Crystal field and magnetism with Wannier functions

Pavel Novák
Institute of Physics, Prague

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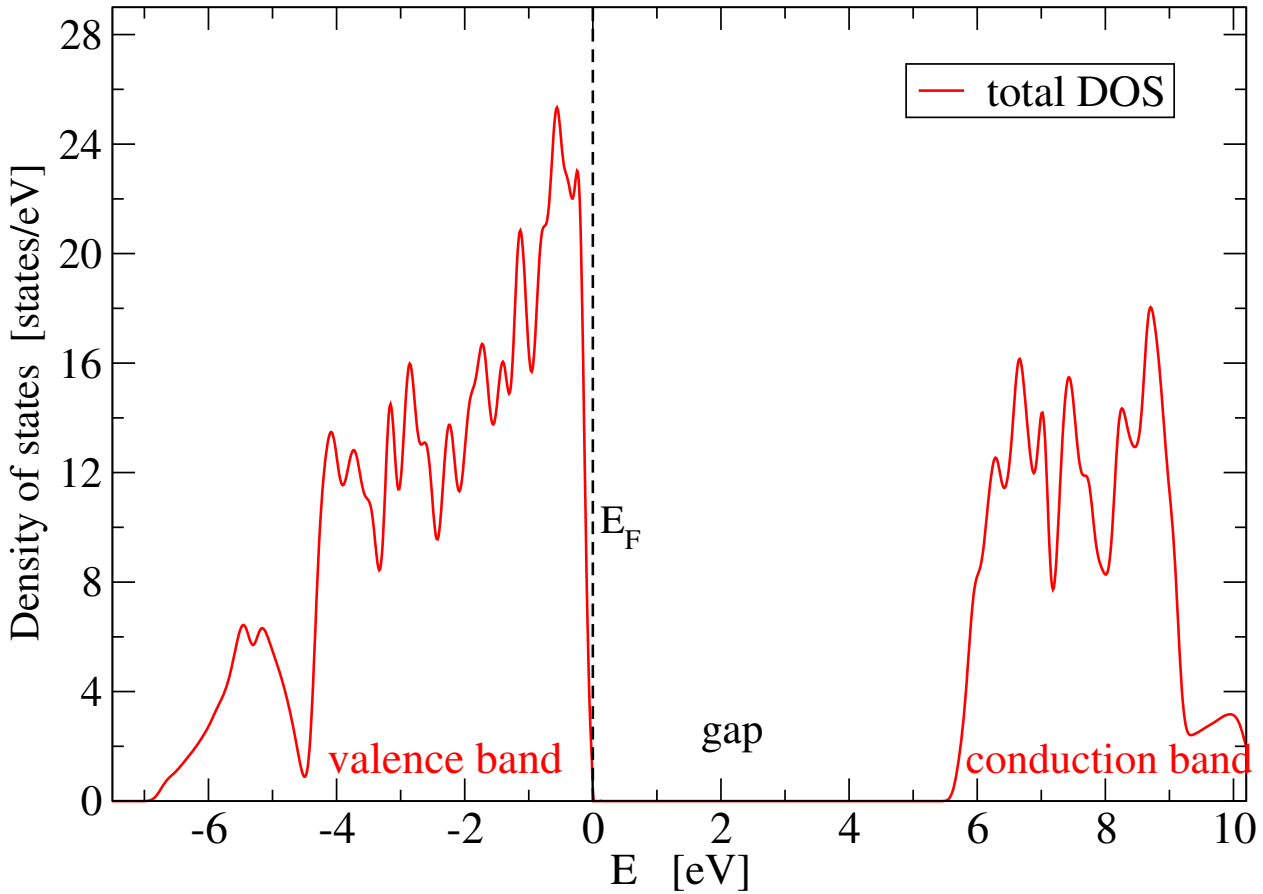
Outline

- Introduction: electronic structure of rare-earth oxides
- Atomic-like hamiltonian
- Crystal field hamiltonian and its parameters
- Calculation of crystal field parameters.
- Determination of multiplet splitting and magnetism
- Results
  - Energy levels
  - Magnetism
- Limitations of method
- Conclusions and outlook

Electron structure of oxide matrix: $YAlO_3$

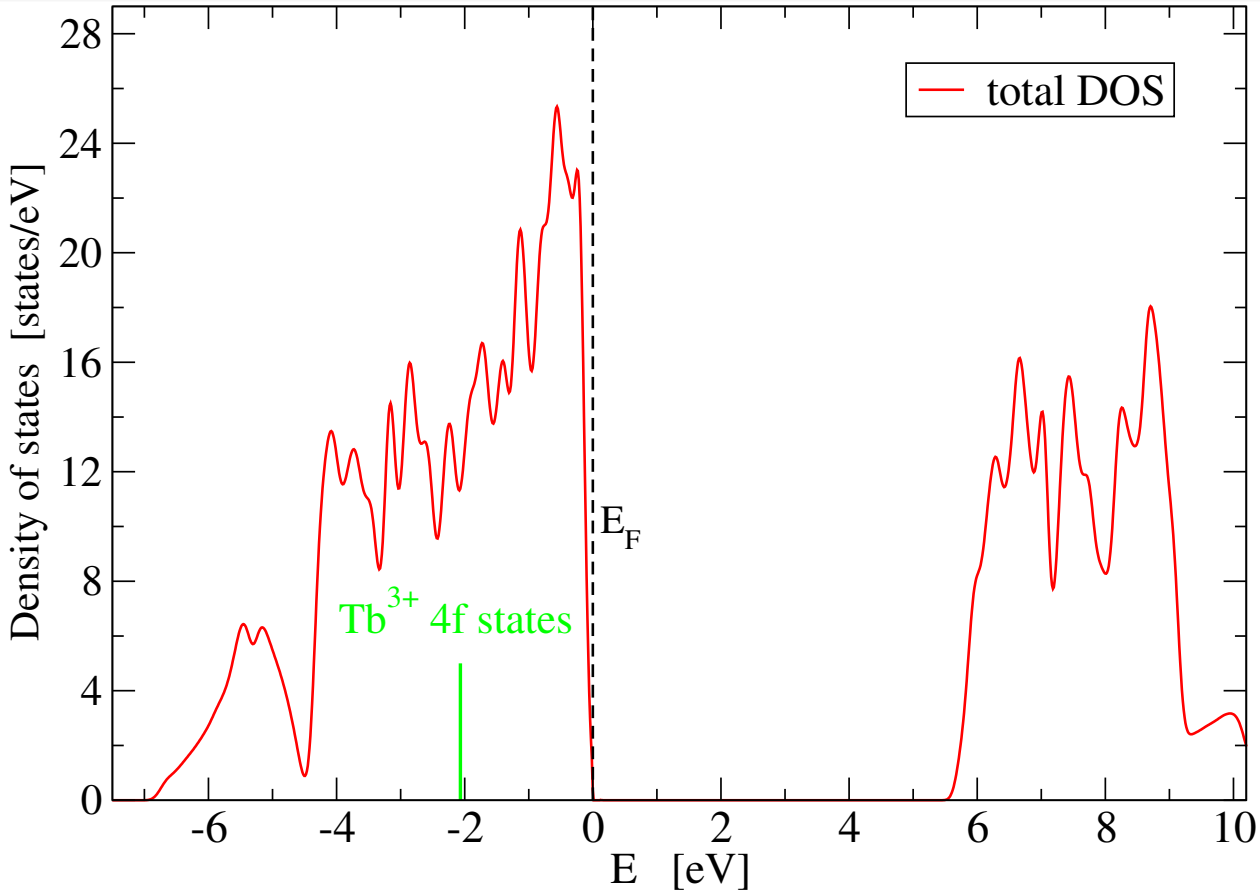
Density of states calculated with WIEN2k package



Tb:$YAlO_3$ ($TbY_{23}Al_{24}O_{72}$)

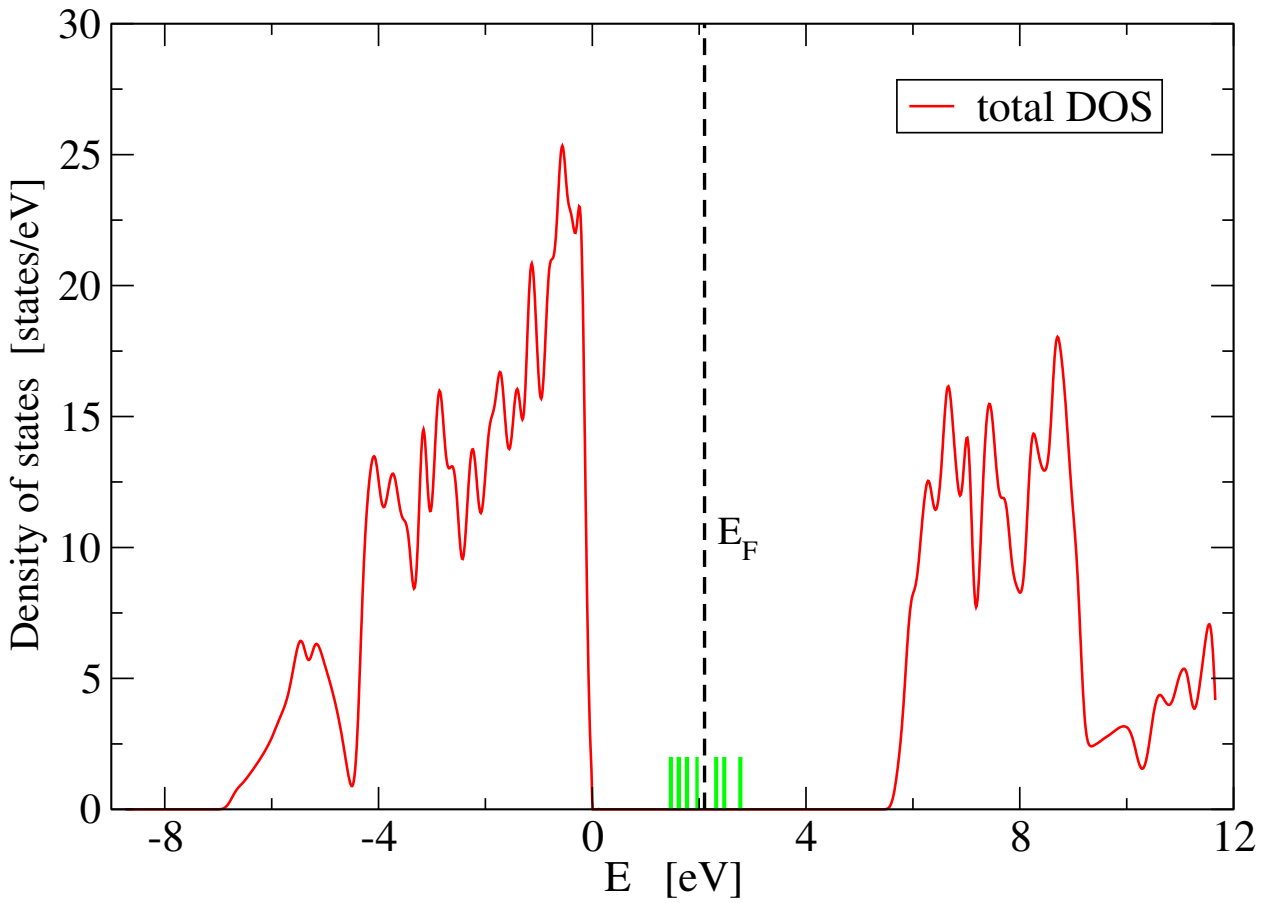
Tb($4f$) states treated as core levels (WIEN2k)

Core states feel only spherical potential,
they are not split by crystal field and do not contribute to it.



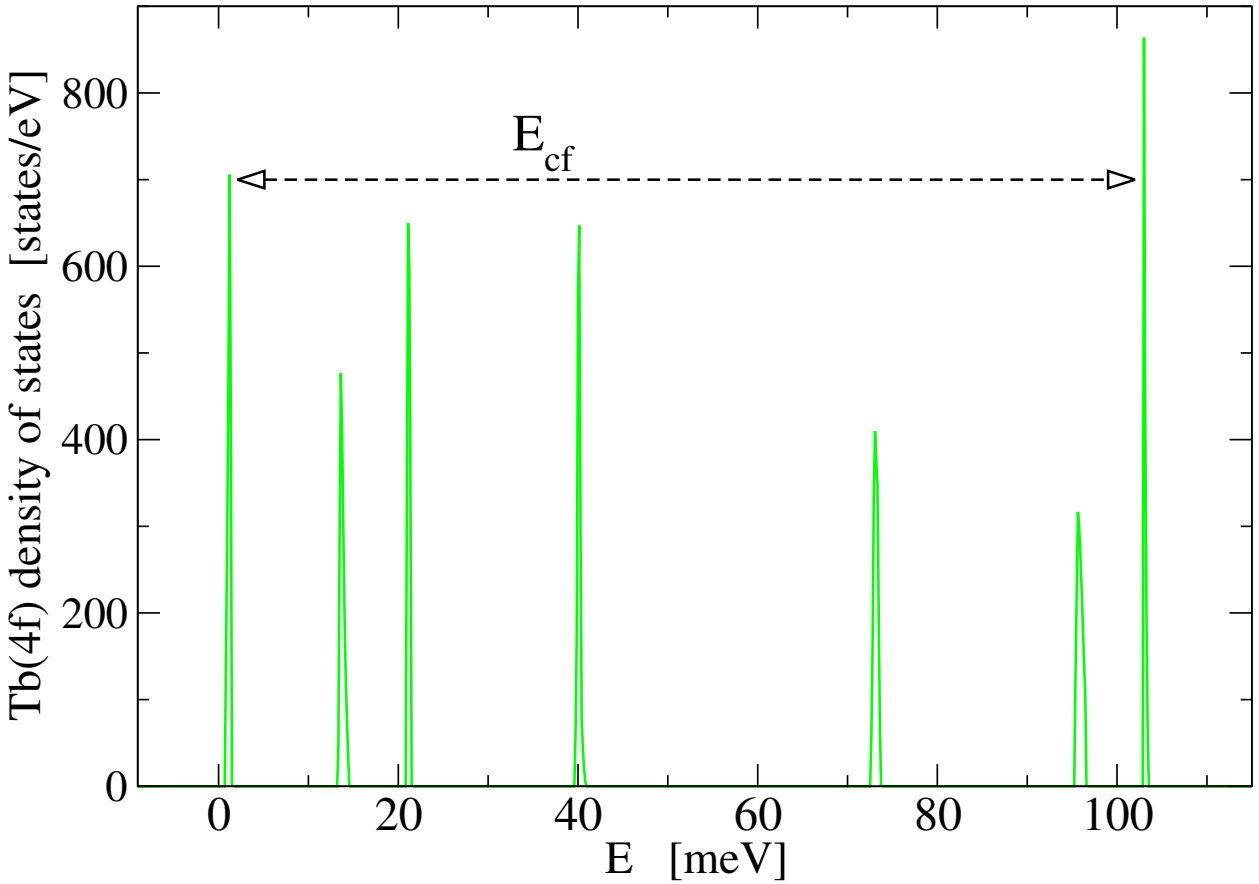
$Tb:YAlO_3$ ($TbY_{23}Al_{24}O_{72}$)

Expected position of Tb($4f$) levels, $4f$ treated as valence states



Splitting of Tb($4f$) levels by crystal field

7 orbital singlets - complete lifting of degeneracy



Crystal field parameters from density of states

Cubic symmetry

$4f$ level split on three states (singlet, 2 triplets).
Crystal field characterized by two parameters
$\Longrightarrow$ energies are sufficient information to determine crystal field.
PrO_2, $PrBaO_3$ Novák, Diviš, phys.stat.sol (b) **244**, 3168 (2007)

C_s symmetry of Tb^{3+} site in $YAlO_3$

7 singlets, 15 parameters of crystal field
$\Longrightarrow$ energies are not sufficient to determine crystal field.
Additional information needed: orbital composition of singlets.
Problem: too many information (48) $\Longrightarrow$ use least squares.
Ambiguous, many local minima, which one is correct?

Way out: Wannier functions

Atomic-like hamiltonian for well localized f electrons

Sum of atomic (free ion), crystal field and Zeeman parts

$$\hat{H} = \hat{H}_A + \hat{H}_{CF} + \hat{H}_Z;\ \hat{H}_Z = \mu_B \vec{B} \sum_{i=1}^{N} (\hat{l}_i + 2\hat{s}_i)$$

Free ion hamiltonian

$$\hat{H}_A = E_{avg} + \sum_{k=2,4,6} F^k \hat{f}_k + \xi_{4f} \sum_{i=1}^{N} \hat{s}_i \hat{l}_i +$$
$$\alpha \hat{L}^2 + \beta \hat{G}(G_2) + \gamma \hat{G}(R_2) +$$
$$\sum_{j=0,2,4} M^j \hat{m}_j + \sum_{k=2,4,6} P^k \hat{p}_k + \sum_{r=2,3,4,6,7,8} T^r \hat{t}(r),$$

$\hat{H}_A$ has spherical symmetry, depends on 20 parameters.
For rare-earth ions approximate values of parameters are known, or they may be calculated *ab initio*

Crystal field hamiltonian

$$\hat{H}_{CF} = \sum_{k=2}^{2L} \sum_{q=-k}^{k} B_q^{(k)} \hat{C}_q^{(k)}$$

$\hat{C}_q^{(k)}$: spherical tensor operator of rank k.
$\hat{C}_q^{(k)}$ form full orthogonal system.
$B_q^{(k)}$: crystal field parameters.
$\hat{H}_{CF}$ acts on one-electron states, it does not depend on spin.

Values of q and k for which $B_q^{(k)} \neq 0$ depend on site symmetry.

f electrons
cubic symmetry: 2 parameters.
C_s symmetry of orthorhombic perovskites: 15 parameters.
LaF_3 no symmetry: 27 parameters.

Determination of crystal field parameters

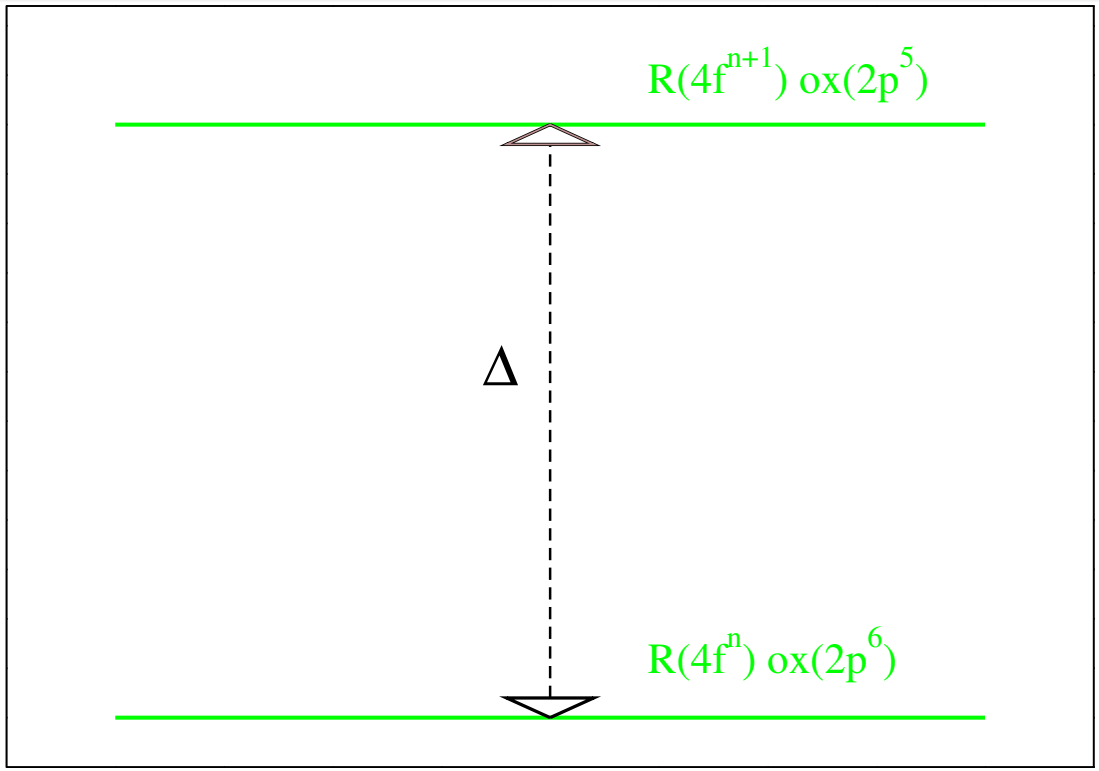
Steps

1. Selfconsistent band calculation with f electrons in core.
   Standard WIEN2k calculation.
2. f states and oxygen ligand treated as valence states
   in a nonselfconsistent calculation, all other states moved away.
   Relative position of 4f and oxygen states is adjusted using
   'hybridization' parameter Δ (the only parameter of method).
   WIEN2k with orbital energy shift potential.
3. Transformation of 4f band states to Wannier basis.
   wien2wannier, wannier90 packages.
4. Extraction of local 4f hamiltonian and its expansion in series
   of spherical tensor operators. program *Bkq*
   coefficients of expansion are crystal field parameters.

Hybridization parameter Δ

Δ is the charge transfer energy between $4f$ and ligand states

Analog in $3d$ compounds (Co:ZnO): Kuzian et al. Phys. Rev. B 74,155201 (2006).



In oxides semiempirical analysis of optical absorption data gives $3\ \text{eV} < \Delta < 10\ \text{eV}$. Δ can also be estimated using WIEN2k.

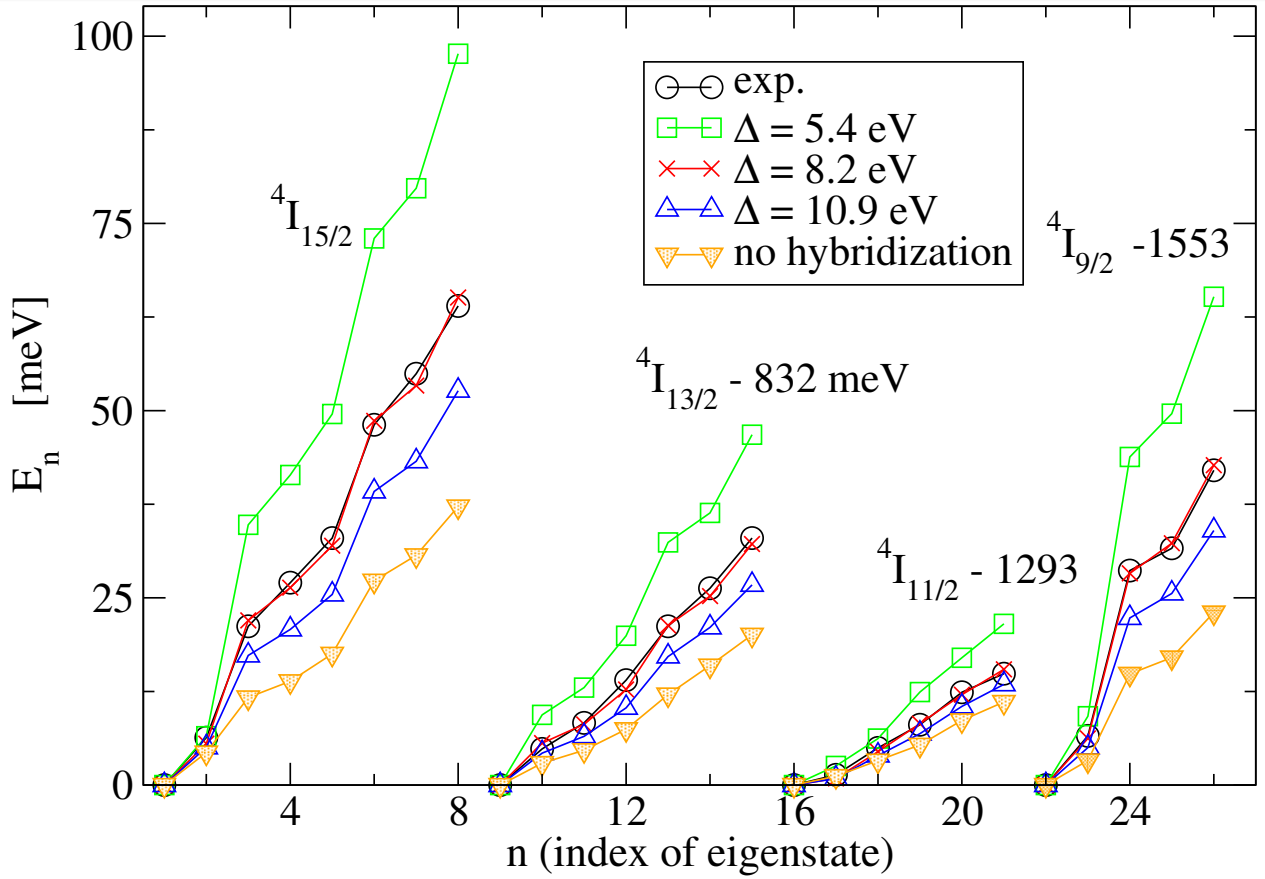
Multiplet splitting and magnetic properties

1. REcfp. Solves eigenproblem for hamiltonian $\hat{H}$, originated from lanthanide package (Edwardsson and Aberg, 2001).
   Result: energies and eigenvectors of all states of $(4f)^n$ electron configuration, and their dependence on external magnetic field.
2. g_chi. Calculation of eigenstates magnetic moments, $\hat{g}$ and $\hat{\chi}$ tensors including their canonical form.
3. temp. Temperature dependence of magnetic moments and susceptibility, optionally averaging for polycrystals.

Multiplet splitting in Er:$YAlO_3$

Splitting of the lowest four multiplets by crystal field.

Experiment: Duan *et al.*, Phys. Rev. B **75**, 195130 (2007).

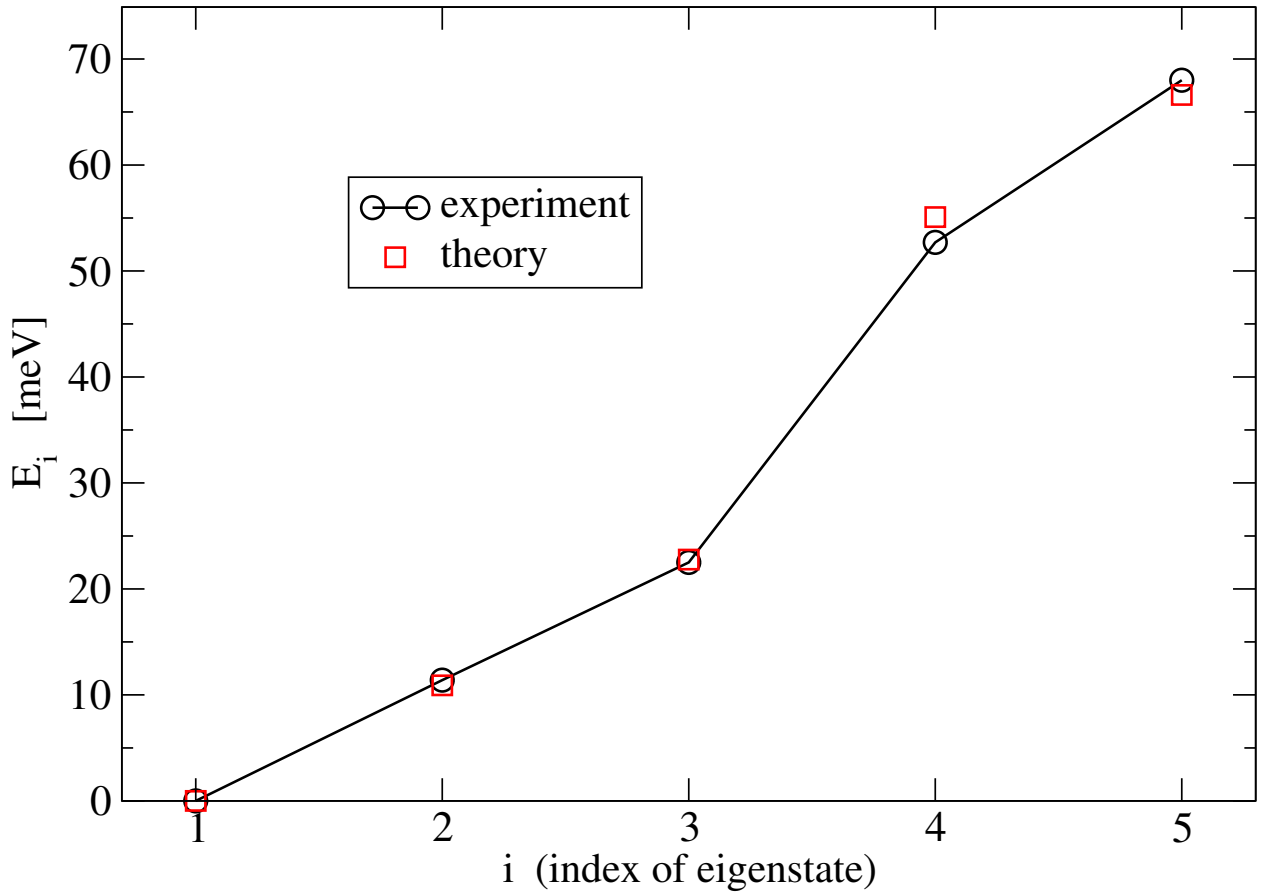


In orthoperovskites Δ was fixed at 8.2 eV (0.6 Ry)

Comparison with experiment: energy levels

$NdGaO_3$: splitting of ground $^4H_{9/2}$ multiplet by crystal field.

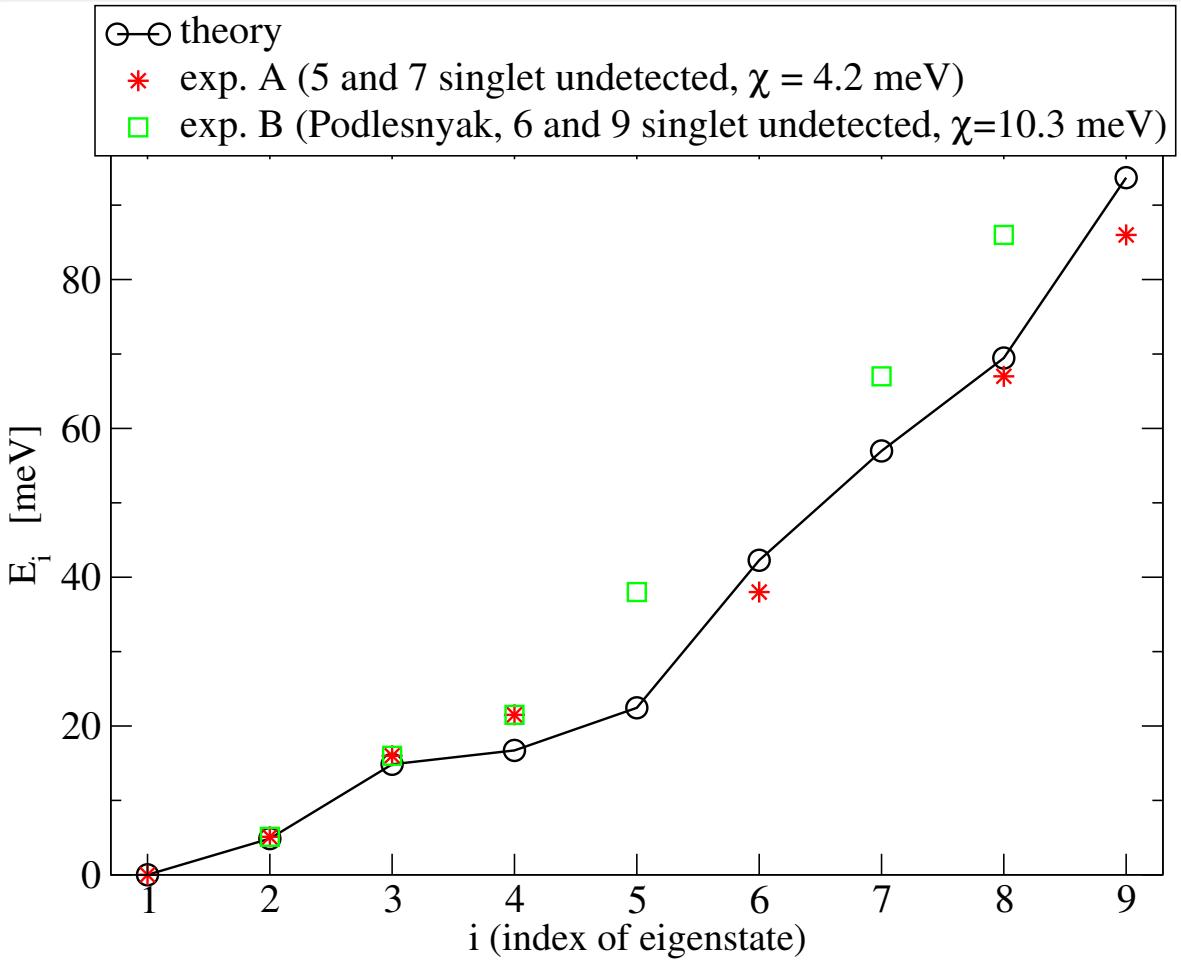
Experiment: Podlesnyak et al., J. Phys.:Condens. Matter **5**, 8973 (1993).



Comparison with experiment: energy levels

$PrGaO_3$: splitting of ground $^3H_4$ multiplet by crystal field.
Only six of eight excited singlets were detected experimentally.

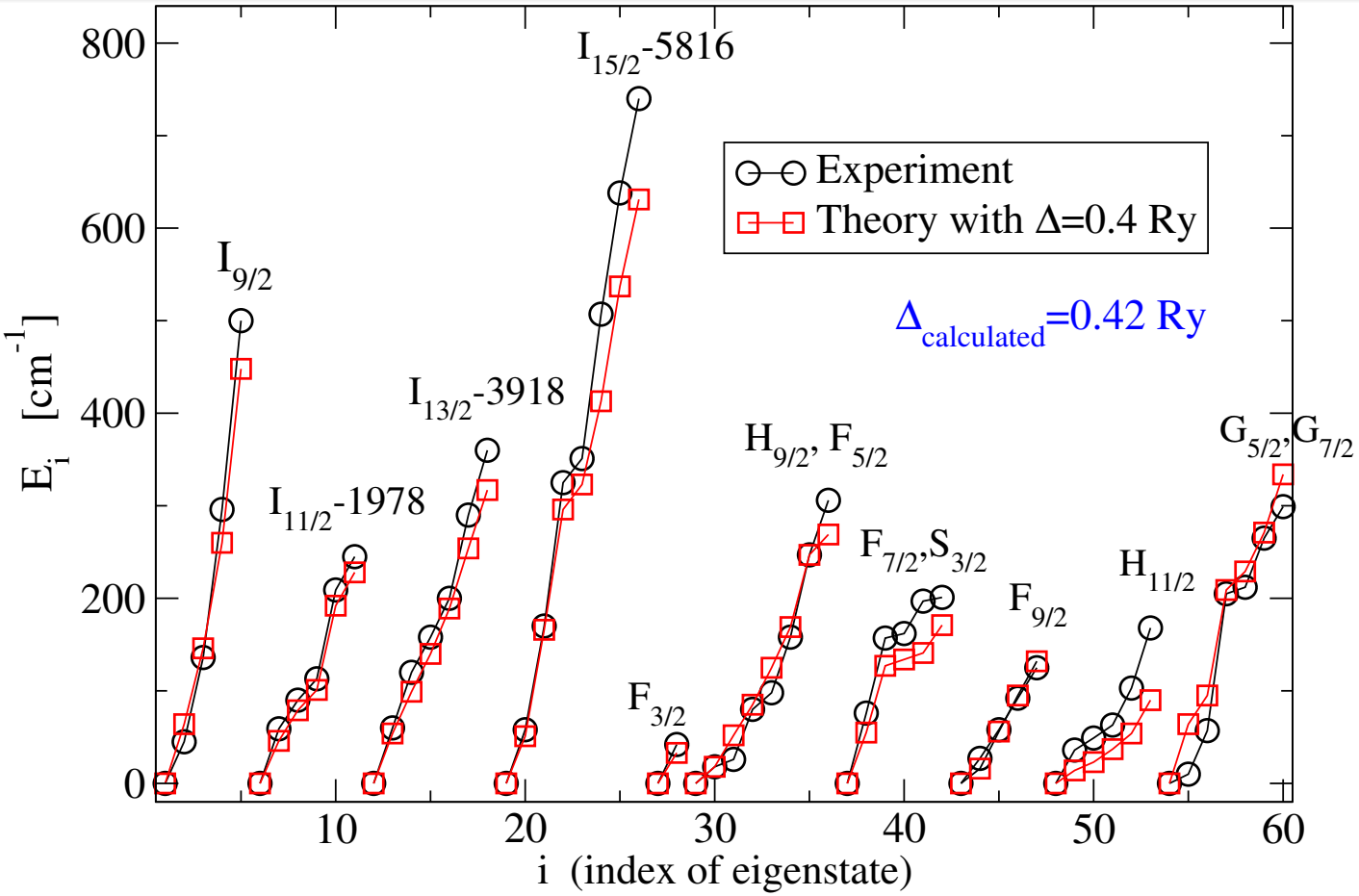
Experiment: Podlesnyak et al., J. Phys.: Condens. Matter **6**, 4099 (1994).



Comparison with experiment: energy levels

Nd:LaF_3: splitting of low lying multiplets by crystal field.
No local symmetry, 27 crystal field parameters calculated.

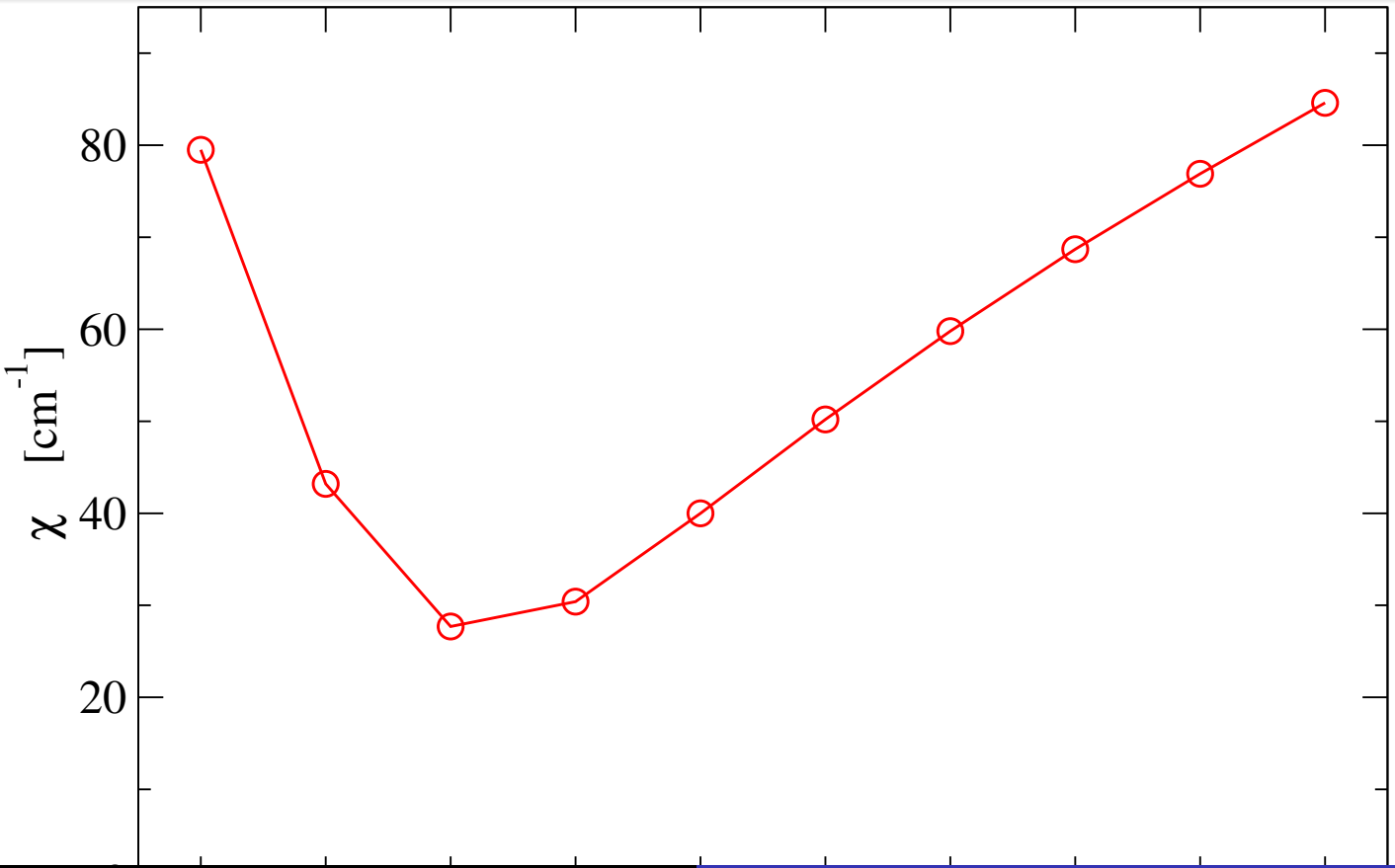
Experiment: Carnall et al., J. Chem. Phys 90, 3443 (1989).



Nd:LaF_3. Experiment vs. calculation

Mean quadratic deviation χ as function of Δ

$$\chi = \frac{1}{N_{levels}} \sqrt{\sum_{i=1}^{N_{levels}} (E_i^{calc} - E_i^{exp})^2}$$

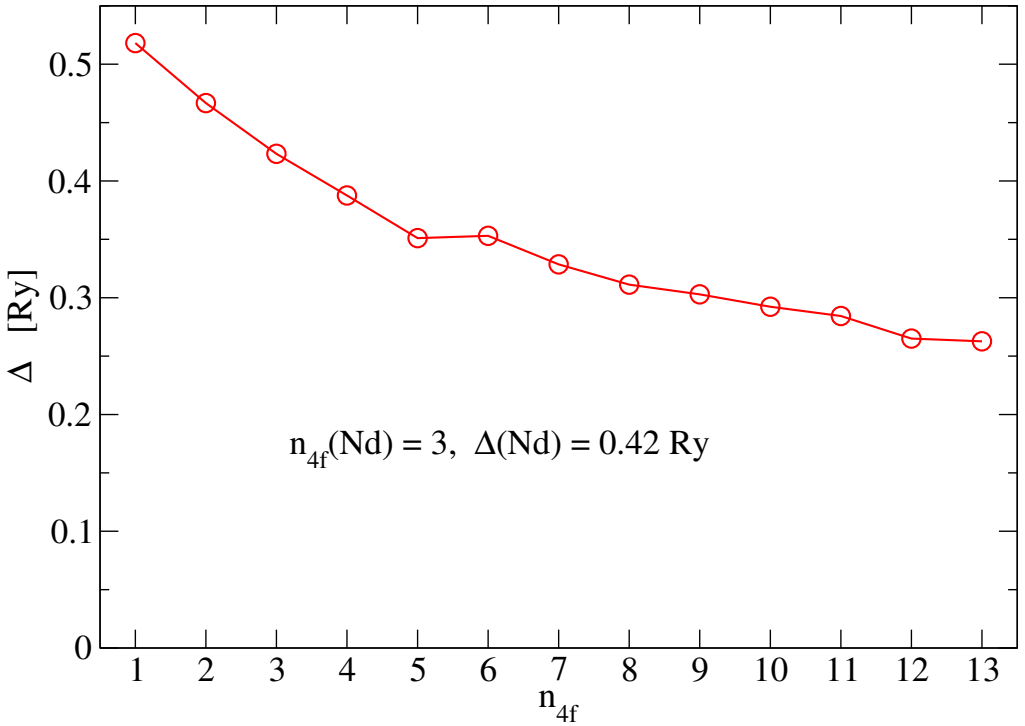


RE:LaF_3. Calculated Δ parameter

Δ as function of number of $4f$ electrons

Calculation with RE($4f$) treated as core electrons

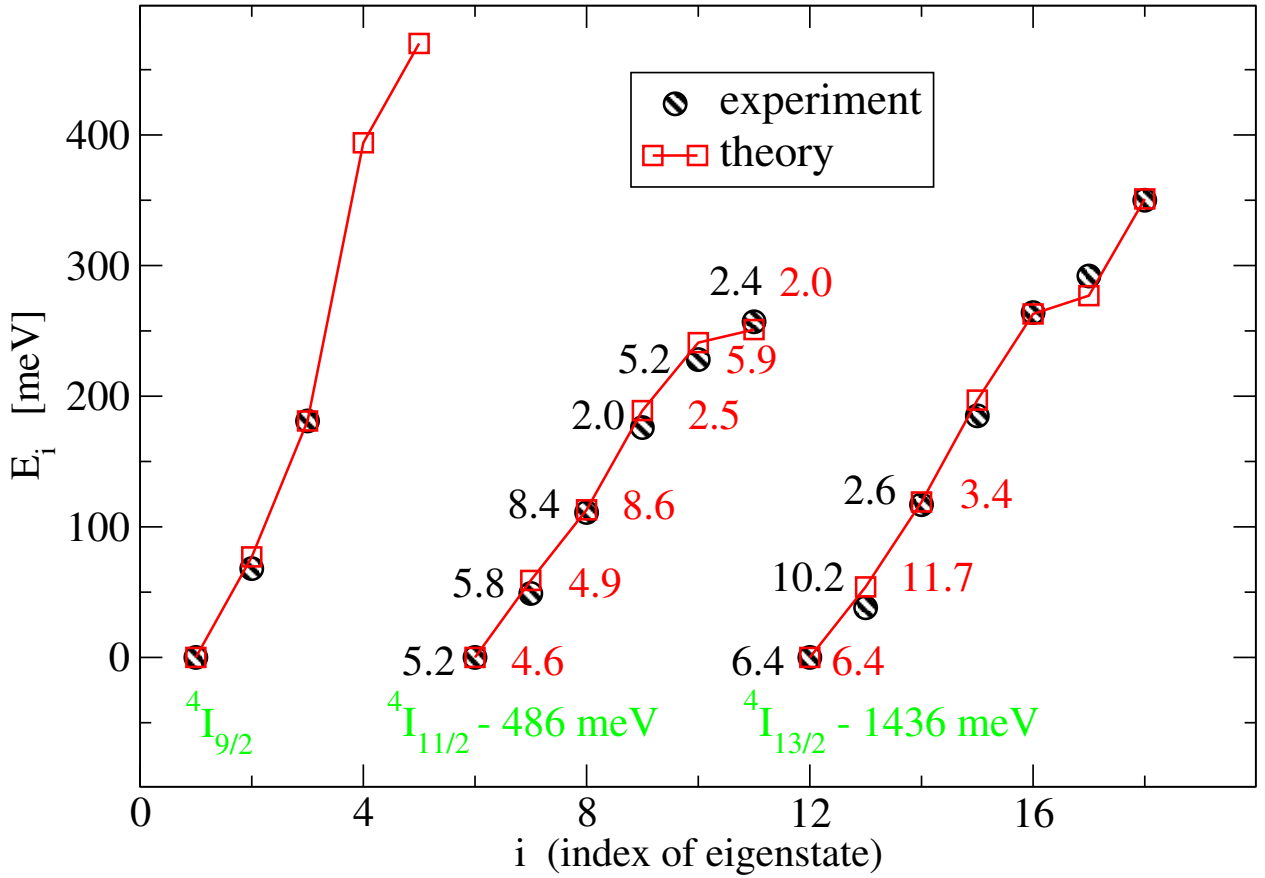
$\Delta = E_{tot}(4f^n, N \text{ val. electrons}) - E_{tot}(4f^{n+1}, N-1 \text{ val. electrons})$



Manganites - magnetism in excited states

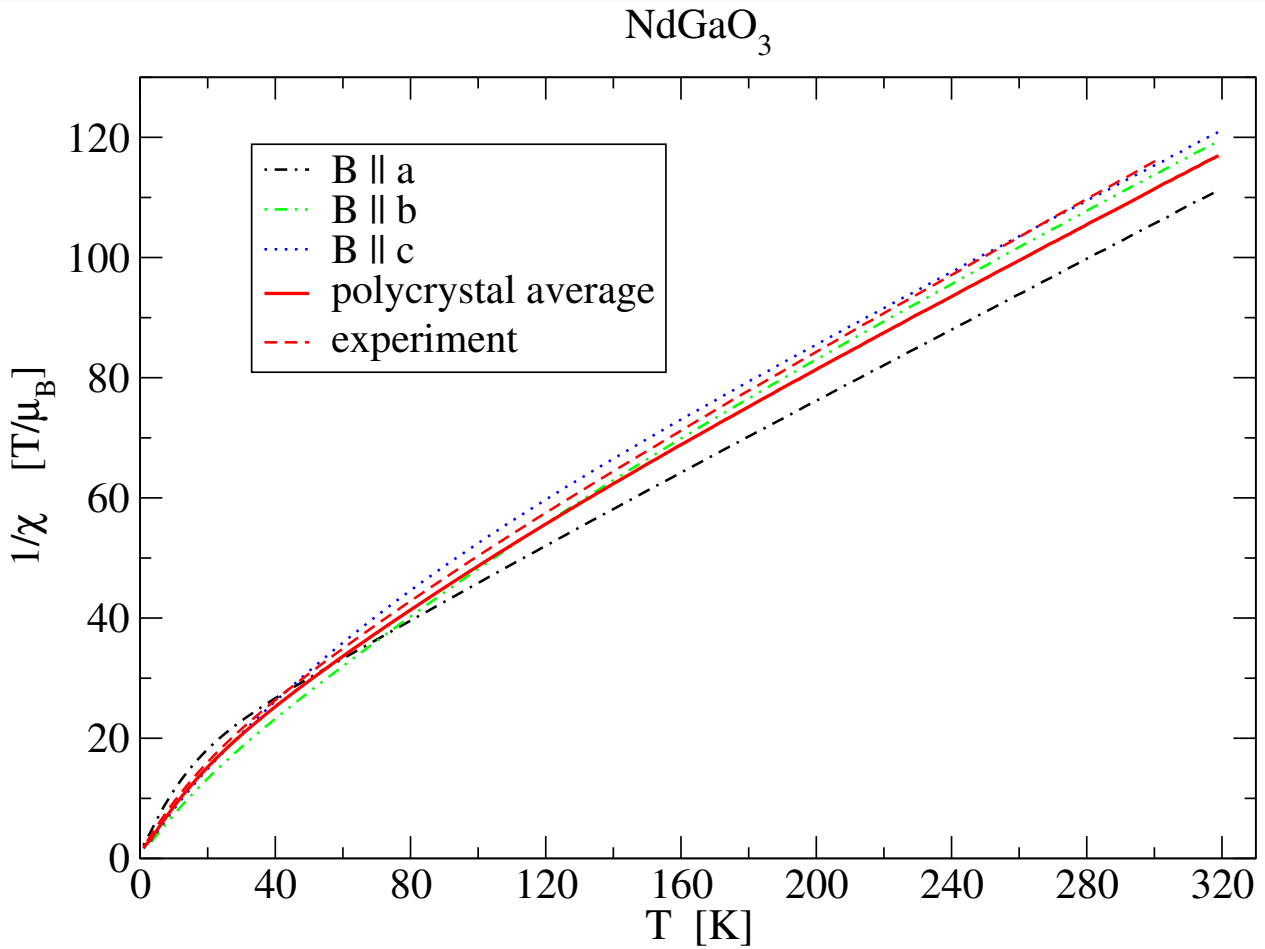
$NdMnO_3$: splitting of the lowest three multiplets by crystal field and g_a factor of nine Kramers doublets.

Experiment: Jandl *et al.*, Phys. Rev. B **71**, 024417 (2005).



$NdGaO_3$: temperature dependence of inverse susceptibility.

Experiment: Novák *et al.*, J. Phys.: Condens. Matter **25**, 446001 (2013).



Limitations, outlook

Limitations

- Hybridization of f electrons should be weak,
  as it is not taken into account selfconsistently.
  If the f-oxygen states hybridization is strong:
  multiplet ligand-field theory using Wannier orbitals.

  M.W. Haverkort *et al.* Phys. Rev. B **85**, 165113 (2012)
- Atomic-like, model hamiltonian is limited to f space.

Outlook

- Intensity of $f - f$ transitions. Instead of Judd-Ofelt method ab-initio approach.
- Application to other rare-earth compounds.
- Is the method applicable to the d and $5f$ states?

Conclusions

- New method to calculate crystal field parameters proposed. Method contains single adjustable parameter, which can be independently estimated.
- Until now method applied to more than sixty compounds:
  - orthorhombic aluminates, gallates, cobaltites and manganites.
  - Rare-earth impurities in aluminium and gallium garnets.
  - Rare-earth layered hexagonal cobaltates.
  - R:LaF_3; R=Ce, Pr ...Yb.
  - $R_2Fe_{14}B$ (cooperation with Tohoku Univ.).
  - $CeCu_2Si_2$ (cooperation with MPI Dresden).
- Agreement with experimental multiplet splitting within meV.
- Good agreement with magnetic properties.
- Present version applicable to arbitrary local symmetry.
- With few modifications method may be used by non-specialists.

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