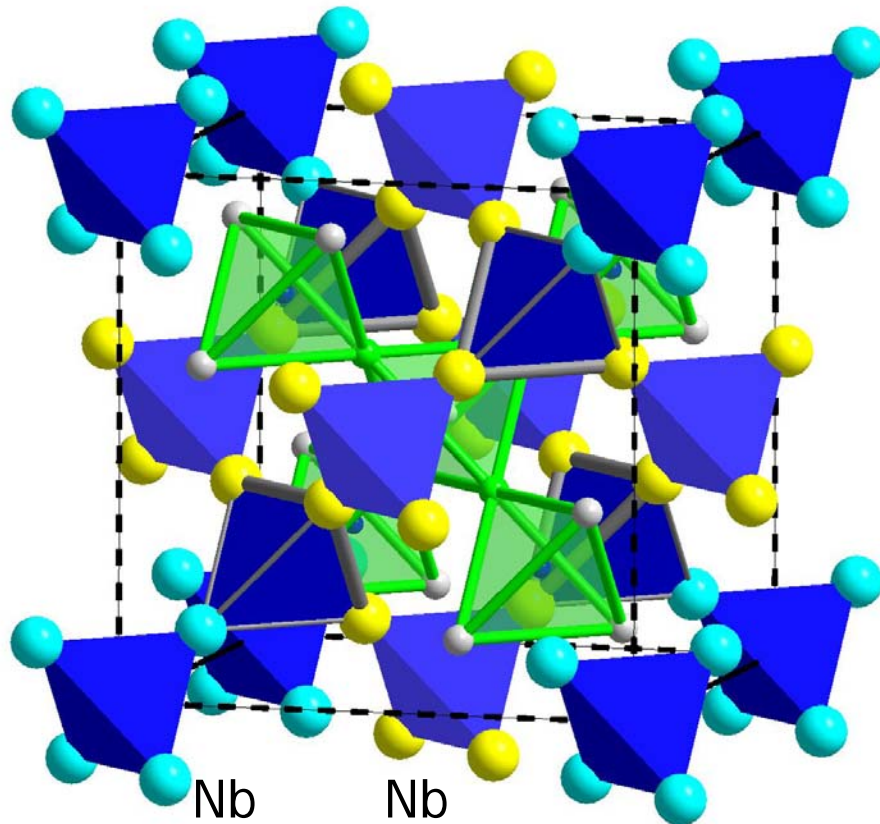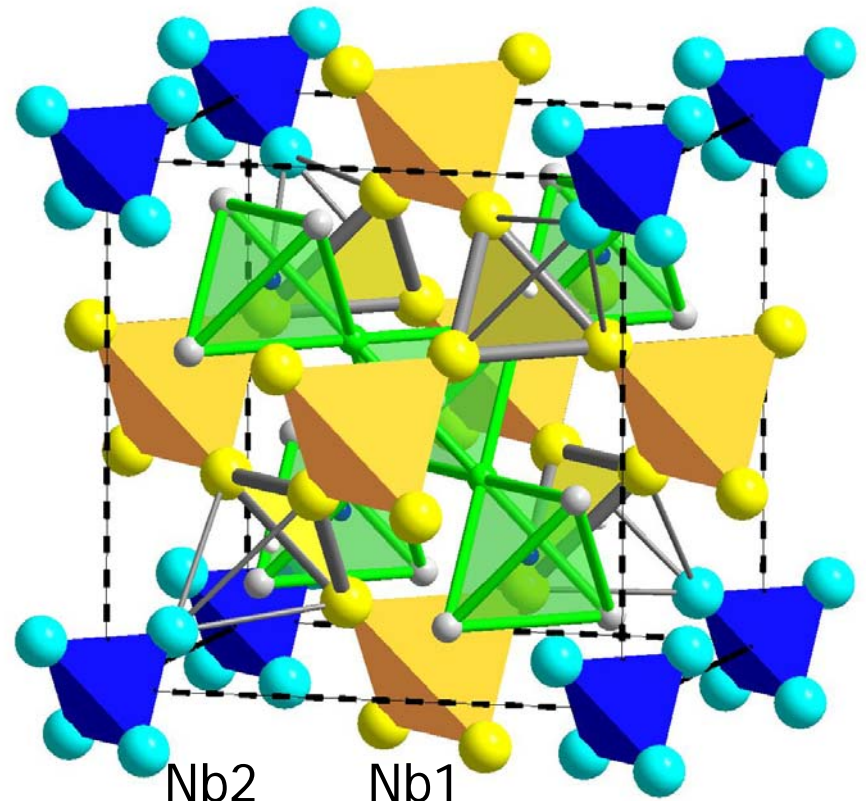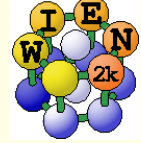
2.91 Å   3.90 Å   3.89 Å

Nb1–triangle: 3.40 Å

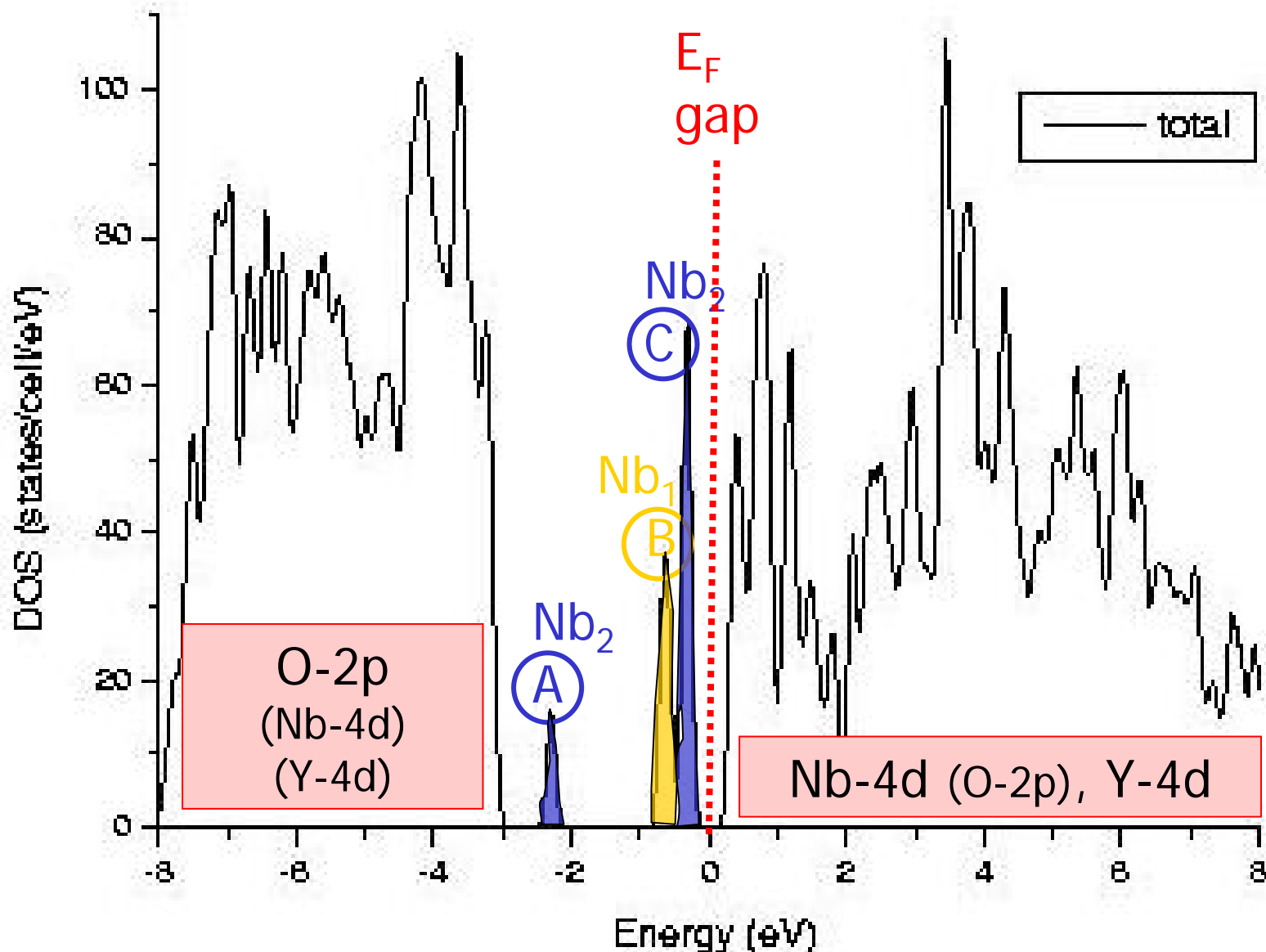peak A: Nb-Nb bonds within the Nb tetrahedra by d-z^2 orbitals

Nb t_{2g}
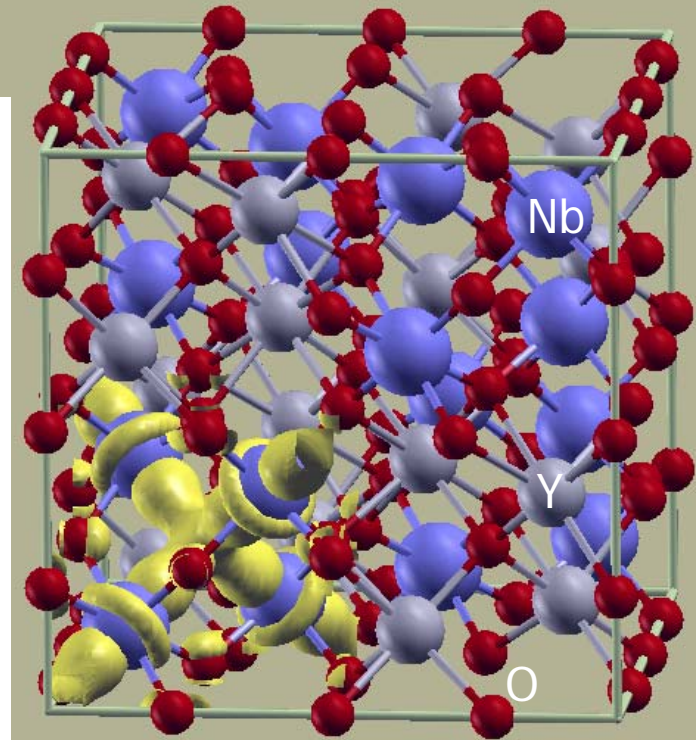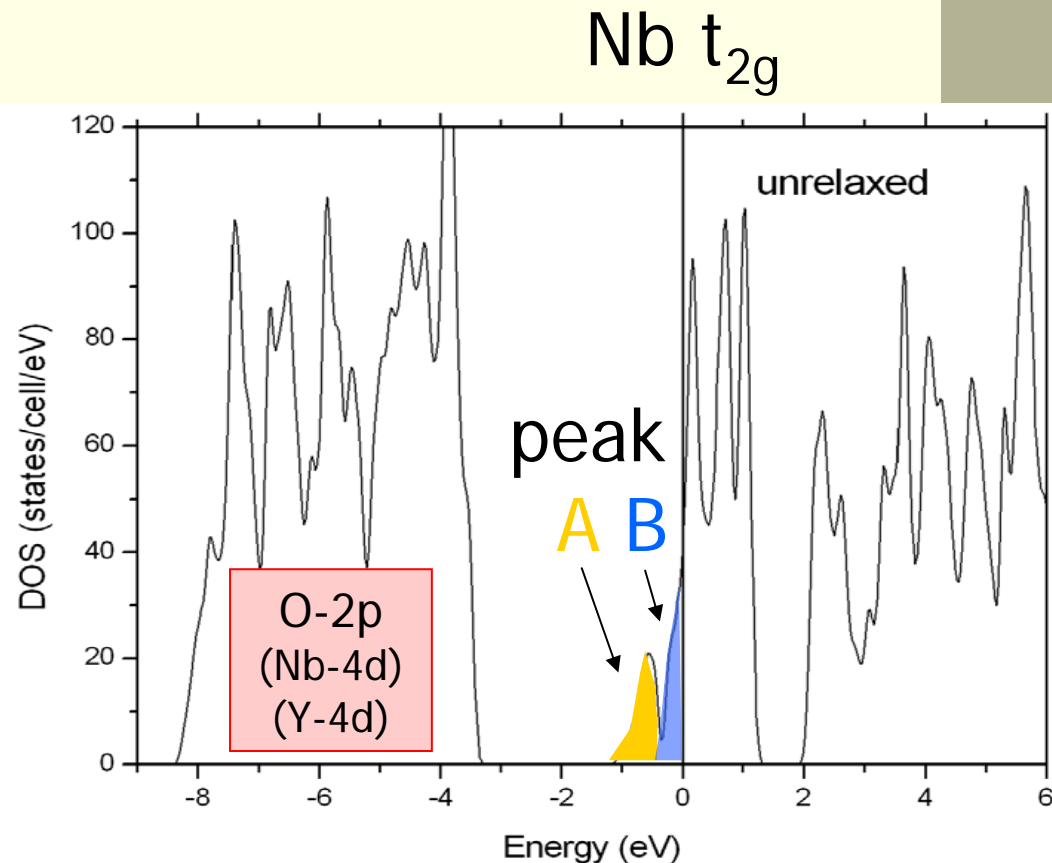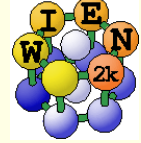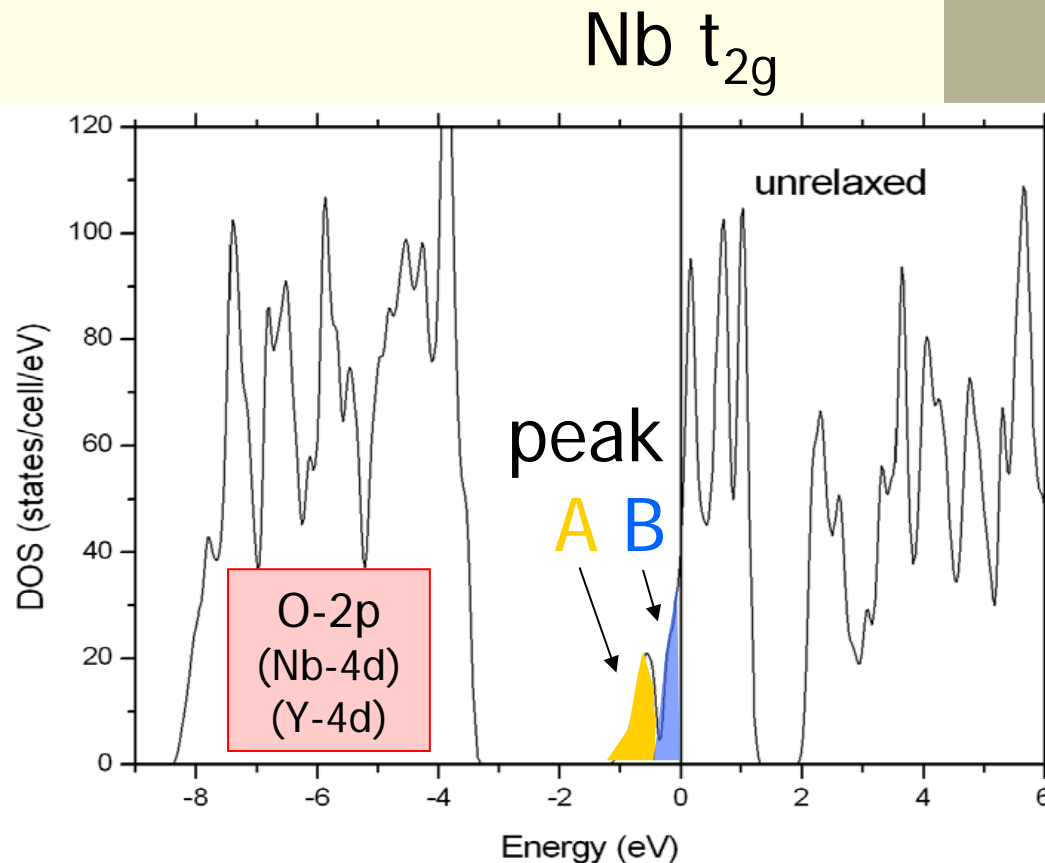
peak B: mixture of all 3 t_{2g} orbitals
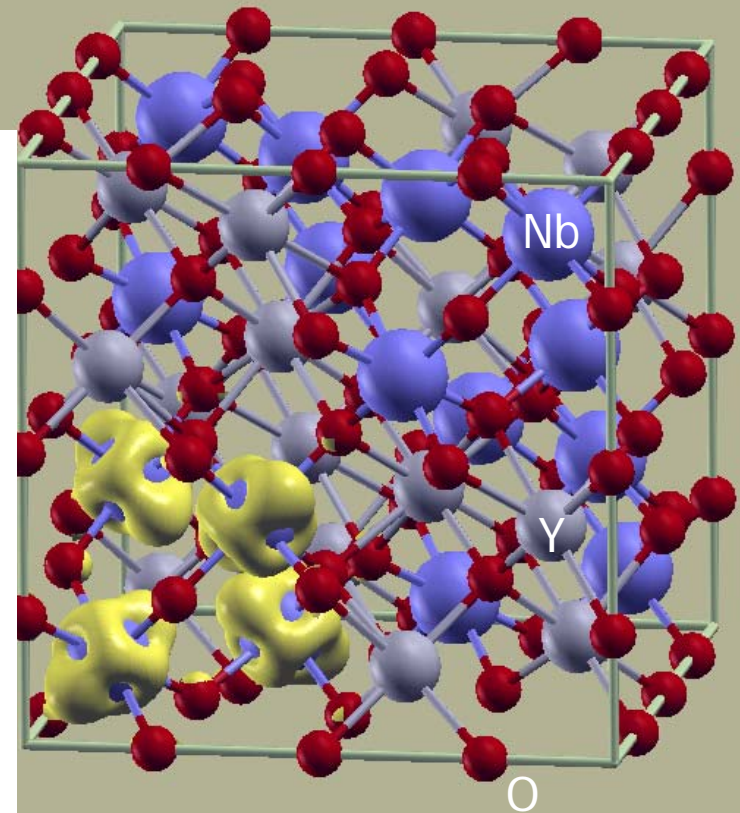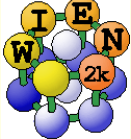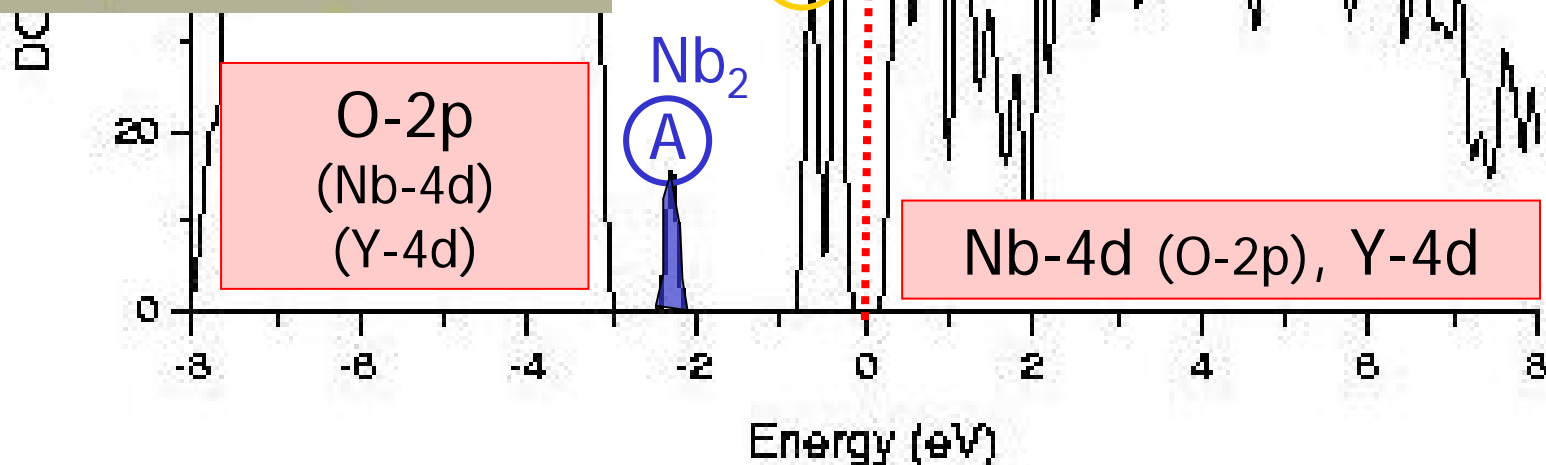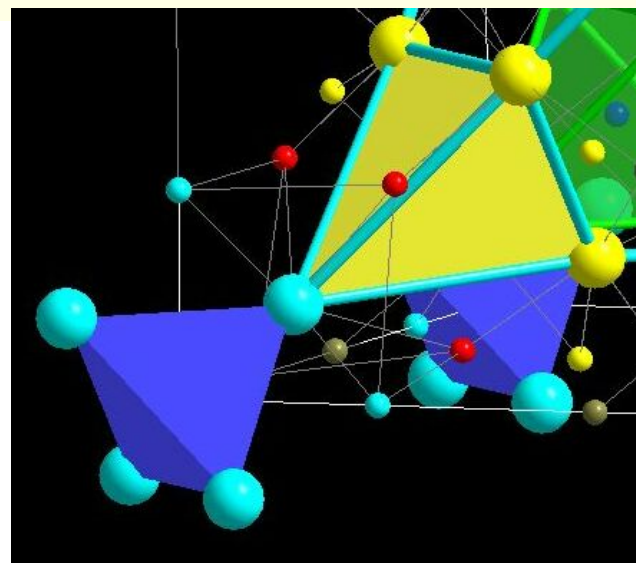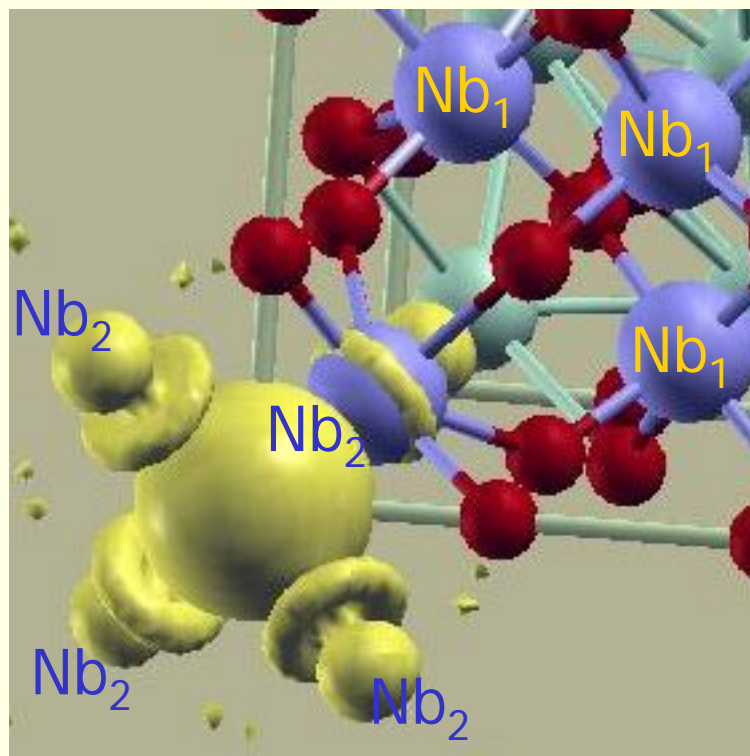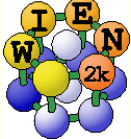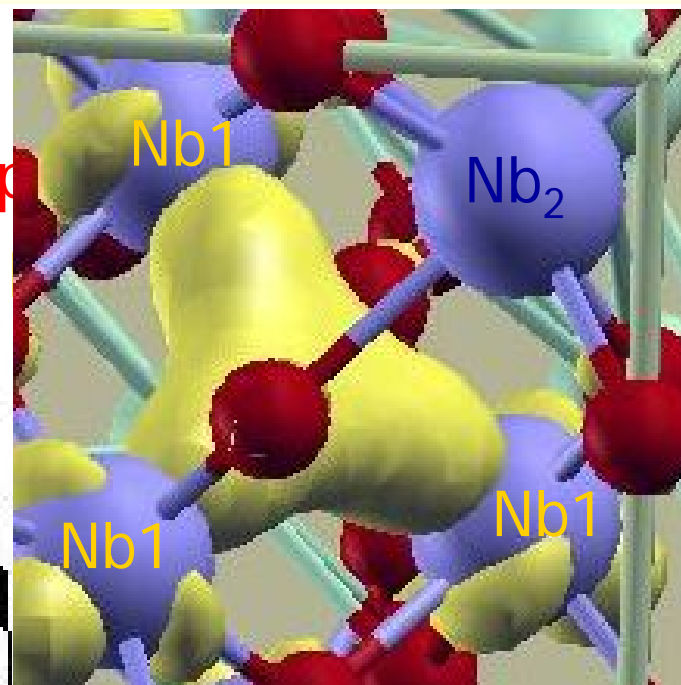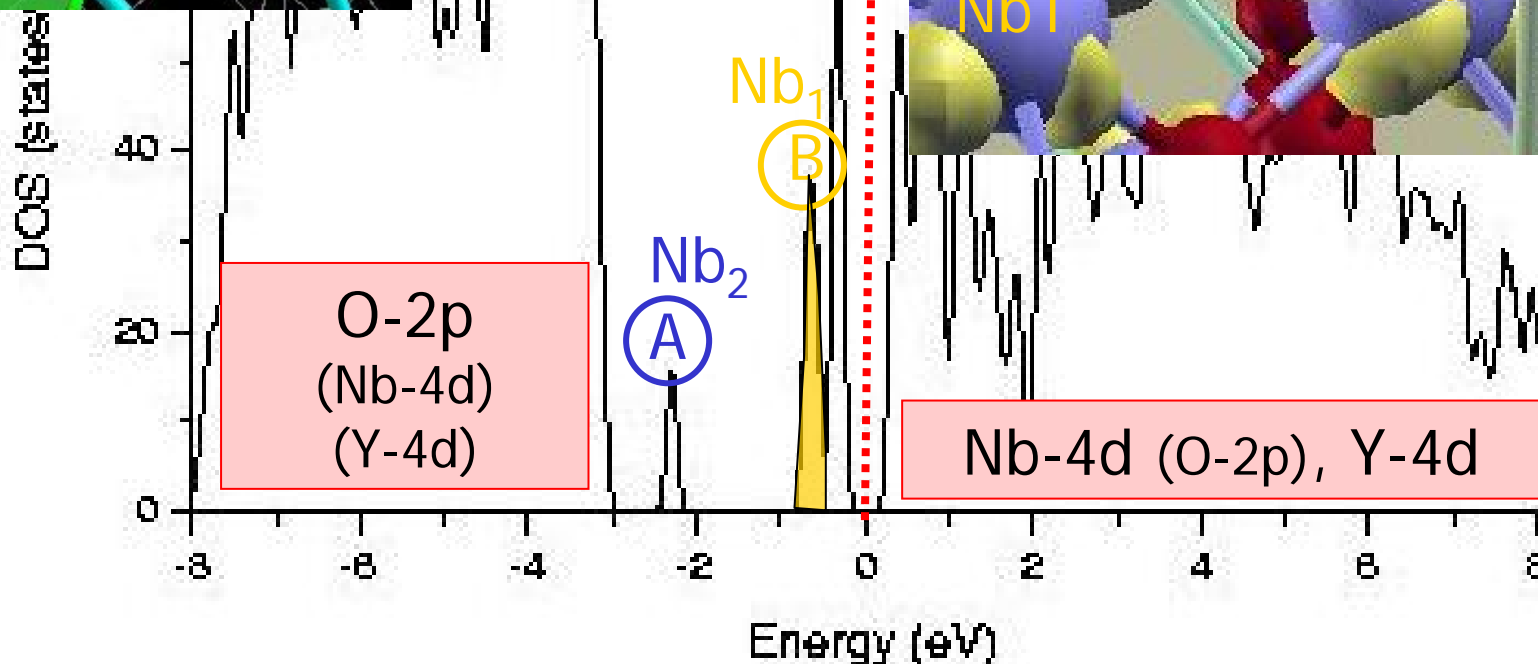
Nb t_{2g}

E_F
gap

Nb_2
Ⓒ

Nb_1
Ⓑ

Nb_2
Ⓐ

O-2p
(Nb-4d)
(Y-4d)

Nb-4d (O-2p), Y-4d

Energy (eV)

DOS (states)

E$_F$
gap

Nb$_2$
C

Nb$_1$
B

Nb$_2$
A

O-2p
(Nb-4d)
(Y-4d)

Nb-4d (O-2p), Y-4d

Nb1
Nb$_2$
Nb1
Nb1

Energy (eV)

DOS (states)

E$_F$
gap

Nb$_2$
Ⓒ

Nb$_1$
Ⓑ

Nb$_2$
Ⓐ

O-2p
(Nb-4d)
(Y-4d)

Nb-4d (O-2p), Y-4d

Nb1 Nb1

Nb$_2$ Nb$_2$ Nb1

Nb$_2$ Nb$_2$

Energy (eV)
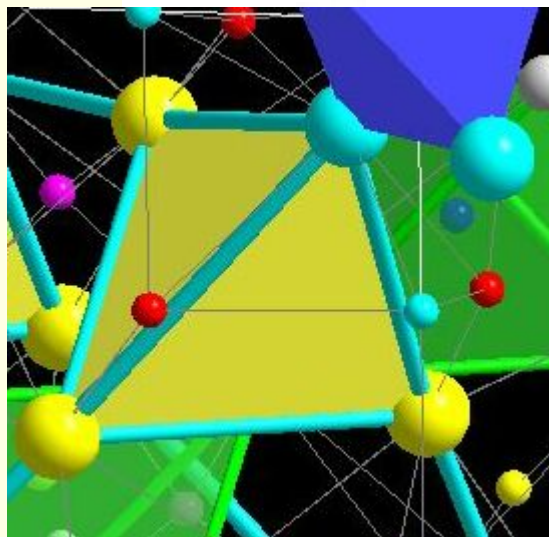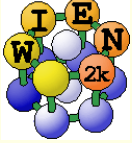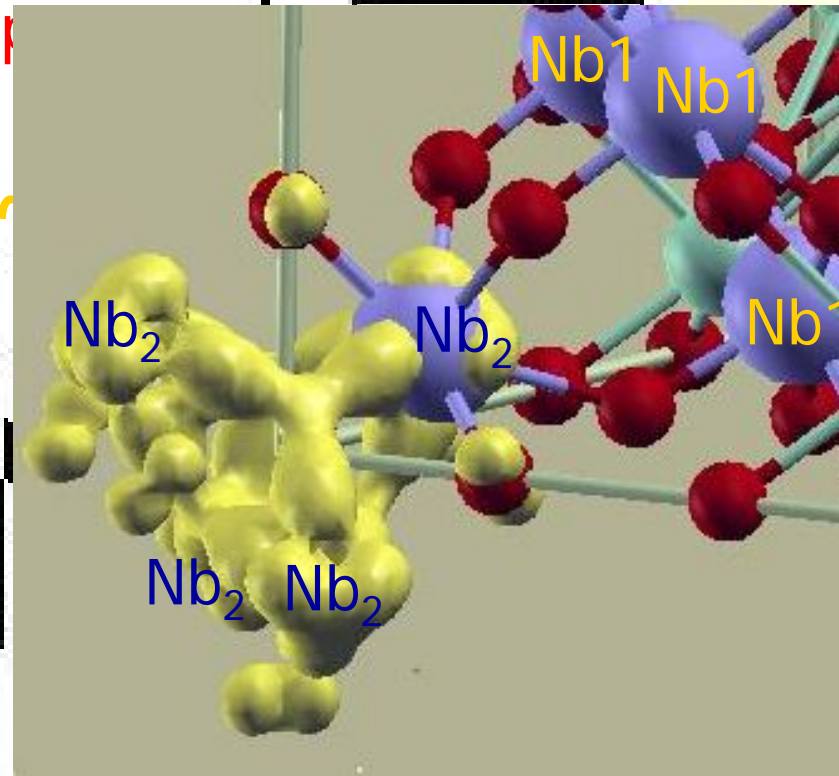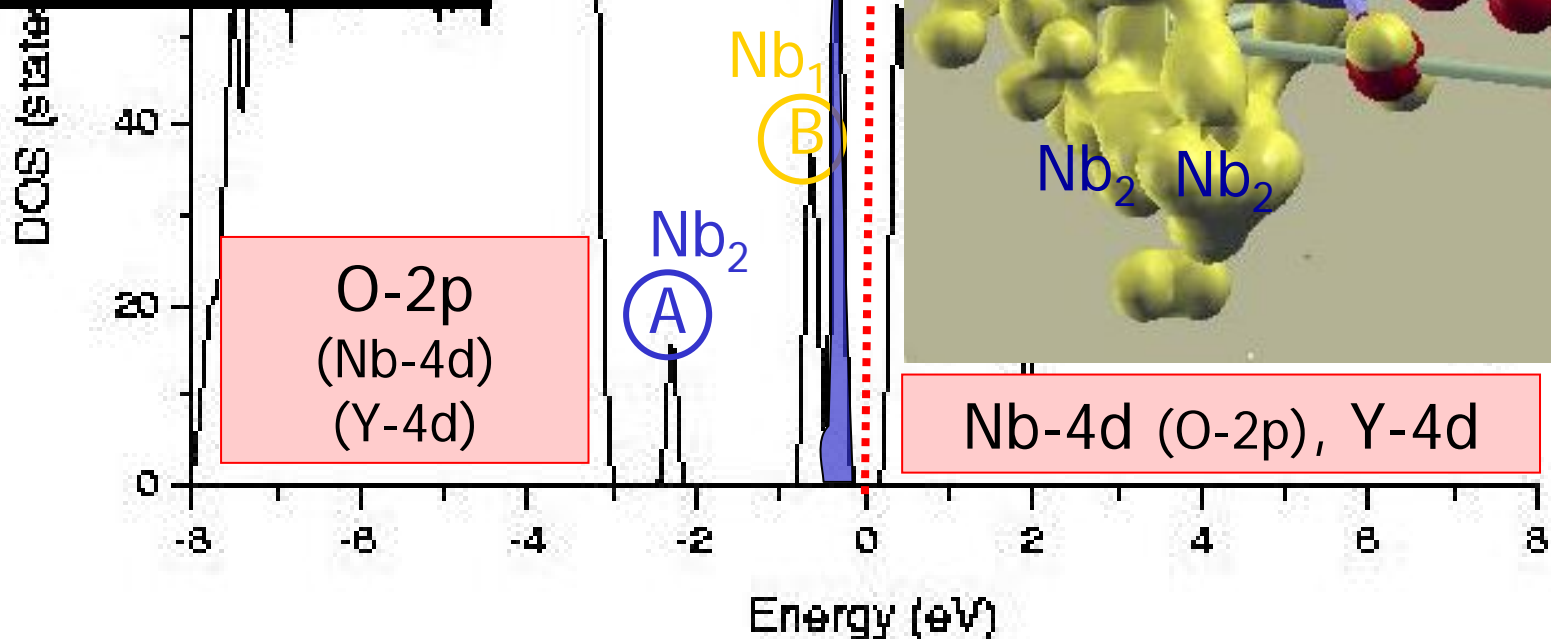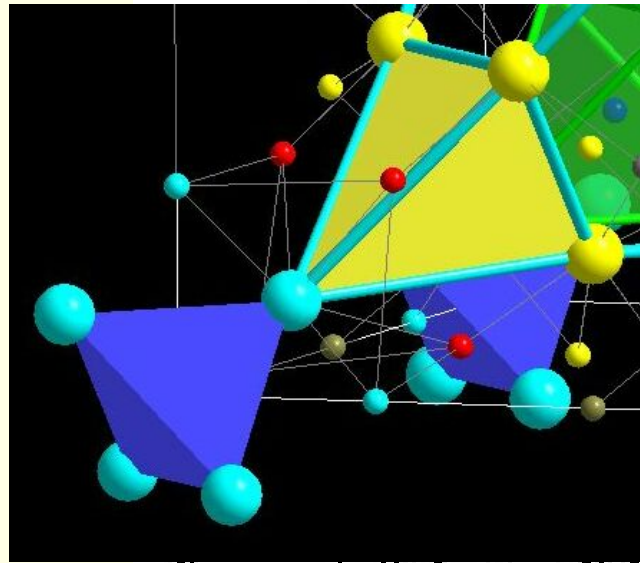
- **Orbital ordering of Nb-4d orbitals and structural distortion !**
  - *Can be described with LDA !!*
- **M-M interaction (second NN): 2 types of bonds:**
  - *strong Nb-Nb 4-center bonds (only Nb2 d_{z^2})*
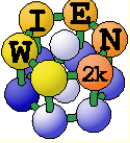 - *strong Nb-Nb 3-center bonds (both, on Nb1 and Nb2)*
- **Relaxation**
  - *Two types of Nb*
    - Nb1 (12i) highly elongated tetradedron along (111)
    - Nb2 (4e) perfect tetrahedron with short distances
- **Metal/insulator**
  - *Ideal structure metallic, relaxed structure insulating*

+ robust all-electron full-potential method

+ unbiased basisset, one convergence parameter (LDA-limit)

+ all elements of periodic table (equal expensive), metals

+ LDA, GGA, meta-GGA, LDA+U, spin-orbit

+ many properties

+ w2web (for novice users)

- ? speed (+ memory requirements)

    + very efficient basis for large spheres (2 bohr) (Fe: 12Ry, O: 9Ry)

    - less efficient for small spheres (1 bohr) (O: 25 Ry)

    - large cells (n^3, iterative diagonalization not perfect)

- no stress tensor

- no linear response

Thank you for your attention !