ABINIT04 workshop (10-12 May, 2004, Paris)

ABINIT applications : Rare-earth Sesquioxides/Oxysulfides and a Photochromic Molecular Crystals

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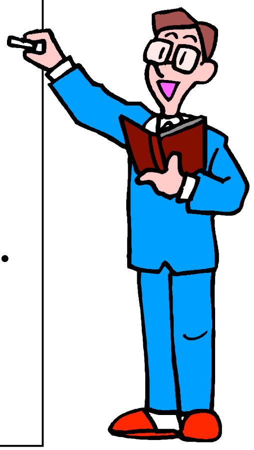
   1.1. Why RE_2O_3/RE_2O_2S ?
   1.2. ABINIT results : Geometry, Band, RF-calculations…
2. A Molecular Crystal : RF-results and discussion
   (for detail, Mikami & Nakamura, PRB69, 134205 (2004))

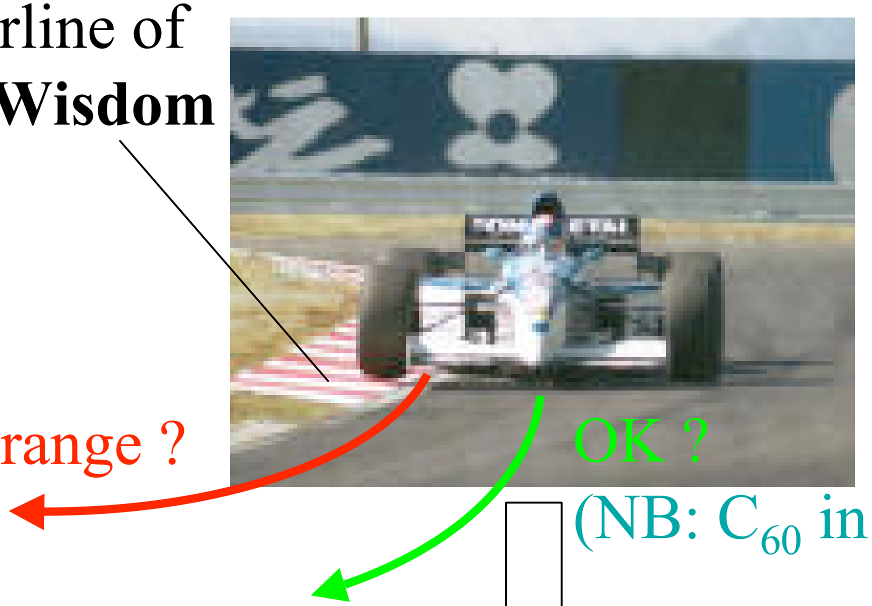


Motivation

Feasibility of first-principles calculation for extraordinary systems ?

Benchmark !

(Fuzzy) borderline of
Conventional Wisdom



Out of range ?

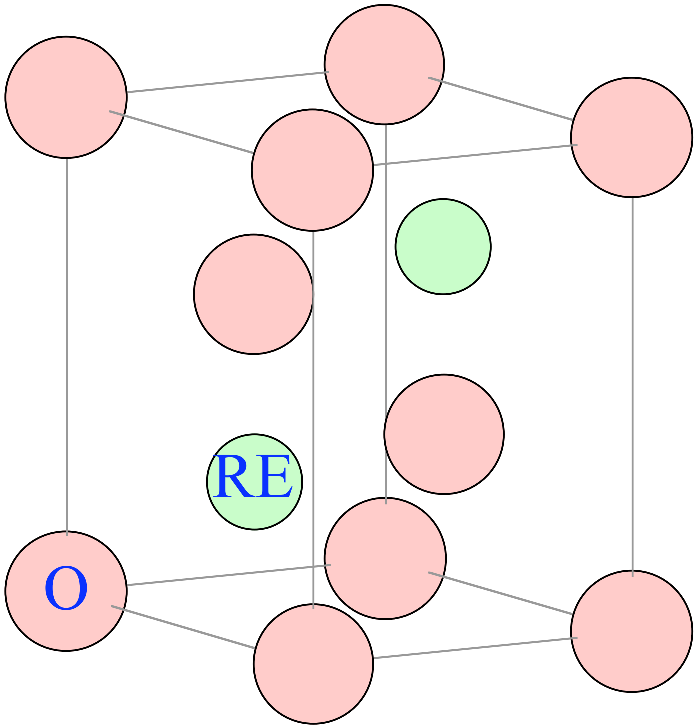
OK ?

(NB: C_{60} in LDA/ not in GGA)

Let us share gained wisdoms & difficulties
–> ***future (possible) functions*** *may be suggested*

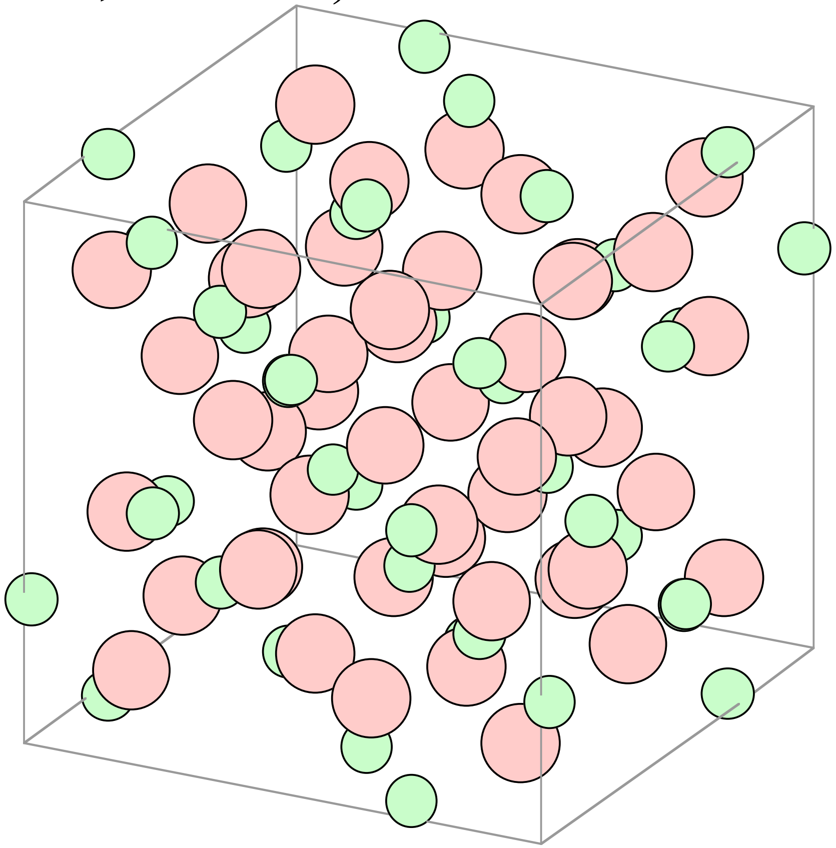
1. Introduction (Why RE_2O_3 ?)

Rare-earth sesquioxides (RE_2O_3: R=Y, La – Lu)



A-type ($P\bar{3}m1$) : ***large*** RE

(RE=La, Ce, Pr, Nd, Pm)



C-type ($Ia3$) : ***small*** RE

(RE=Y, Sm, Eu, Gd, Tb, …, Lu)

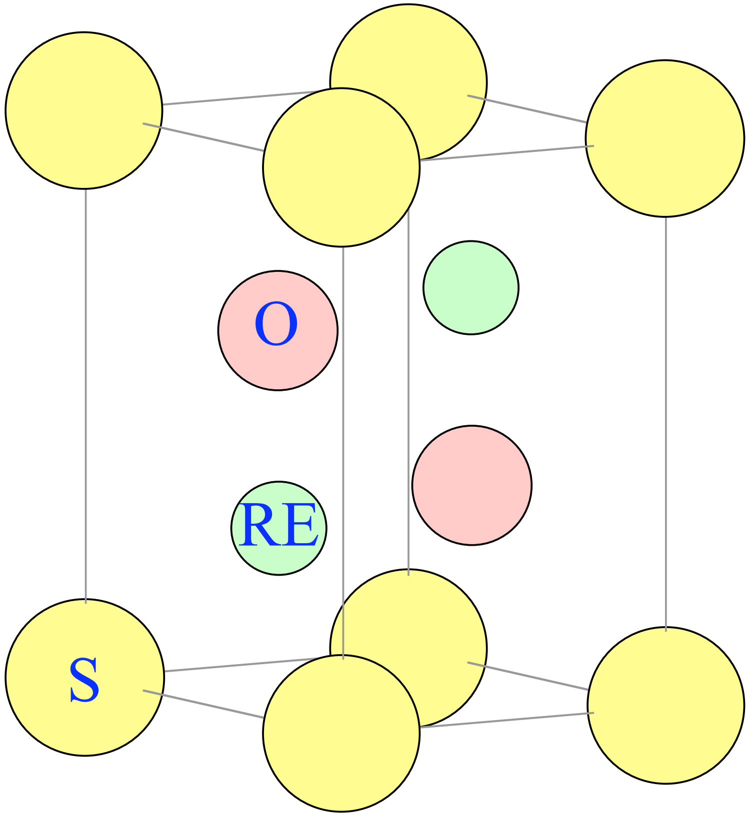
- High-***k***, Catalyst (O_2 storage in Ceria), Additive, Coating, …

  few studies on electronic structure/physical properties

- Feasibility of RE pseudopotentials ? (e.g. treatment of 4*f*)

1. Introduction (Why Oxysulfide ?)

Rare-earth Oxysulfides (RE_2O_2S: RE=Y, La – Lu)

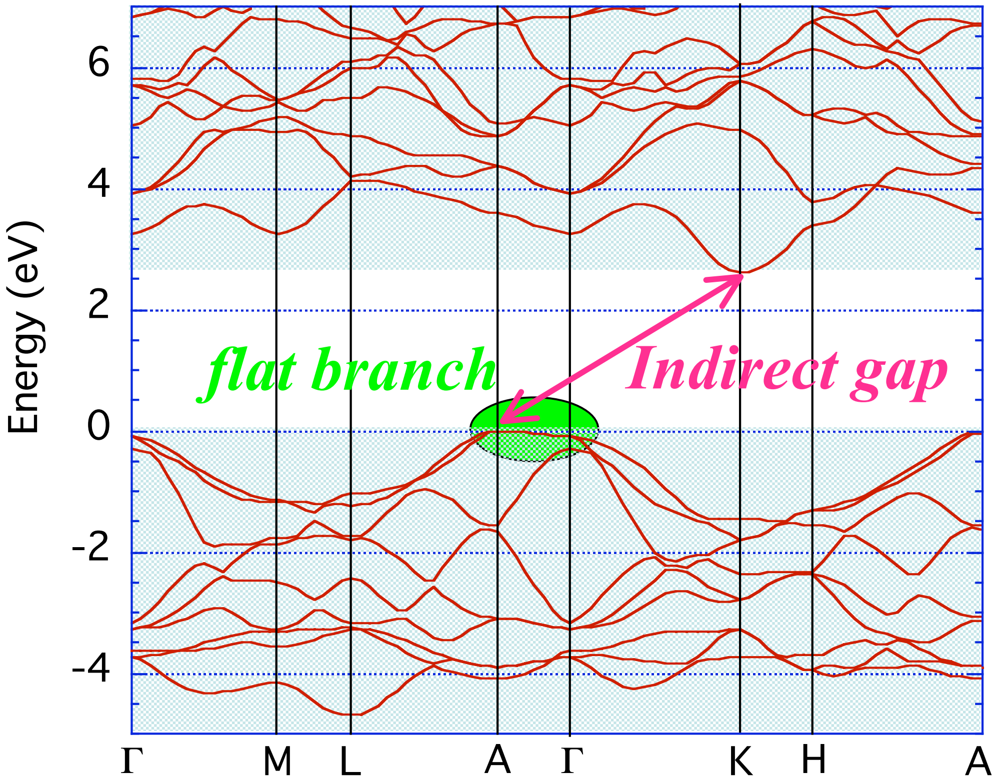


efficient hosts for phosphors

Y_2O_2S: Eu ••• red for TV

Gd_2O_2S: Pr ••• scintillator

Y_2O_2S band-structure



M. Mikami & A. Oshiyama,
Phys.Rev.B57, 8939 (1998)

RF calc. (phonon/ ε) also performed
M.Mikami et al. PRB65, 094302 (2002)

similarity/difference between RE_2O_3 and RE_2O_2S ?

Variation of the band gap in RE_2O_3 / Body-color in RE_2O_2S

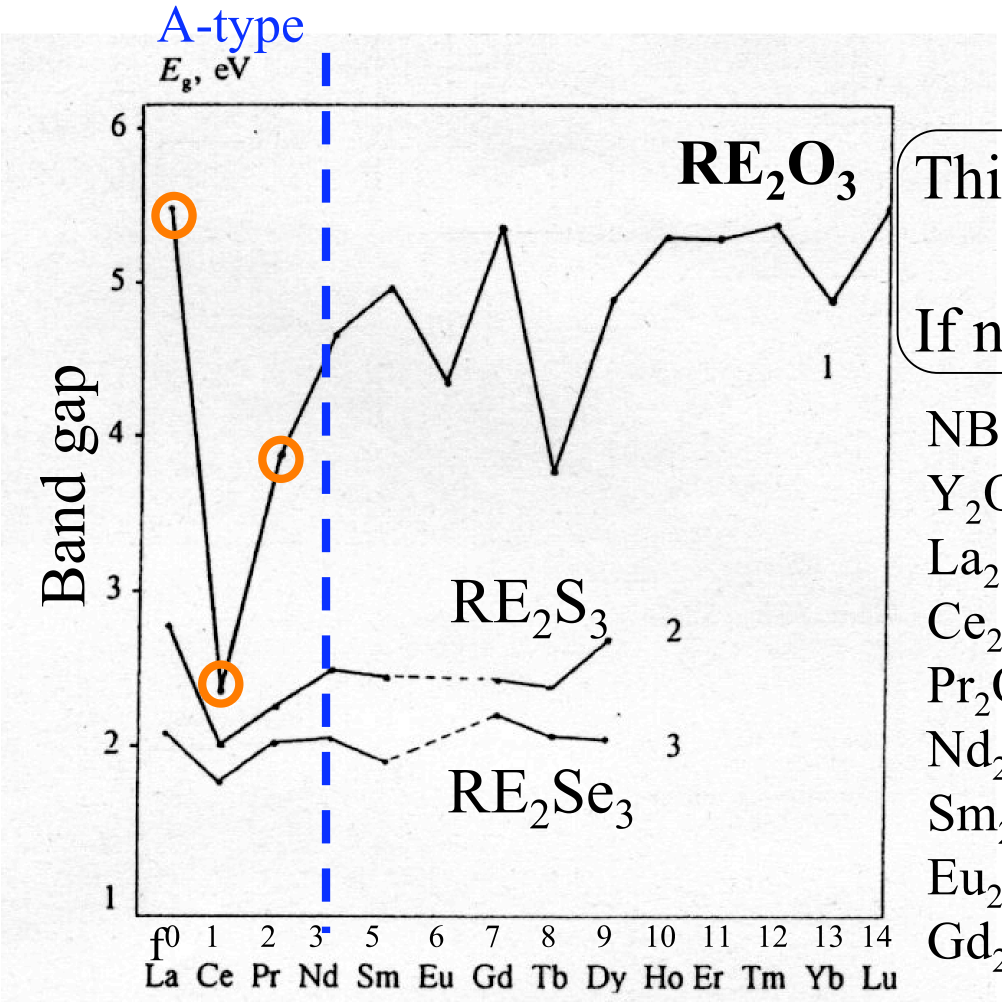


Fig. 1. Variation of the band gap E_g of Ln_2X_3 in the lanthanide series: (1) oxides; (2) sulphides; (3) selenides.

A.V.Prokofiev et al., J.Alloys Compd. 242, 41 (1996)
cited in Chem.Rev.98, 1479 (1998)

This variation may be explained from
VB (O-2*p*) => CB (RE-*s*/*d*) ?
If not, 4*f*-state may be involved...

NB: Body Color of RE_2O_2S

Y_2O_2S	white		
La_2O_2S	white-yellowish	Tb_2O_2S	**brown**
Ce_2O_2S	**brown-black**	Dy_2O_2S	gray
Pr_2O_2S	**black**	Ho_2O_2S	beige
Nd_2O_2S	bluish	Er_2O_2S	rose
Sm_2O_2S	pale beige	Tm_2O_2S	beige
Eu_2O_2S	**rose**	Yb_2O_2S	gray
Gd_2O_2S	white	Lu_2O_2S	yellowish

E_g variation or *crystal quality* ?
(intrinsic) (extrinsic)

2. Calculation Method

Density **F**unctional **T**heory – **Lo**cal **D**ensity **A**pproximation :

xc functional : Ceperley-Alder -> Perdew-Zunger

First-Principles Band Calculation : **ABINIT code** (www.abinit.org)

Reference: X. Gonze et al., Comp. Mater. Sci. 25, 478 (2002)
(see also :M.Mikami "Kotai-Butsuri" p.219 (2003) for Japanese)

Troullier-Martins-type pseudopotentials, prepared with **FHI98PP code**

FHI98PP : www.fhi-berlin.mpg.de/th/fhi98md/fhi98PP
M. Fuchs and M. Scheffler, Comp. Phys. Comm. 119, 67 (1999)
RE PP: **4*f* as "core"**, **shallow-core (5s/5p) as "valence"**
([Kr]$4d^{10}4f^{x}$ $5s^2 5p^6 5d^1 6s^2$, x=0,1,2 for La,Ce,Pr, respectively)
to avoid difficulties (ghost-bands, 4*f*-states at E_F & fractional occ.)
=> ***Feasiblity check !*** (geometries, energy bands except *f*-state, …)
We will see if our "***cats***" are effective … (from a Chinese saying)

Energy cut-off: 160Ry (due to RE's shallow-core states)

1st BZ integral : Monkhorst-Pack grid (4x4x2)

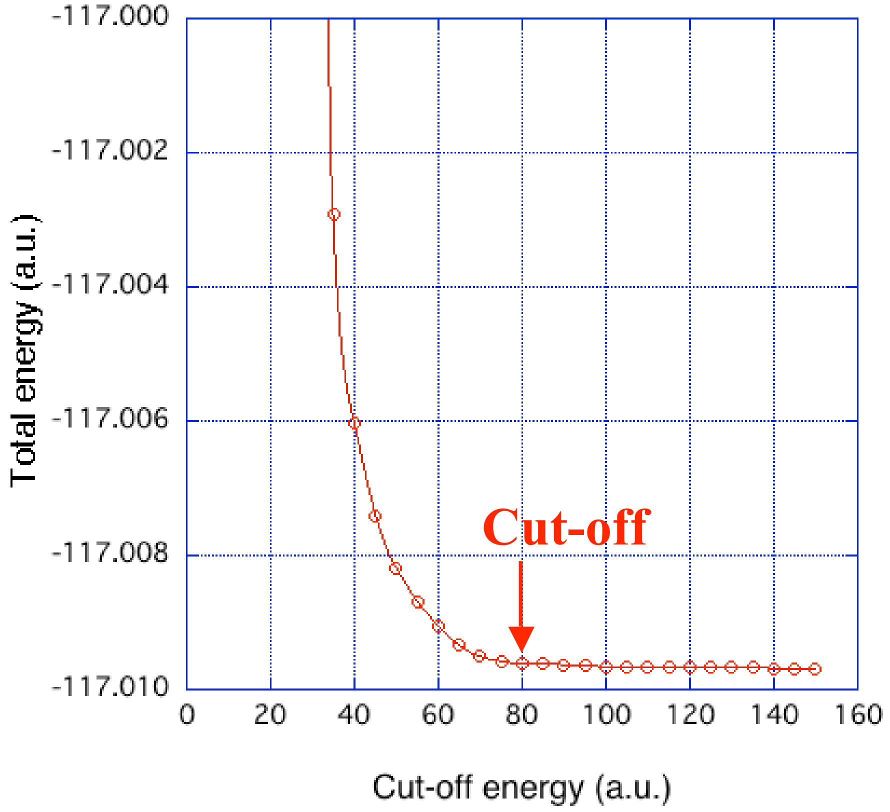
SCF sycle : Conjugate Gradient based on the minimum of the energy

X. Gonze, Phys. Rev. B54, 4383 (1996)

Geomerty optimization : Broyden-Fletcher-Goldfarb-Shanno minimization

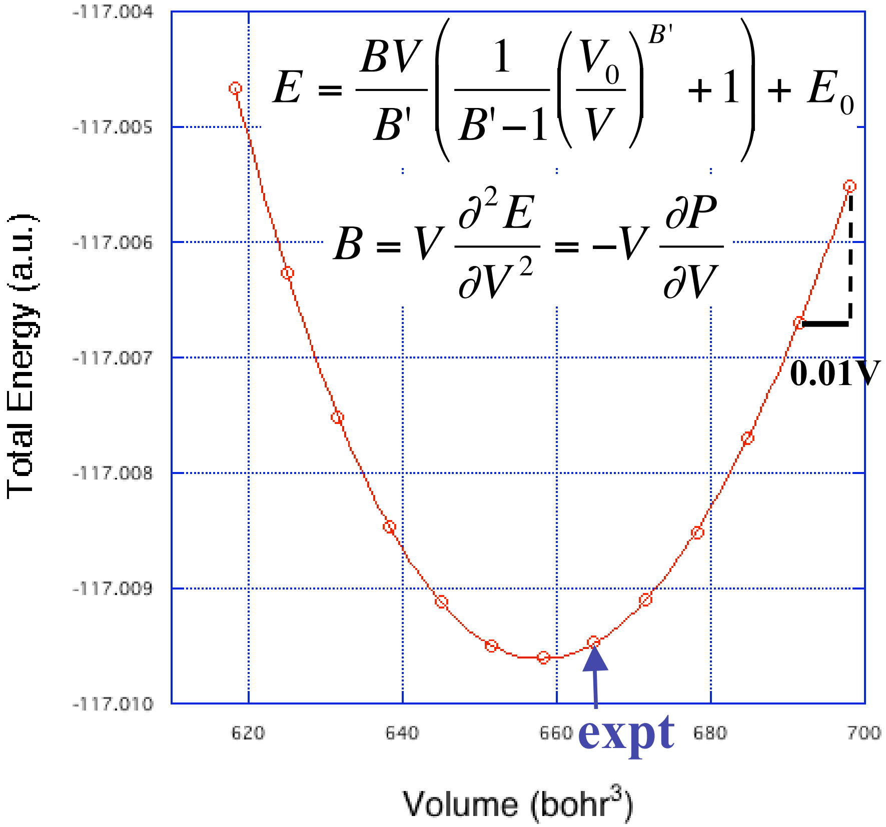
Typical examples from La_2O_2S calc.

Energy v.s. Cut-off



80 a.u. (160 Ry) adopted as the Cut-off energy

Volume v.s. Energy @ 160 Ry.



$$E = \frac{BV}{B'}\left(\frac{1}{B'-1}\left(\frac{V_0}{V}\right)^{B'}+1\right)+E_0$$

$$B = V\frac{\partial^2 E}{\partial V^2} = -V\frac{\partial P}{\partial V}$$

Murnaghan’s equation fitting

=> V_0, Bulk Modulus: B

3. Structures

calc.
(expt.)

This work & Previous work (PRB57,8939)

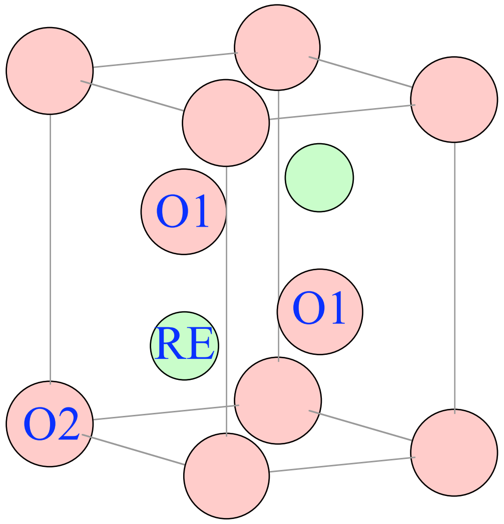
	a (Å)	***c*** (Å)	***c/a***	***u***	***v***	***B*** (GPa)
La_2O_3	**3.933** (3.940)	**6.086** (6.130)	**1.547** (1.556)	**0.247** (0.245)	**0.645** (0.645)	**118**
Ce_2O_3	**3.871** (*3.888*)	**6.001** (*6.026*)	**1.550** (1.550)	**0.247** (0.245)	**0.645** (0.647)	**124**
Pr_2O_3	**3.824** (*3.859*)	**5.934** (*6.013*)	**1.552** (1.558)	**0.247** (0.246)	**0.645** (0.656)	**130**

La_2O_2S	**4.035** (4.049)	**6.915** (6.939)	**1.714** (1.714)	**0.279** (0.279)	**0.629** (0.629)	**109**
Ce_2O_2S	**3.976** (4.008)	**6.822** (6.886)	**1.716** (1.718)	**0.280**	**0.629**	**114**
Pr_2O_2S	**3.930** (3.976)	**6.752** (6.831)	**1.718** (1.718)	**0.281**	**0.629**	**119**
Y_2O_2S	**3.750** (3.791)	**6.525** (6.596)	**1.740** (1.740)	**0.282**	**0.631**	**142**

NB: ionic radii(Å): La (1.10), Ce (1.07), Pr (0.99-1.126), Y (0.96)

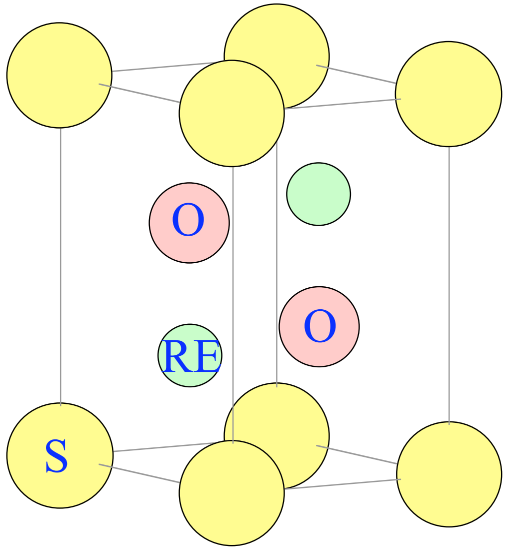
Bond length : calc. (sum of ionic radii (Σ))

	La_2O_3	Ce_2O_3	Pr_2O_3
RE–O1	2.364,2.422 (2.50)	2.327,2.388 (2.47)	2.299,2.362 (2.46)
RE–O2	2.723 (2.50)	2.682 (2.47)	2.650 (2.46)
O1–O2	3.134 (2.80)	3.088 (2.80)	3.052 (2.80)



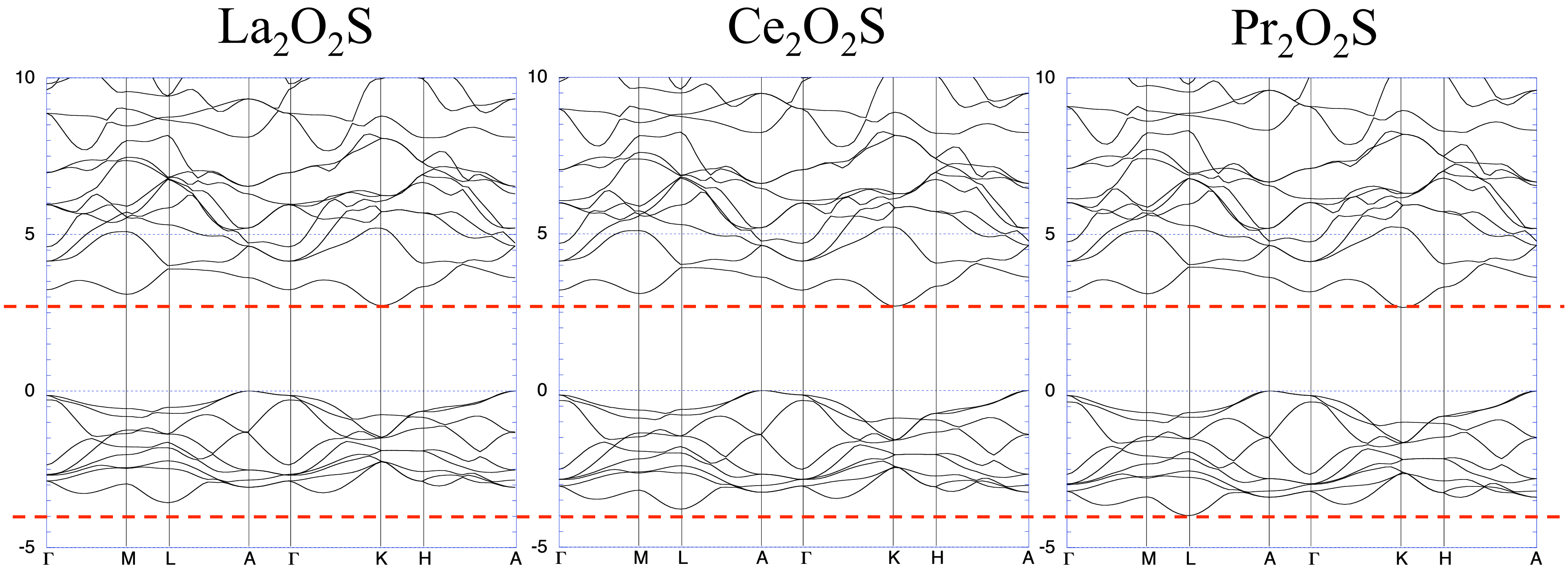
RE-O1 $< \Sigma$, RE-O2 $> \Sigma$

	La_2O_2S	Ce_2O_2S	Pr_2O_2S
RE–O	2.415,2.420 (2.50)	2.378,2.381 (2.47)	2.349,2.350 (2.46)
RE–S	3.025 (2.94)	2.986 (2.91)	2.958 (2.90)
O–S	3.465 (3.24)	3.417 (3.24)	3.380 (3.24)



RE-O $< \Sigma$, RE-S $> \Sigma$

RE_2O_2S Bandstructures (without f-states)



- indirect gap ∼ 3 eV (underestimated due to LDA)

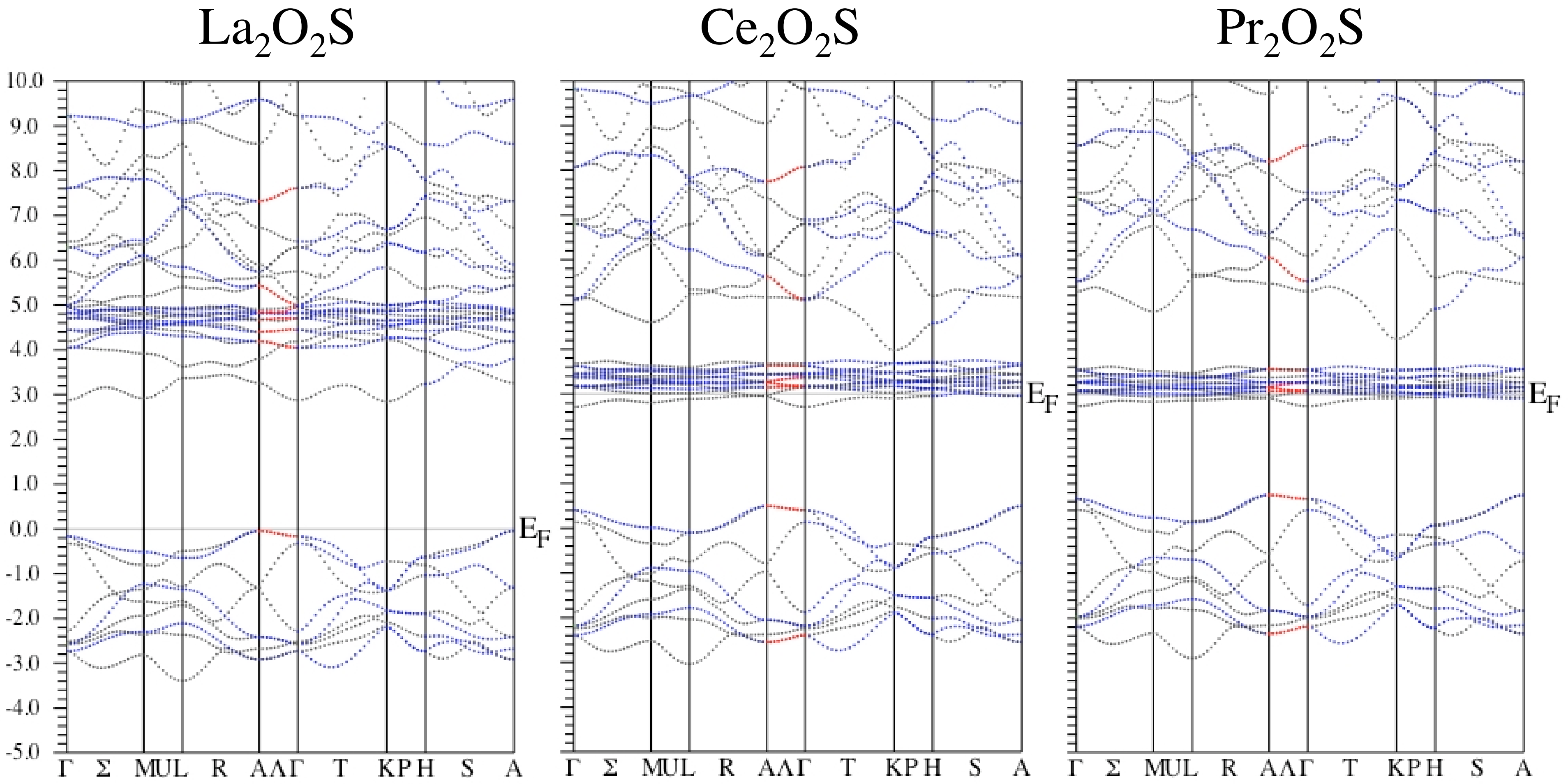
expt: La_2O_2S: 4.6 eV, Gd_2O_2S: 4.7 eV, Y_2O_2S: 4.9 eV, Lu_2O_2S: 5.1 eV
ionic .... covalent

- flat top branch (A–G) in VB
- wider VB (La –> Pr) : may reflect “covalency”

	La_2O_2S	**Ce_2O_2S**	**Pr_2O_2S**
VB width (eV)	**3.4**	**3.6**	**3.8**
Δ E (a.u.)	**-1.515**	**-1.532**	**-1.543**

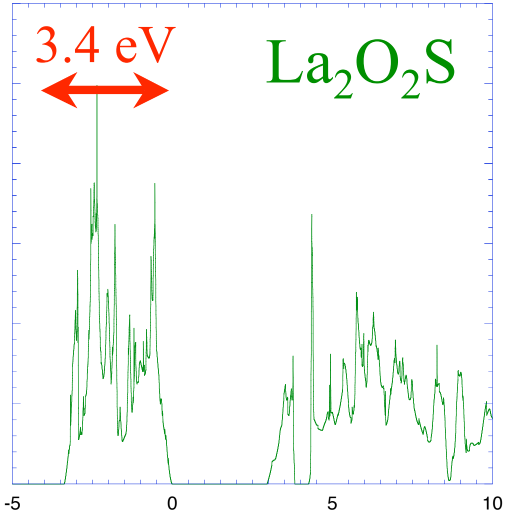
(NB: $\Delta E = E(RE_2O_3) - 2E(RE) - 2E(O) - E(S)$)

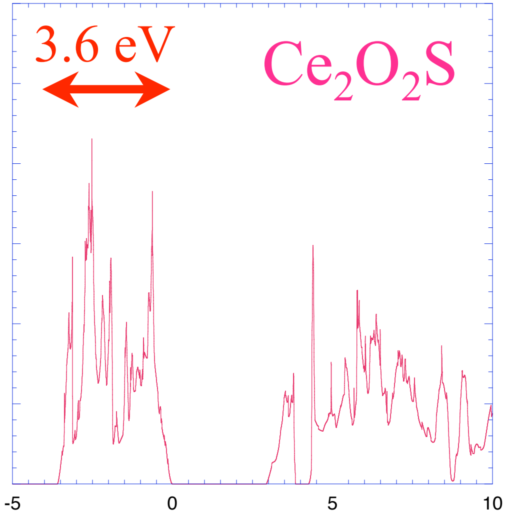
Band structures calculated with FLAPW (WIEN2k)

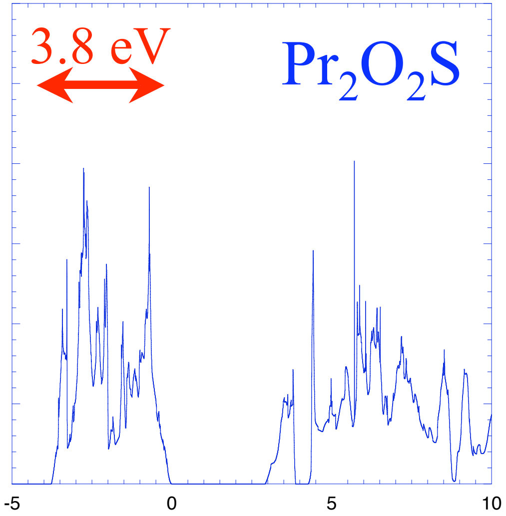


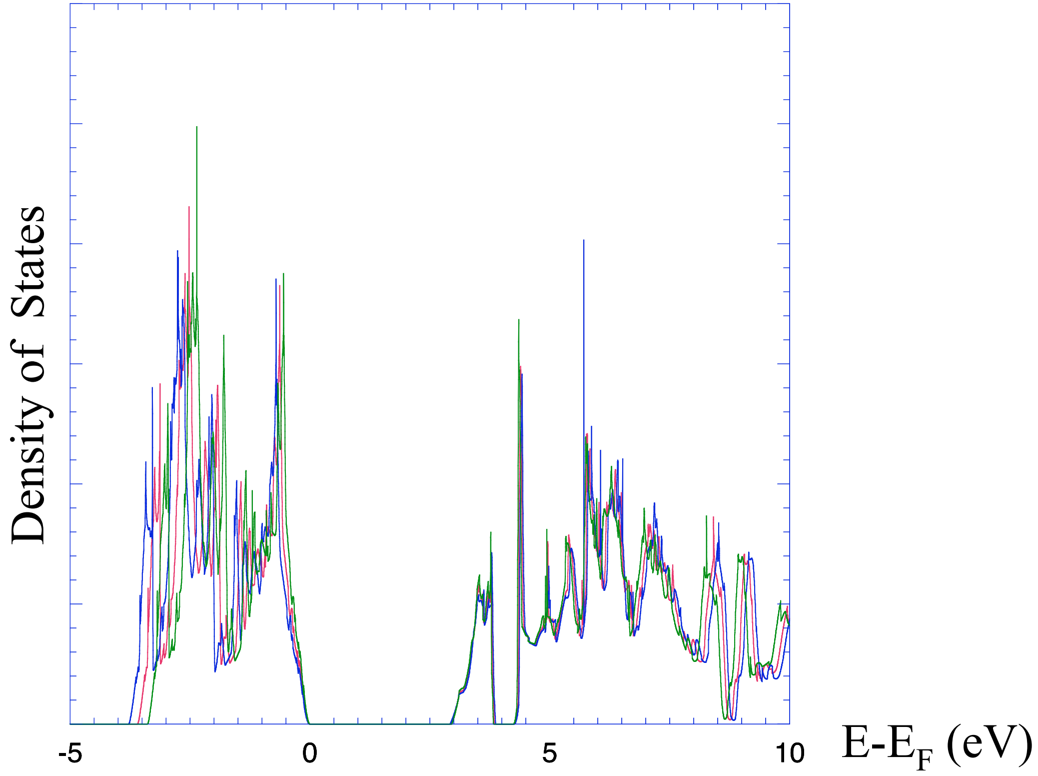
La_2O_2S Ce_2O_2S Pr_2O_2S

RE$_2$O$_2$S Density of States (without f-states)

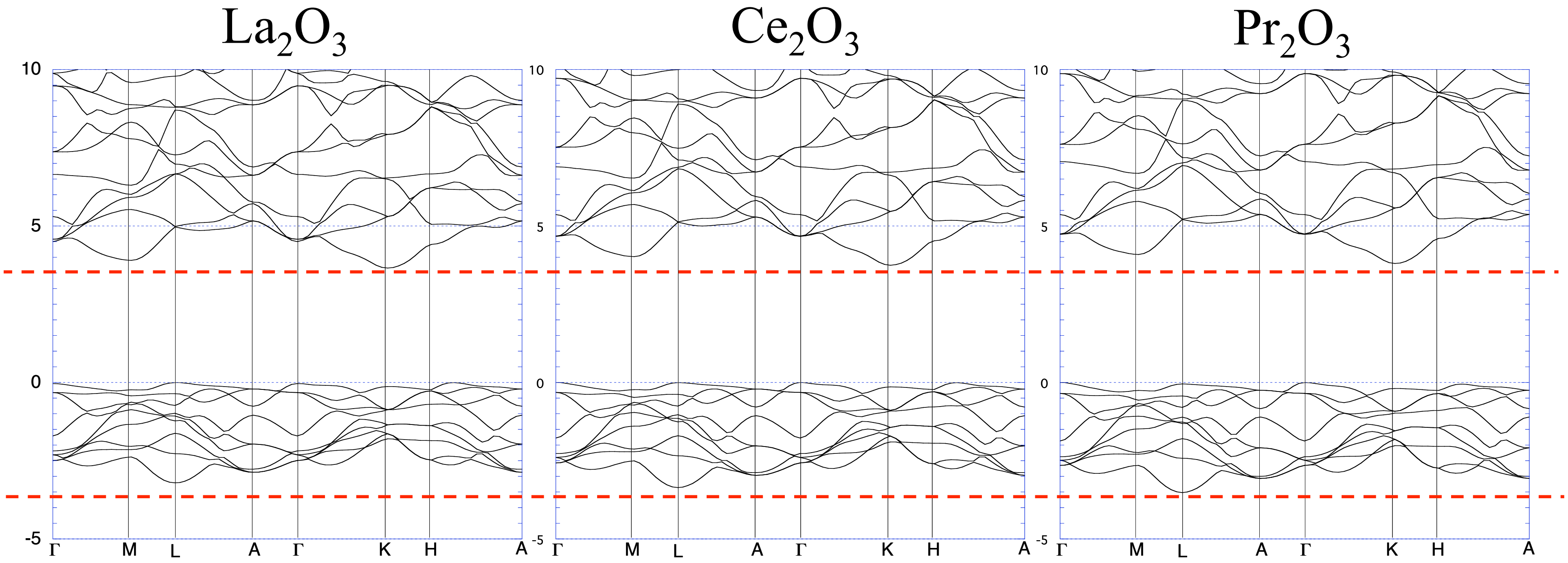








RE_2O_3 Bandstructures (without f-states)


La_2O_3 Ce_2O_3 Pr_2O_3

- indirect gap ∼ 4.0 eV: (underestimated due to LDA)

  expt: La_2O_3: 5.5 eV, Ce_2O_3: 2.4 eV, Pr_2O_3: 3.9 eV

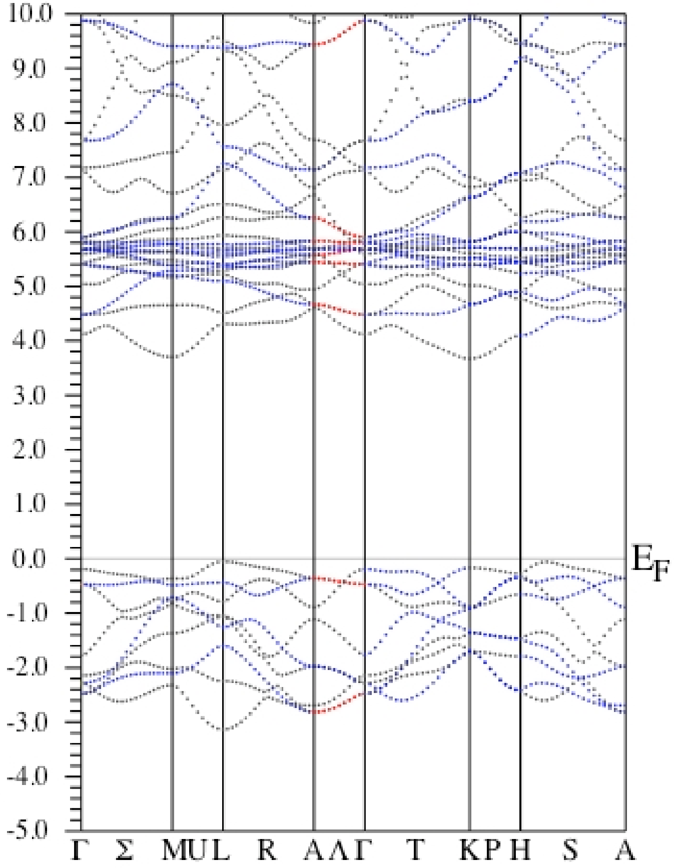
  => ***"f"-states must be explicitly considered*** (as discussed later)
- flat VB top, but different from that of RE_2O_2S
- wider VB (La –> Pr) : may reflect "covalency"

	La_2O_3	**Ce_2O_3**	**Pr_2O_3**
VB width (eV)	**3.0**	**3.1**	**3.2**
ΔE (a.u.)	**-1.590**	**-1.612**	**-1.625**

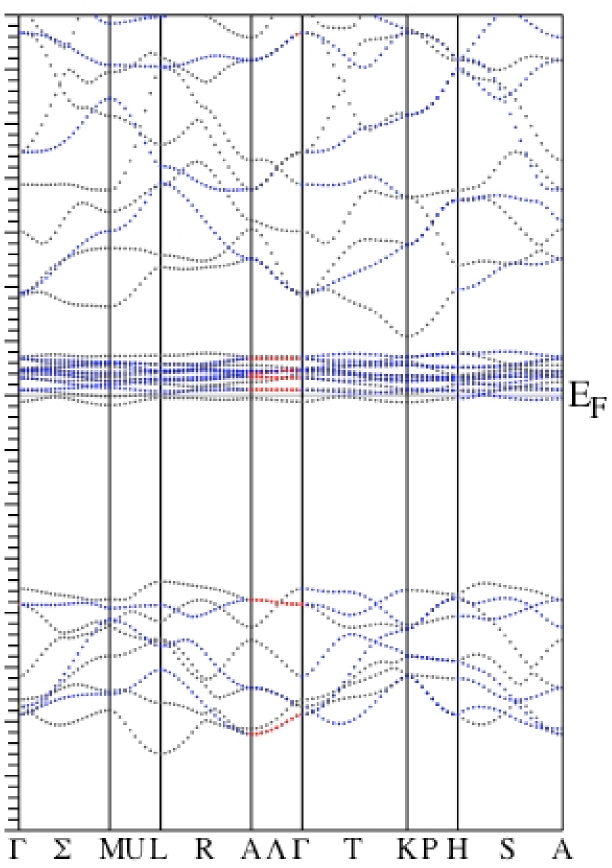
(NB: $\Delta E = E(RE_2O_3) - 2E(RE) - 3E(O)$)

Band structures calculated with FLAPW (WIEN2k)

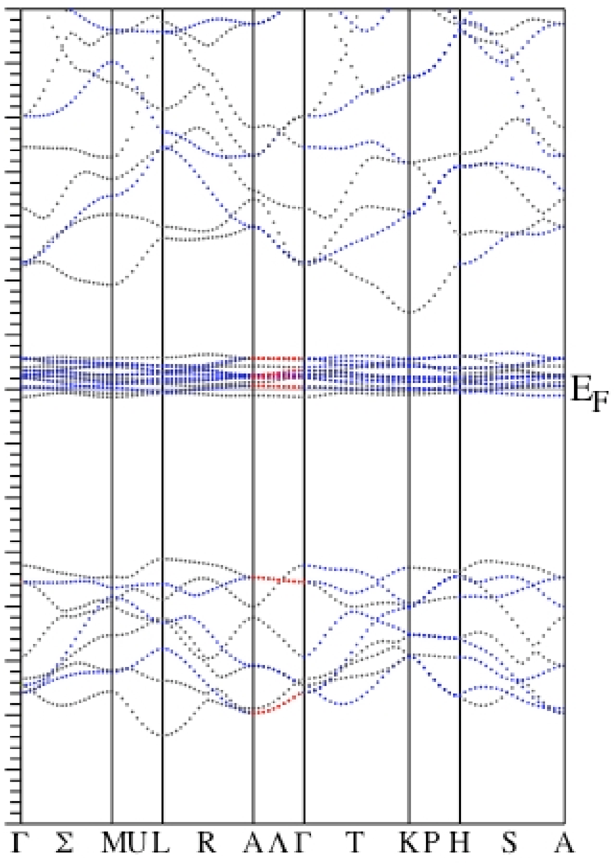
La_2O_3



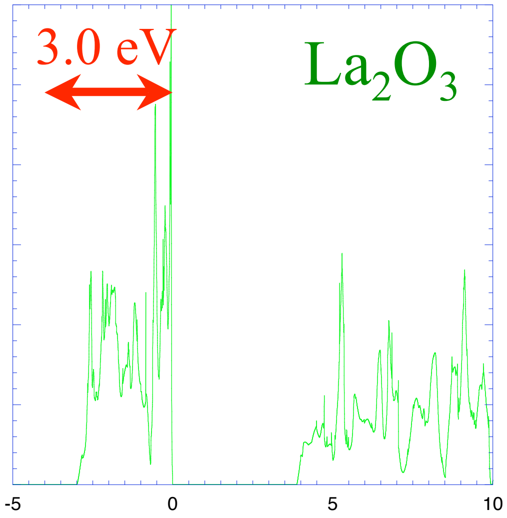
Ce_2O_3

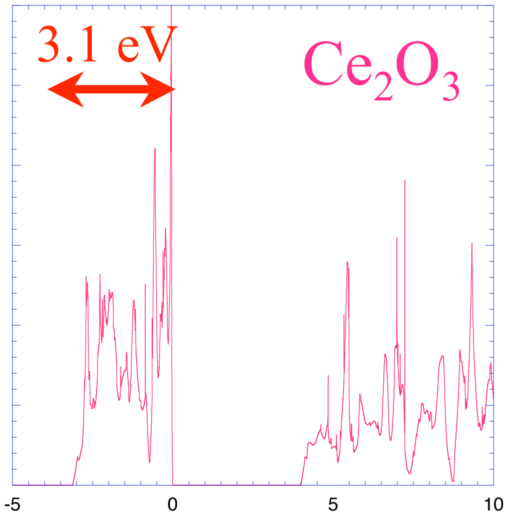


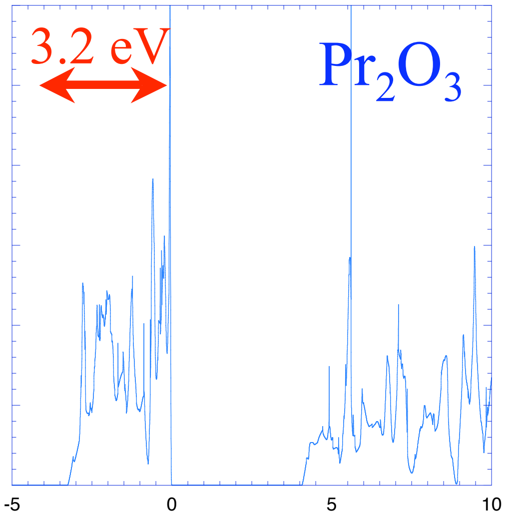
Pr_2O_3

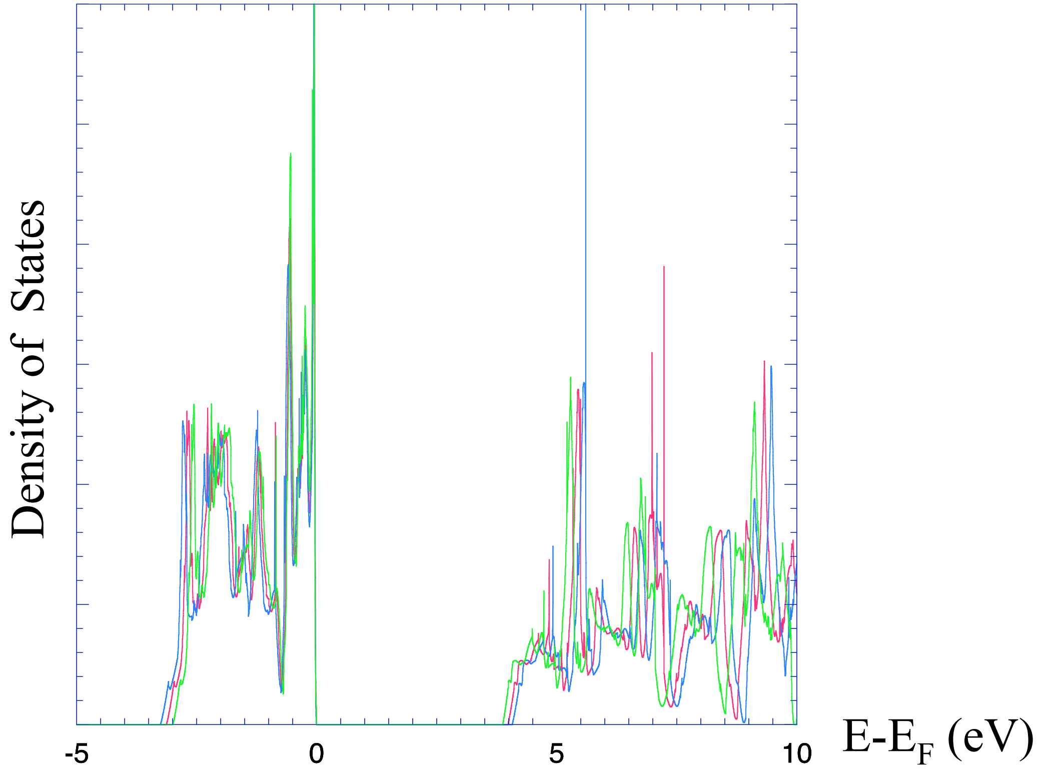


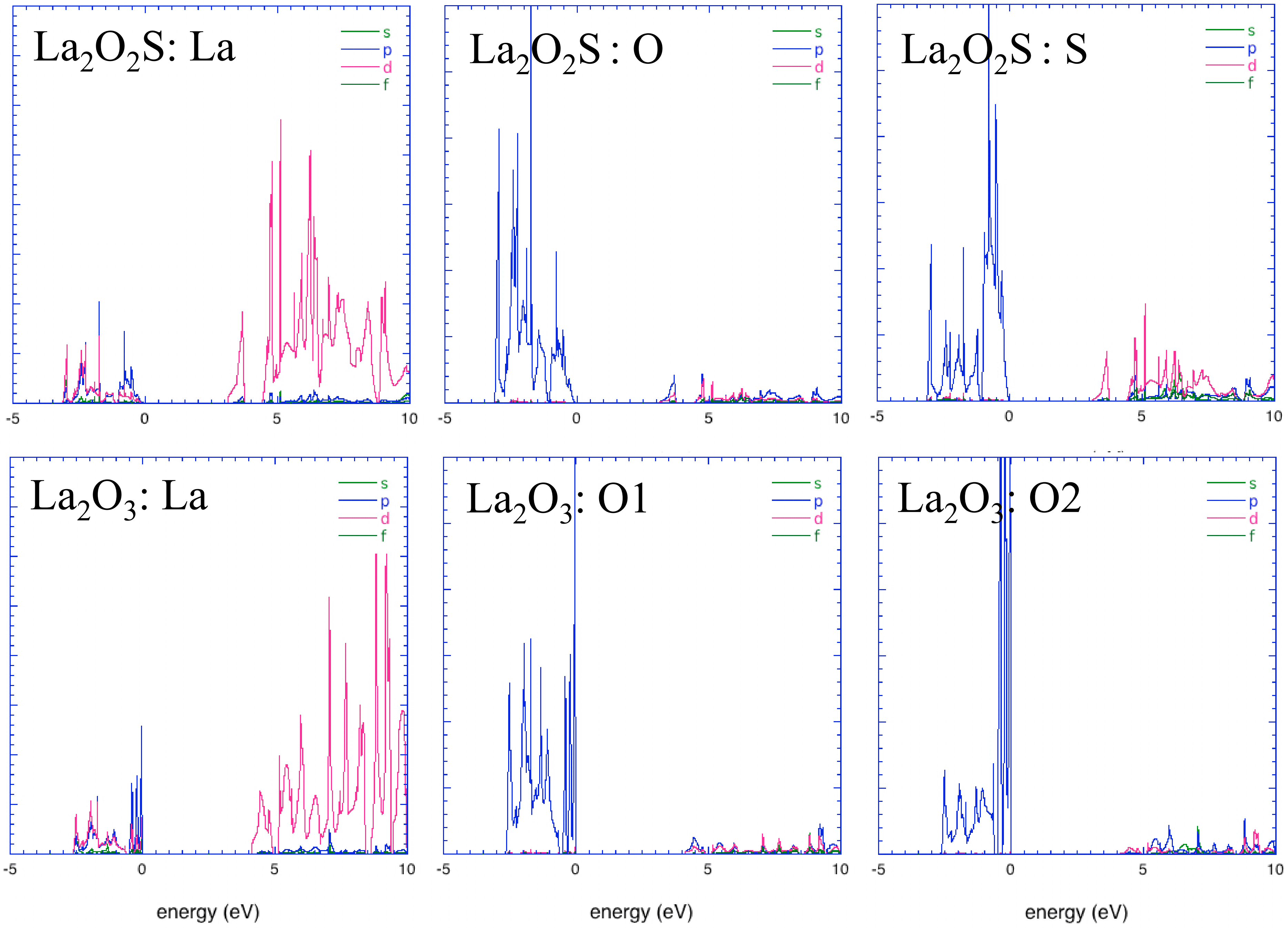
RE$_2$O$_3$ Density of States (without f-states)










La$_2$O$_2$S: La
La$_2$O$_2$S : O
La$_2$O$_2$S : S
La$_2$O$_3$: La
La$_2$O$_3$: O1
La$_2$O$_3$: O2
s
p
d
f
-5
0
5
10
energy (eV)

Lattice vibrations of RE_2O_2S

unit: cm^{-1}

	La_2O_2S		Ce_2O_2S		Pr_2O_2S	
	Theory	Expt.	Theory	Expt.	Theory	Expt.
Raman						
E_g	107	104	109	106	111	101
A_{1g}	201	196	203	–	205	190
E_g	383	360	394	–	404	372
A_{1g}	398	392	410	409	421	412
IR						
E_u	193(TO) 223(LO)	262 276	197(TO) 228(LO)	248 282	200(TO) 231(LO)	–
A_{2u}	201(TO) 297(LO)	212	237(TO) 303(LO)	200	241(TO) 308(LO)	–
E_u	333(TO) 474(LO)	420 458	342(TO) 483(LO)	417 450sh	349(TO) 491(LO)	–
A_{2u}	406(TO) 513(LO)	370	415(TO) 524(LO)	348	423(TO) 533(LO)	–

Lattice vibrations of RE_2O_3

unit: cm^{-1}

	La_2O_3		Ce_2O_3		Pr_2O_3	
	Theory	Expt.	Theory	Expt.	Theory	Expt.
Raman						
E_g	106	74	108	–	110	–
A_{1g}	201	108	203	–	205	–
E_g	430	444	445	–	457	–
A_{1g}	403	408	416	–	428	–
IR						
E_u	191(TO) 299(LO)	242	198(TO) 308(LO)	–	203(TO) 316(LO)	–
A_{2u}	216(TO) 397(LO)	242	227(TO) 408(LO)	–	228(TO) 417(LO)	–
E_u	397(TO) 556(LO)	435	409(TO) 569(LO)	–	418(TO) 580(LO)	–
A_{2u}	440(TO) 512(LO)	386	451(TO) 523(LO)	–	460(TO) 539(LO)	–

Born effective charge, high-frequency/static dielectric tensor of La_2O_2S

	$Z^*_{\alpha\alpha}$(La)	$Z^*_{\alpha\alpha}$(O)	$Z^*_{\alpha\alpha}$(S)	$\varepsilon^{\infty}_{\alpha\alpha}$	$\varepsilon^{0}_{\alpha\alpha}$
xx, yy	+3.95	-2.78	-2.33	5.45 (4.53)	14.72
zz	+3.99	-2.79	-2.40	5.23 (4.40)	13.80

Born effective charge, high-frequency/static dielectric tensor of Y_2O_2S

	$Z^*_{\alpha\alpha}$(La)	$Z^*_{\alpha\alpha}$(O)	$Z^*_{\alpha\alpha}$(S)	$\varepsilon^{\infty}_{\alpha\alpha}$	$\varepsilon^{0}_{\alpha\alpha}$
xx, yy	+3.66	-2.53	-2.28	5.23 (4.29)	12.51
zz	+3.71	-2.63	-2.16	4.87 (4.07)	12.20

Born effective charge, high-frequency/static dielectric tensor of La_2O_2S

	$Z^*_{\alpha\alpha}$(La)	$Z^*_{\alpha\alpha}$(O)	$Z^*_{\alpha\alpha}$(S)	$\varepsilon^{\infty}_{\alpha\alpha}$	$\varepsilon^{0}_{\alpha\alpha}$
xx, yy	+3.95	-2.78	-2.34	5.45 (4.53~4.7)	14.72
zz	+3.99	-2.79	-2.40	5.23 (4.40~4.7)	13.80

Born effective charge, high-frequency/static dielectric tensor of La_2O_3

	$Z^*_{\alpha\alpha}$(La)	$Z^*_{\alpha\alpha}$(O_1)	$Z^*_{\alpha\alpha}$(O_2)	$\varepsilon^{\infty}_{\alpha\alpha}$	$\varepsilon^{0}_{\alpha\alpha}$
xx, yy	+4.09	-2.74	-2.71	4.83 (4.13 ~ 4)	23.20~20
zz	+3.78	-2.49	-2.57	4.69 (4.02 ~ 4)	21.54~20

Band-by-band decomposition of Z^* in La_2O_2S

Band	Z_{xx}^*(La)	Z_{zz}^*(La)	Z_{xx}^*(O)	Z_{zz}^*(O)	Z_{xx}^*(S)	Z_{zz}^*(S)
Z_κ	+11.00	+11.00	+6.00	+6.00	+6.00	+6.00
La 5s	-2-0.06	-2-0.06	0+0.05	0+0.05	0+0.01	0+0.00
O 2s	0+*2.15*	0+*0.84*	-2-*2.23*	-2-*0.20*	0+*0.06*	0-*1.28*
La 5p	-6-*2.48*	-6-*1.19*	0+*2.23*	0+*0.08*	0+*0.56*	0+*2.23*
S 3s	0+*0.23*	0+*0.29*	0+*0.09*	0+*0.22*	-2-*0.63*	-2-*1.02*
O 2p S 3p	0+*1.08*	0+*1.14*	-6-*0.95*	-6-*0.92*	-6-*0.36*	-6-*0.30*
Total	+3.95	+3.99	-2.78	-2.79	-2.34	-2.40

roughly compensated

Band-by-band decomposition of Z^* in La_2O_3

Band	Z_{xx}^*(La)	Z_{zz}^*(La)	Z_{xx}^*(O_1)	Z_{zz}^*(O_1)	Z_{xx}^*(O_2)	Z_{zz}^*(O_2)
Z_κ	+11.00	+11.00	+6.00	+6.00	+6.00	+6.00
La 5s	-2-0.07	-2-0.05	0+0.07	0+0.05	0-0.01	0-0.01
O 2s	0+*4.67*	0+*2.66*	-2-*2.99*	-2-*1.72*	-2-*3.57*	-2-*1.64*
La 5p	-6-*4.76*	-6-*2.73*	0+*3.12*	0+*1.83*	0+*3.50*	0+*1.57*
O 2p	0+*1.25*	0+*0.91*	-6-*0.95*	-6-*0.62*	-6-*0.62*	-6-*0.47*
Total	+4.09	+3.78	-2.74	-2.49	-2.71	-2.57

roughly compensated

A reasoning about the E_g variation in RE_2O_3

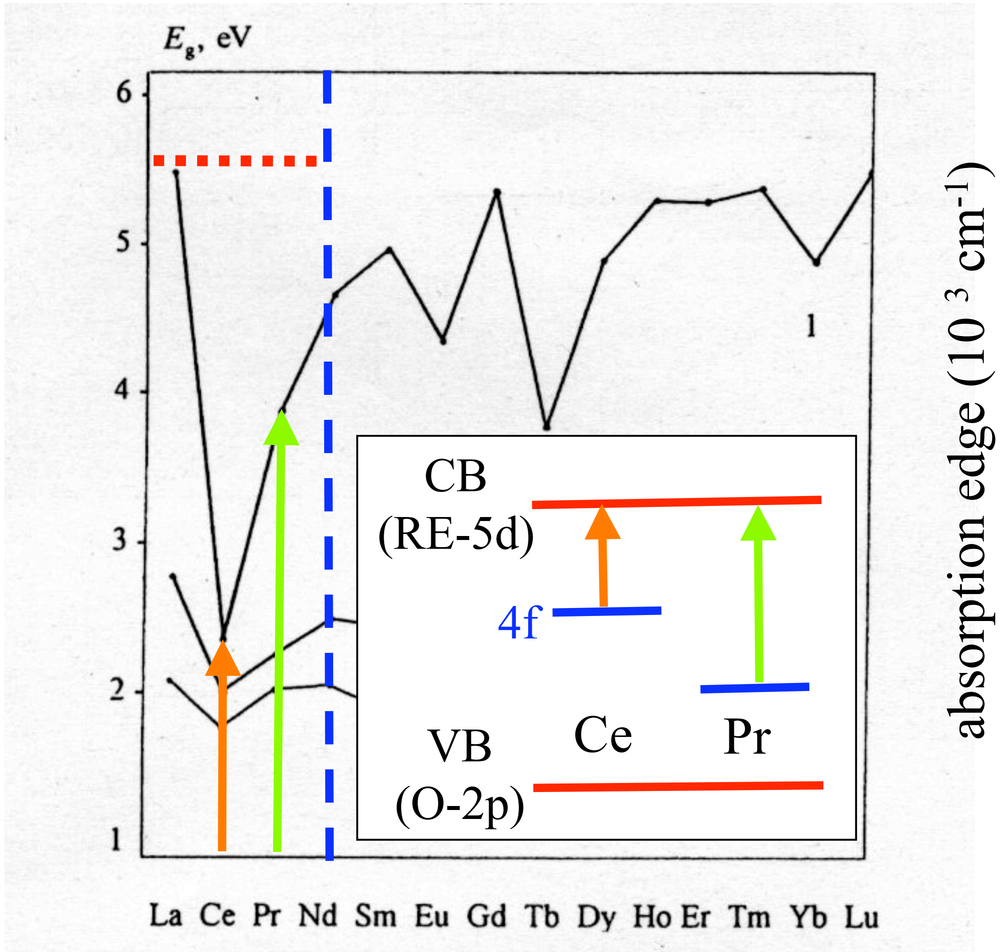
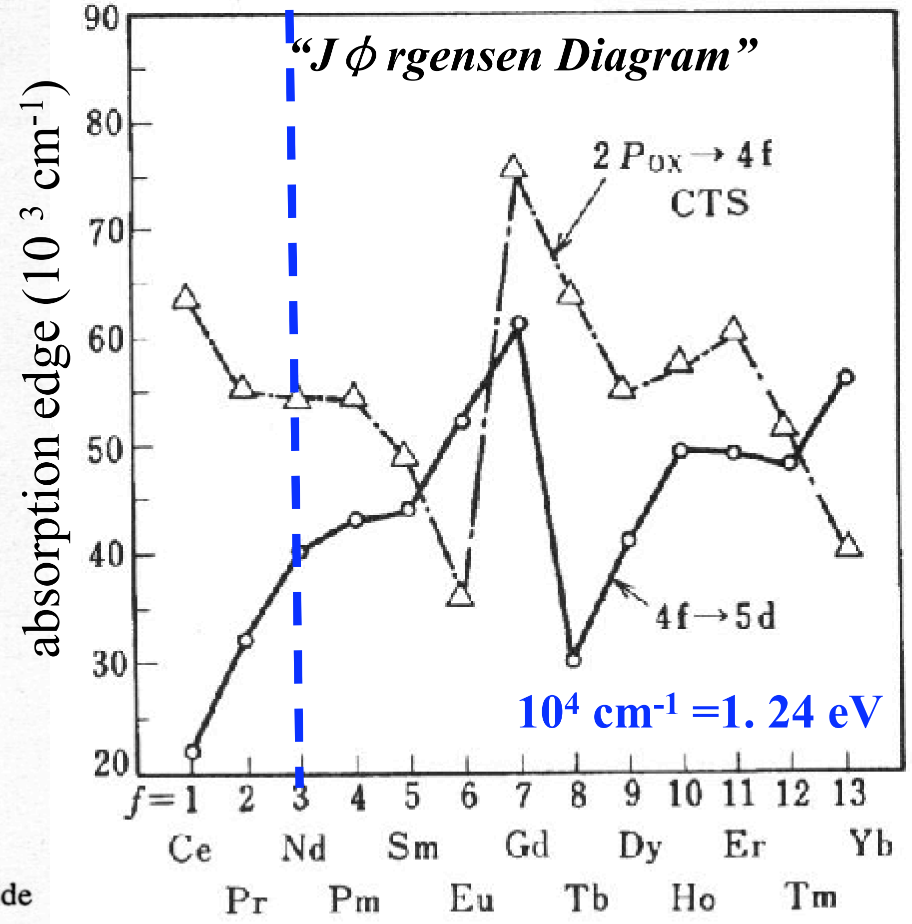


Fig. 1. Variation of the band gap E_g of Ln_2X_3 in the lanthanide series: (1) oxides; (2) sulphides; (3) selenides.

RE-dopant absorption in oxides



from
"Phosphor Handbook"
(Shionoya & Yen)

$4f^1$(Ce)/$4f^2$(Pr) may lie between VB and CB(RE-d).
NB: prediction of *f*-states needs "***beyond-LDA***" methods

PHYSICAL REVIEW B **64** 085107

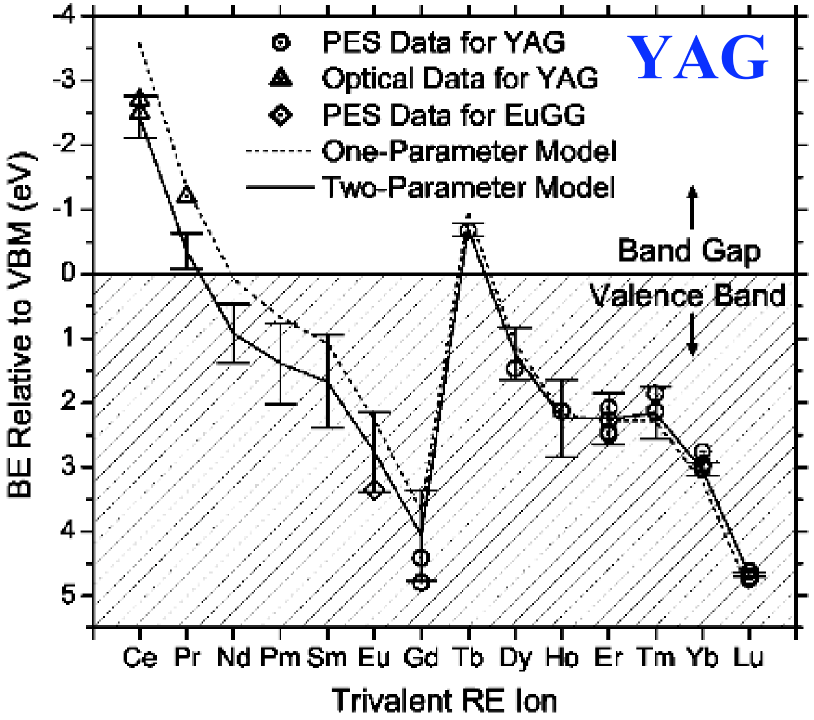


FIG. 6. Systematic behavior of 4*f* binding energies relative to the valence band maximum. Circles represent our measured binding energies relative to the VBM (at 8.7 eV); negative binding energies are within the band gap of the host and positive energies are below the VBM. The dotted line is the fit of the empirical model to our measured values without considering the effect of ionic radius. The solid line is the fit of the model to our measured values including the effect of ionic radius. The error bars on the model are due to uncertainty in the values of the free-ion ionization potentials and the error bars on the extrapolated values for Eu^{3+} through Ce^{3+} include the uncertainty due to the accuracy of the fitting parameters. The triangles represent estimated positions from excited-state absorption and photoconductivity measurements in Refs. 4, 5, and 20. The diamond is the estimated position in EuGG from Ref. 52. Note that the bottom of the conduction band lies at about −6.5 eV.

PHYSICAL REVIEW B **65** 235116

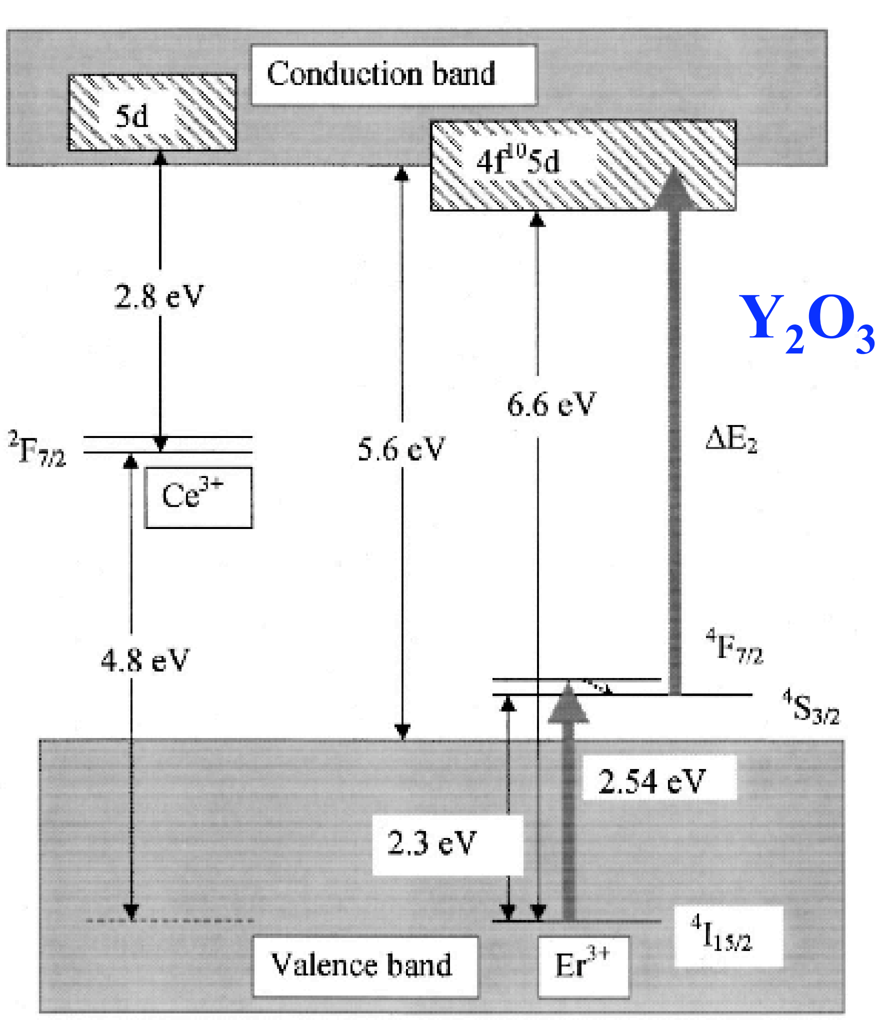


FIG. 2. Energy diagram of Er^{3+} and Ce^{3+} relative to the band gap of Y_2O_3 (only relevant levels are drawn).

“Locating lanthanide impurity levels in the forbidden band” by Pieter Dorenbos (J. Lumin., in press)

Empirical scheme based on his database (4f-5d/CTS) predicts :

CaF_2

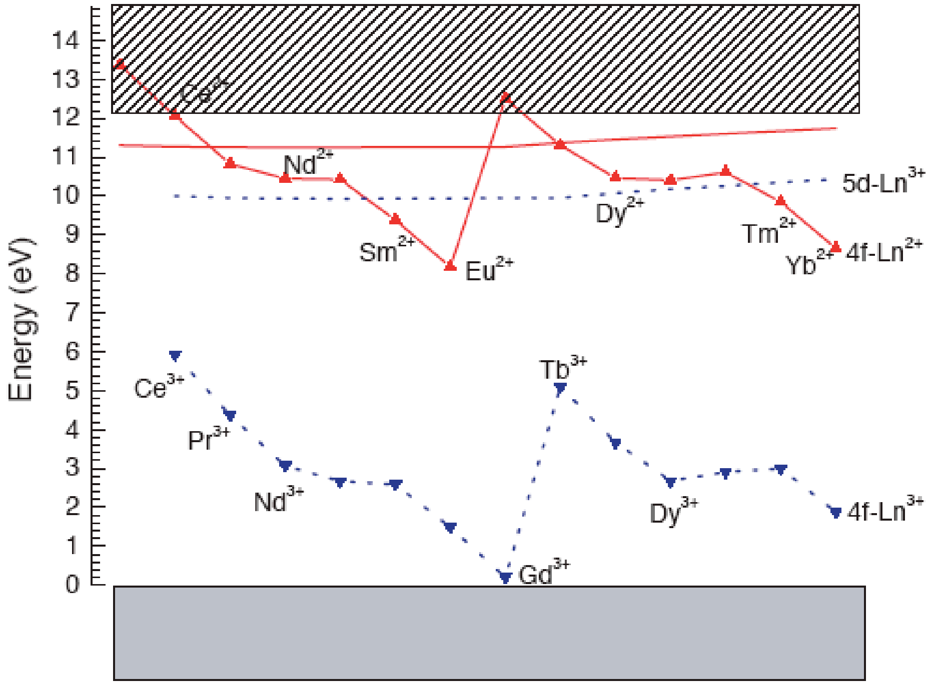


Fig. 4. Energy-level schemes of divalent and trivalent lanthanides in CaF_2.

YPO_4

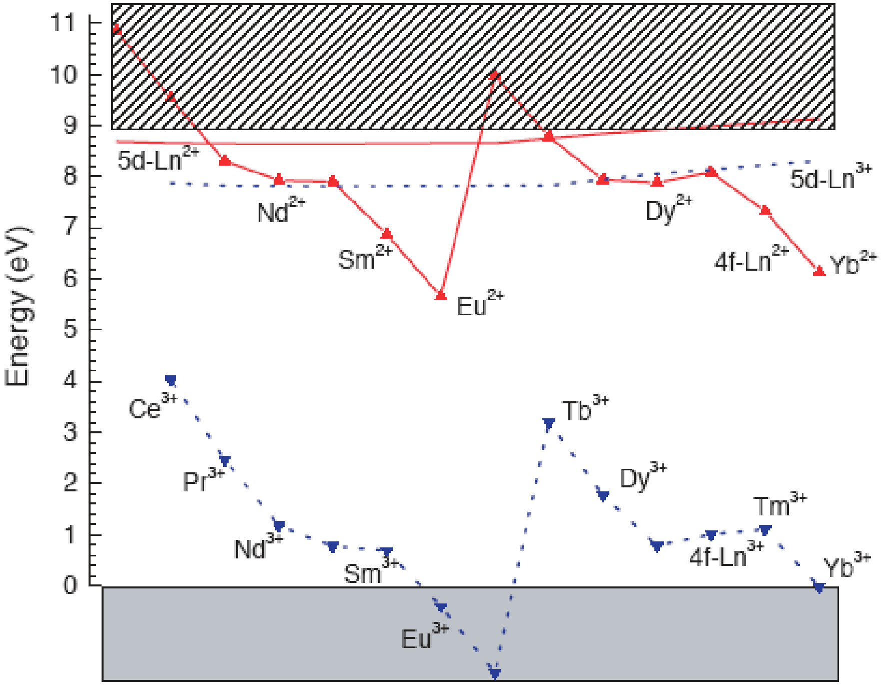


Fig. 5. Energy-level schemes of divalent and trivalent lanthanides in YPO_4.

Important for design of trap level/absorption …

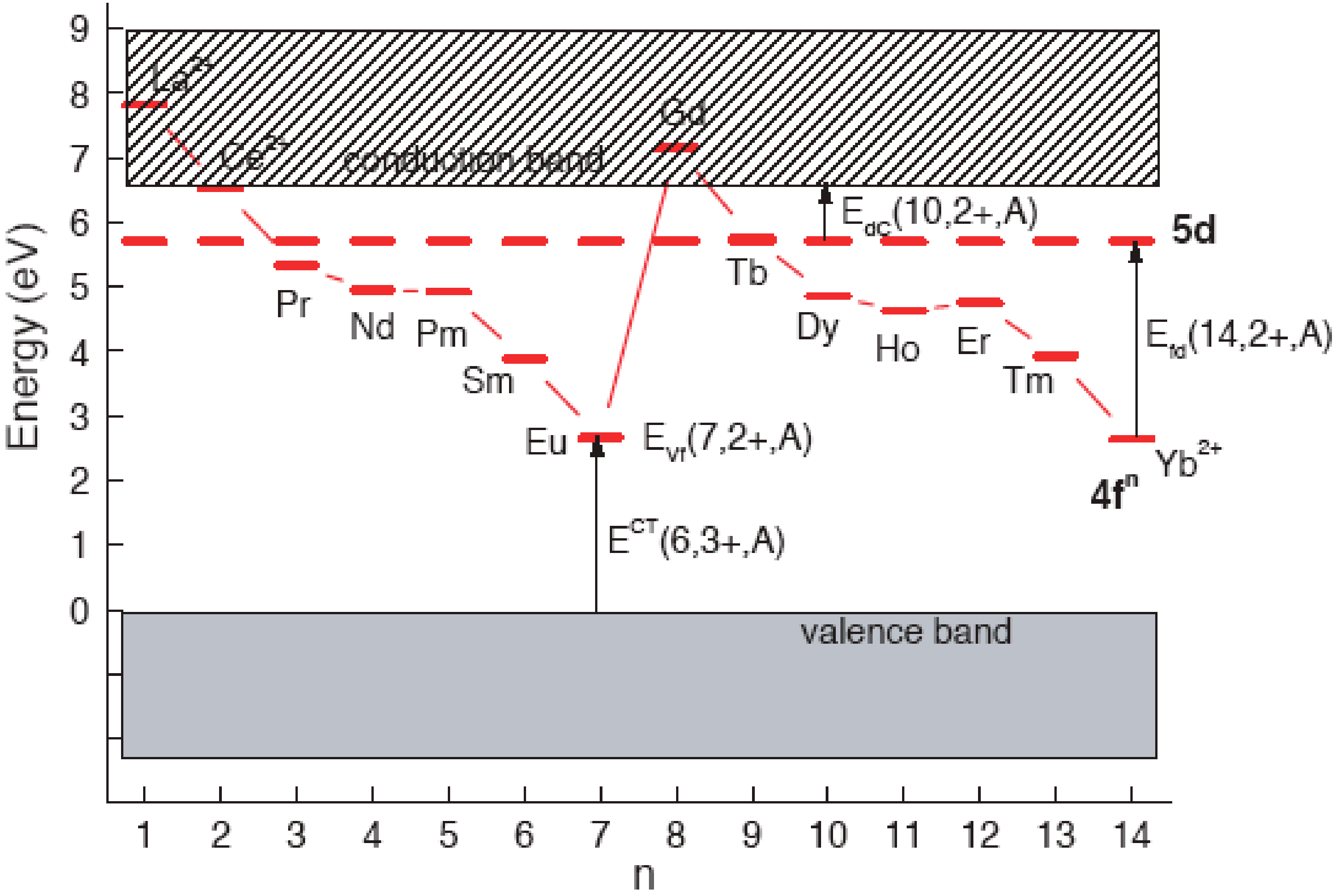


Fig. 1. Idealized systematic in the energy-level positions of divalent lanthanides in a wide band gap ionic crystal.

P. Dorenbos, J. Lumin (in press)

2. Summary for the 1st part of my talk

- Geometries well-reproduced with PPs (within ∼1 % in lattice const.)

  smaller RE … smaller a & c … larger Bulk modulus(B)

  $B(RE_2O_3) > B(RE_2O_2S)$

- *Indirect* bandstructure of RE_2O_3/RE_2O_2S (NB: without *f*-states)

  RE_2O_2S bandstructure ∼ Y_2O_2S bandstructure

  bottom of CB : *K* … due to the similar geometries

  smaller RE … wider VB width … larger covalency

ionic				***covalent***
La ….	**Ce ….**	**Pr ….**	**Y ….**	
large				***small***

  similar band gap between VB and CB(RE-d) among RE_2O_3 (RE_2O_2S)

  but different E_g (from absorption/body-color)

  → 4*f*→5*d*/CTS transition (from Jϕrgensen diagram)

  $4f^1$(Ce)/$4f^2$(Pr) may lie between VB and CB(RE-d)

- *Response function calculation for phonon/ ε seems satisfactory …*

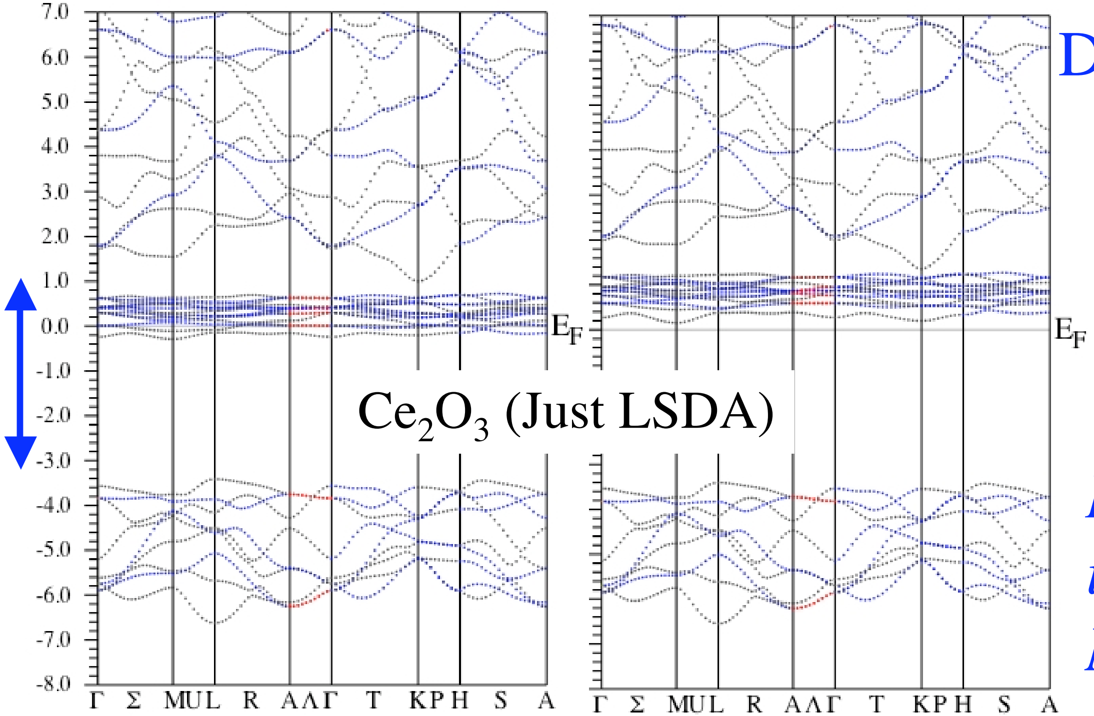
The transferable RE-PPs may be applied
to other "simple" RE-compounds for GS/RF calc.

(*Mikami & Nakamura, submitted to RE'04*)

(possible) Future works awaited …

- explicit treatment of *f*-state for optical transitions (e.g. LSDA+U ?)

Underestimation of Gap between O-2p and Ce-d



Ce_2O_3 (Just LSDA)

Difficulties will remain...

with U

——> ??

How to choose U
in meaningful way ?
NB: Ce_2S_3 (E.Wimmer)

- application of other ABINIT functions:
  Comparison with PAW calculations (accuracy & speed …)
  Charge analysis (Bader)
  Other RF calculations (stress, non-linear optical properties, …)

2nd part of my talk taken from …

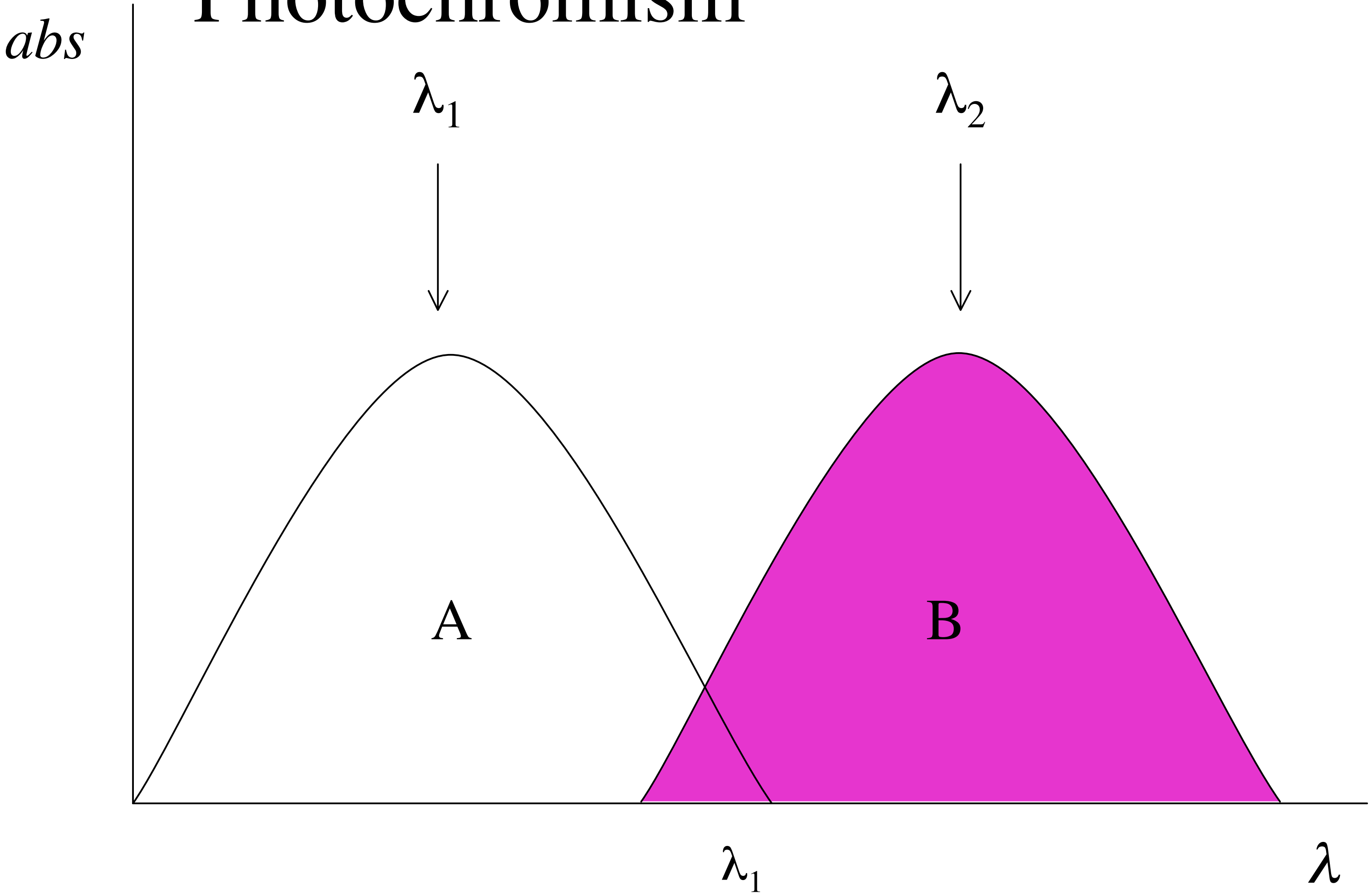
Seminar@UCL (May 7, 2004)

First-principles study of Photochromic Molecular Crystals

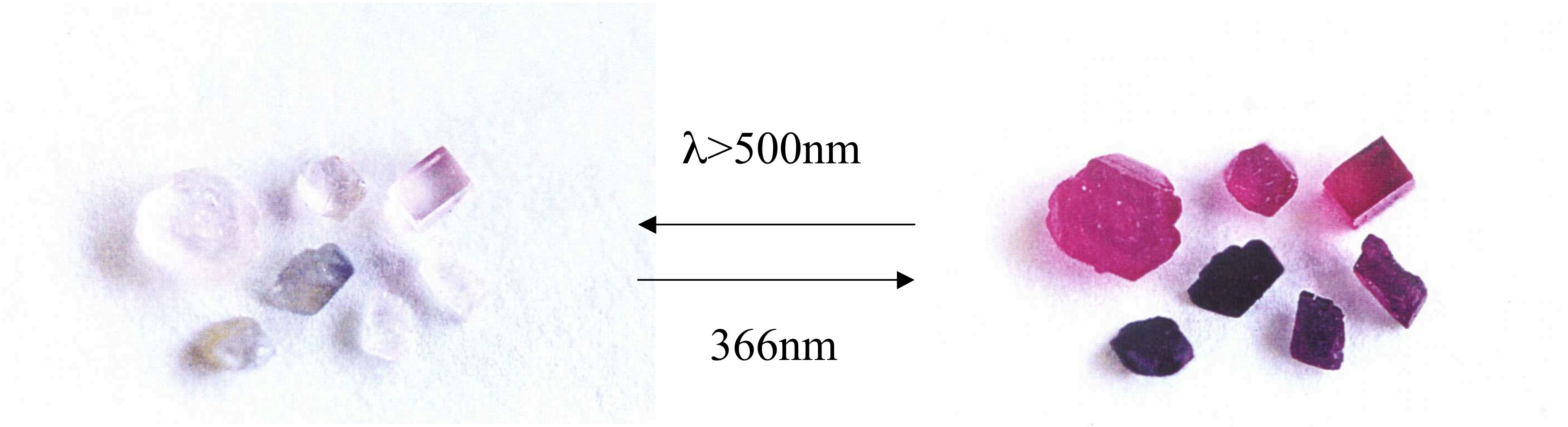
Mitsubishi Chemical Group
Science and Technology Research Center, Inc.
Masayoshi Mikami, Takao Kobayashi, Shinichiro Nakamura

1. Background
2. Computational Method
3. Result: ***Salicylideneaniline*** –> structures, energetics, dielectric
   Diarylethene–> structures, energetics, photo-absorption
4. Summary

Photochromism



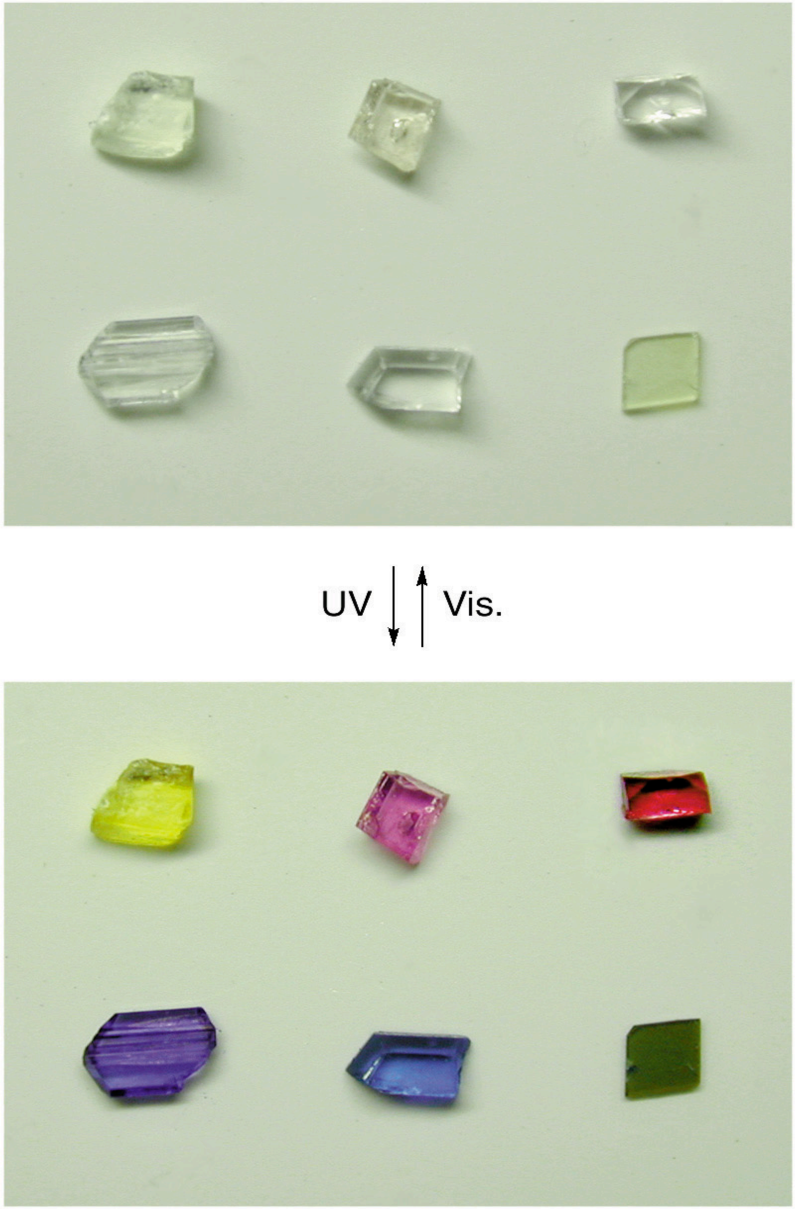
$$A \underset{\lambda_2 \text{ or } \Delta}{\overset{\lambda_1}{\rightleftarrows}} B$$



$\lambda > 500$nm

366nm

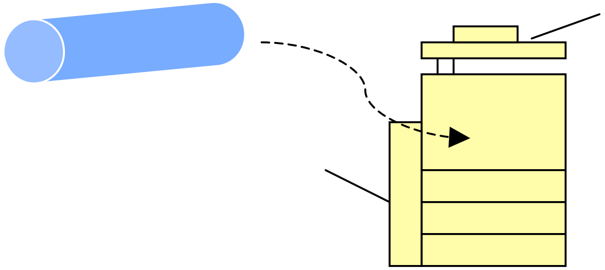
（Prof. M. Irie）



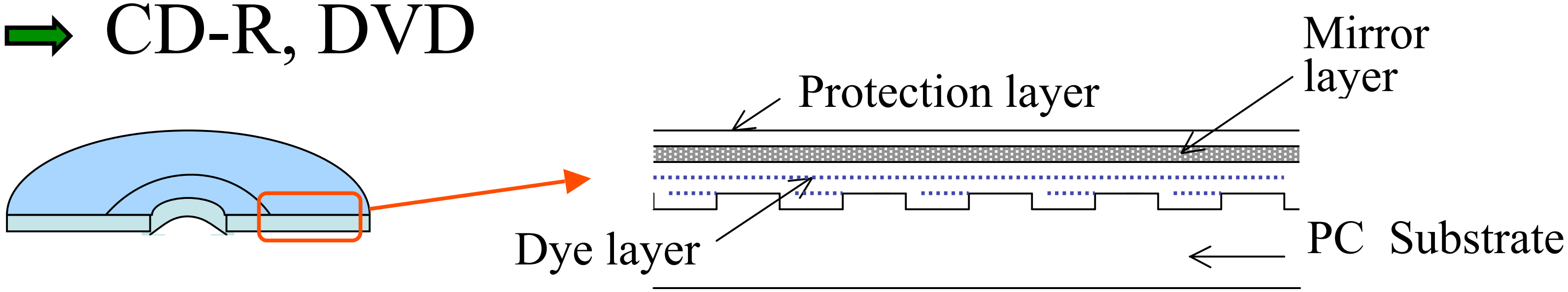
（Prof. M. Irie）

Industrial background：Functional Dyes

Now
in market ➡ Organic Photo Conductor (Copy Materials)



Now
in market ➡ CD-R, DVD



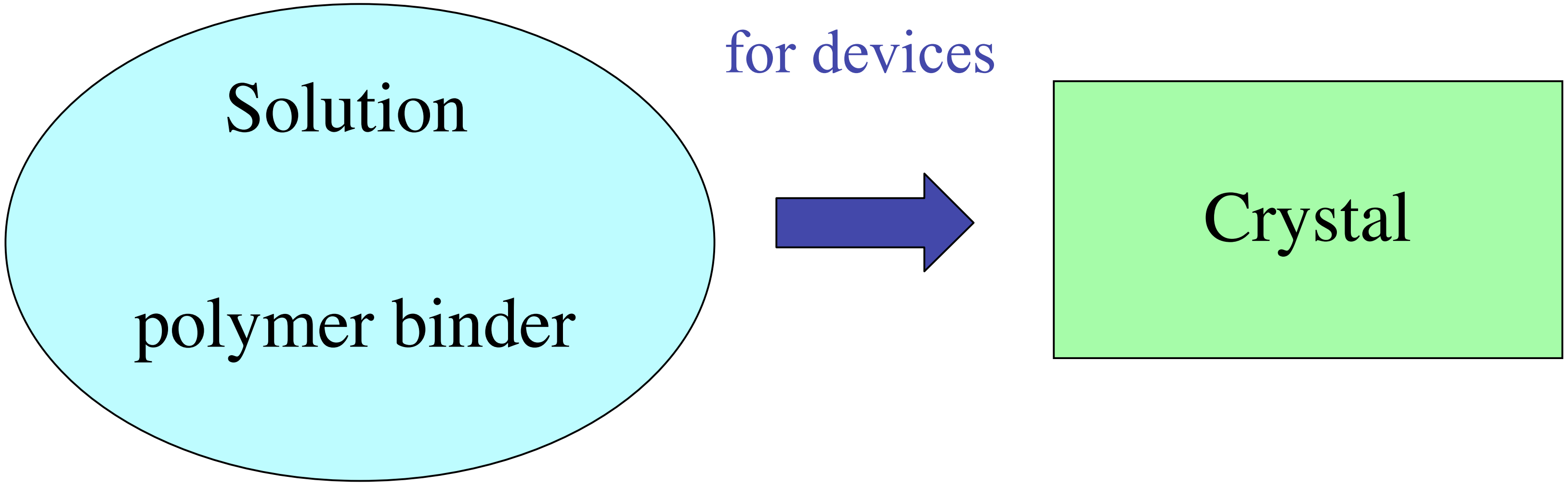
☛ Today

Molecular Memory and Molecular Switching Device.

→ *Photochromic molecular device*

Background

More potential in photochromic systems for devices



Solution

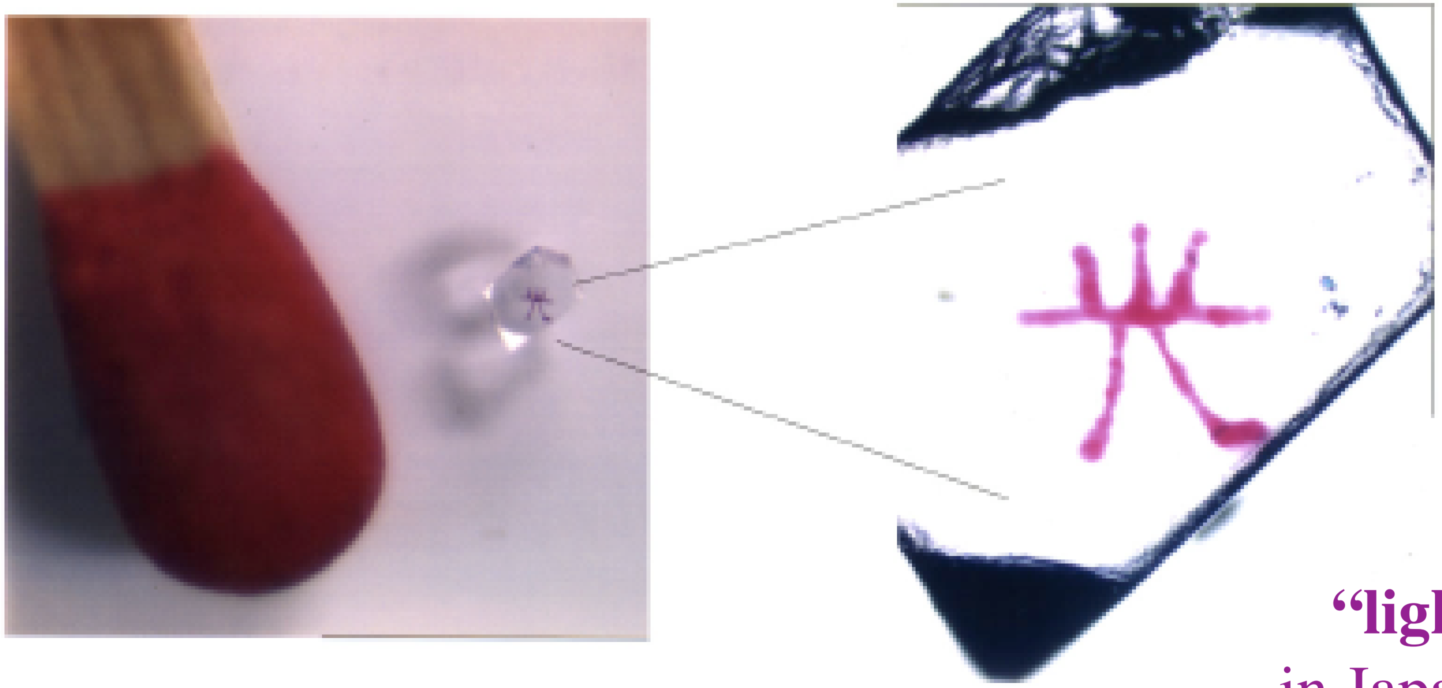
polymer binder

for devices

Crystal

M.Irie., *Chem.Rev.*100,1685 (2000)

UV light writing in *Diarylethene crystals*



“light”
in Japanese

図3　結晶に書き込んだ「光」という文字

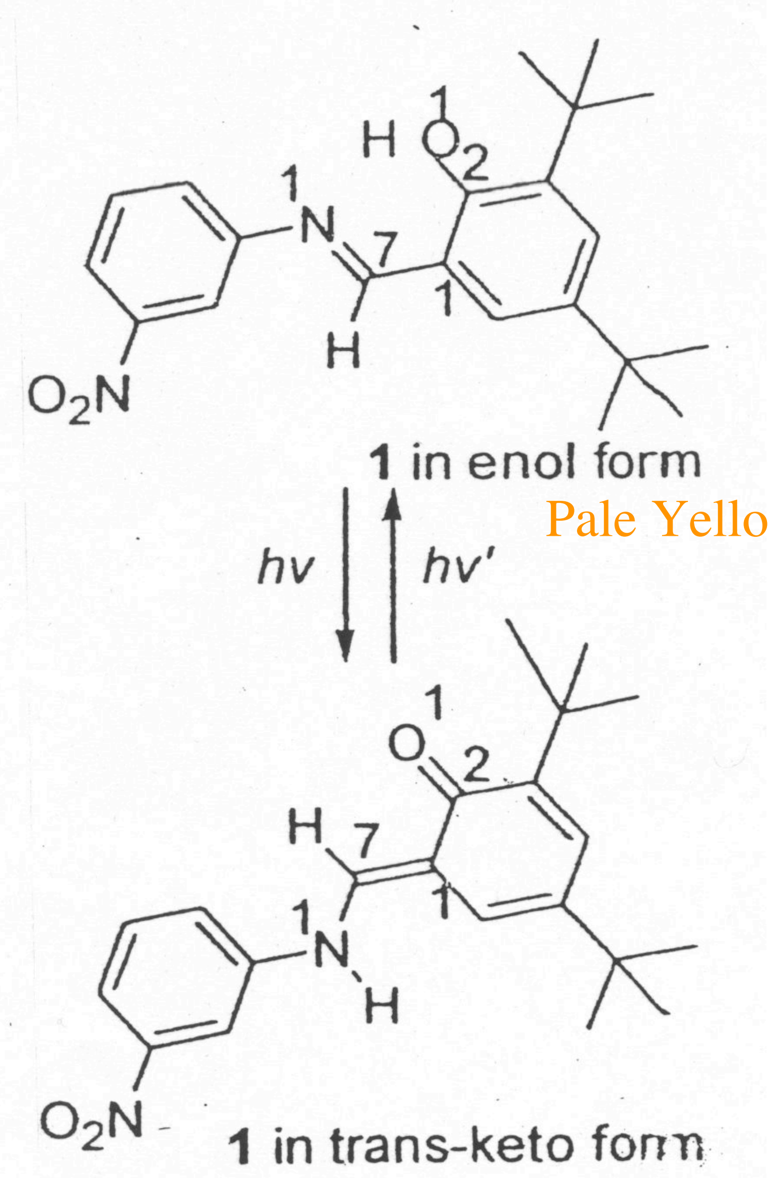
From Prof. Irie laboratory Home Page
(http://www.cstf.kyushu-u.ac.jp/irie/irie.html)

Motivation

From Molecular Design
(Ab-initio MO method)
to **Band Engineering**
(First-Principles Study).

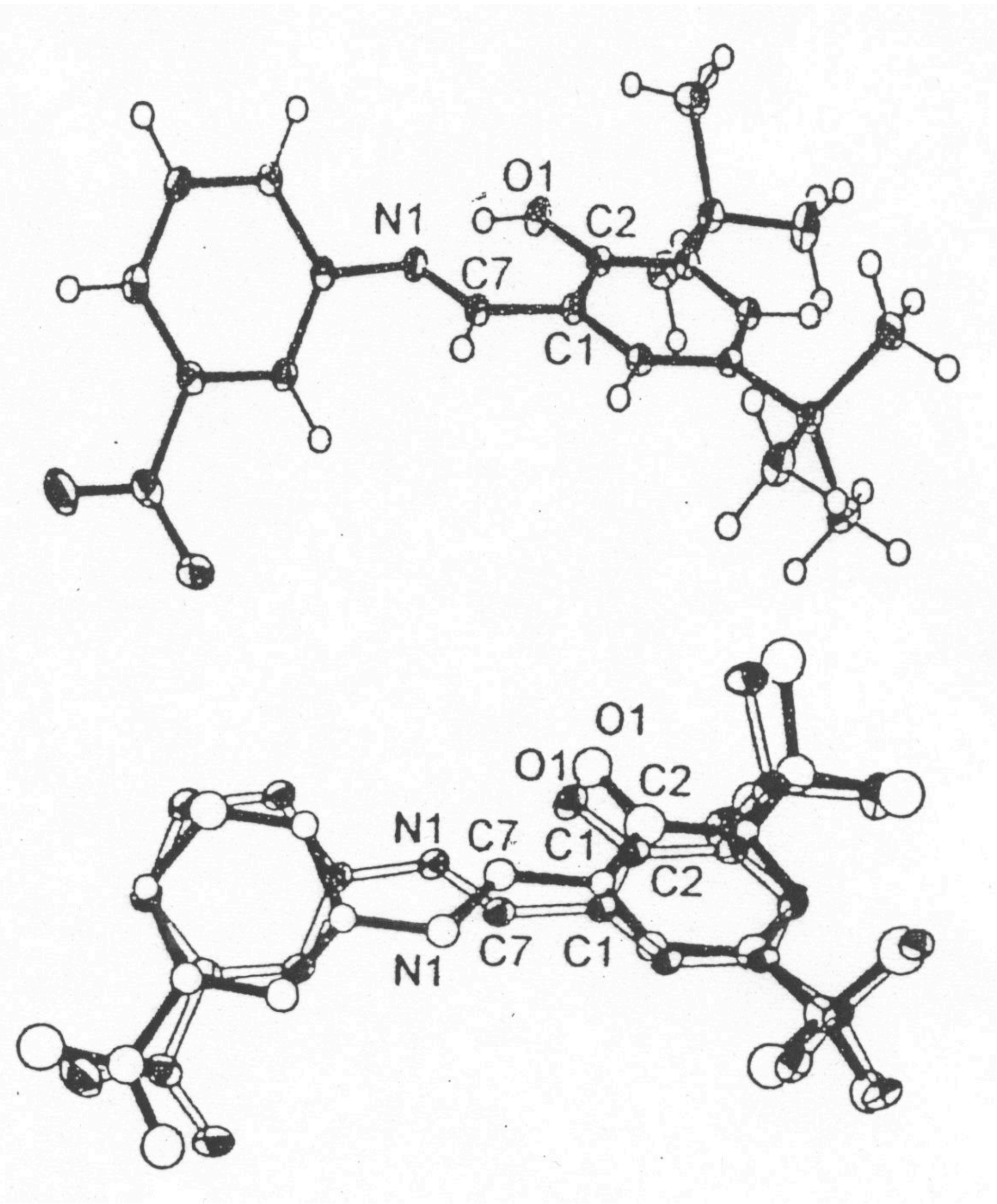
NB: Extraordinary stability of
the trans-keto form in solid state
(400 times longer life than
other ketos unsubsitituted with NO_2)

J. Harada et al.
JACS (1999) 121 5809
T. Kawato et al.
J.Photochem (1985) 28, 103



Pale Yellow

Red



“Crankshaft motion”

J. Harada et al. *JACS (1999) 121 5809*

Calculation Method

Density **F**unctional **T**heory – **G**eneralized **G**radient **A**pproximation :
Perdew-Burke-Ernzerhof (PBE)-type functional :
Phys. Rev. Lett. 77, 3865 (1996), ibid 80, 891 (1998)
Density Functional Perturbation Theory (for dielectric permittivity tensor)

First-Principles Band Calculation : **ABINIT code** (www.abinit.org)
Reference: X. Gonze et al., Comp. Mater. Sci. 25, 478 (2002)

Troullier-Martins-type **pseudopotentials**, prepared with **FHI98PP code**
FHI98PP : www.fhi-berlin.mpg.de/th/fhi98md/fhi98PP
M. Fuchs and M. Scheffler, Comp. Phys. Comm. 119, 67 (1999)

Energy cut-off: 60Ry(salicylideneaniline)、70Ry(diarylethene)
k-point sampling : Γ-point

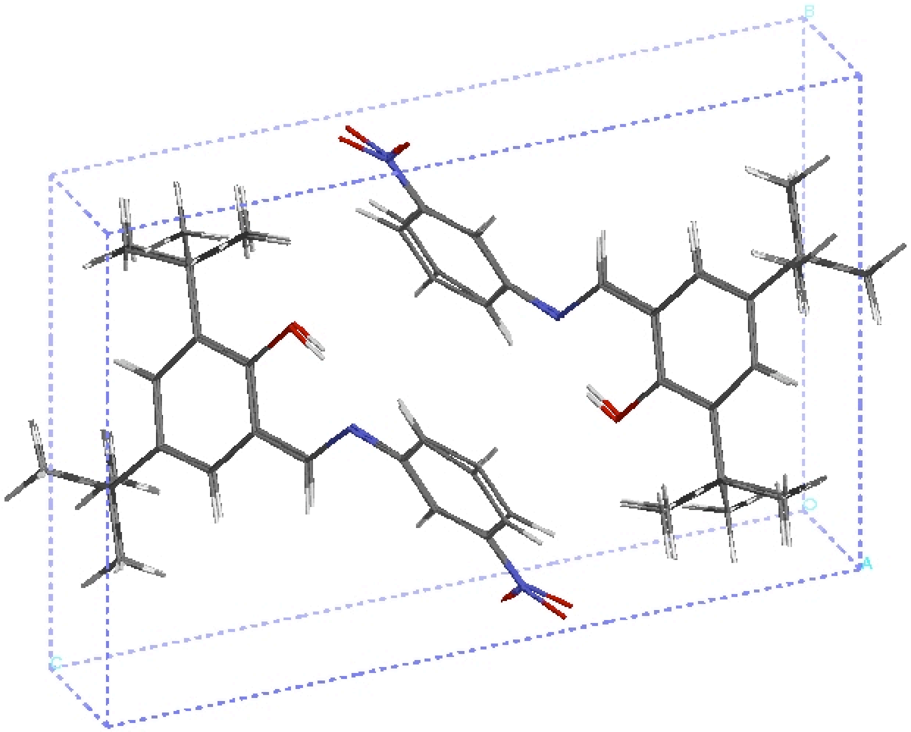
SCF sycle : Conjugate Gradient based on the minimum of the energy
X. Gonze, Phys. Rev. B54, 4383 (1996)

Geometry optimization : Broyden-Fletcher-Goldfarb-Shanno minimization
Convergence ≤ 1 kcal/mol should be expected for energetics

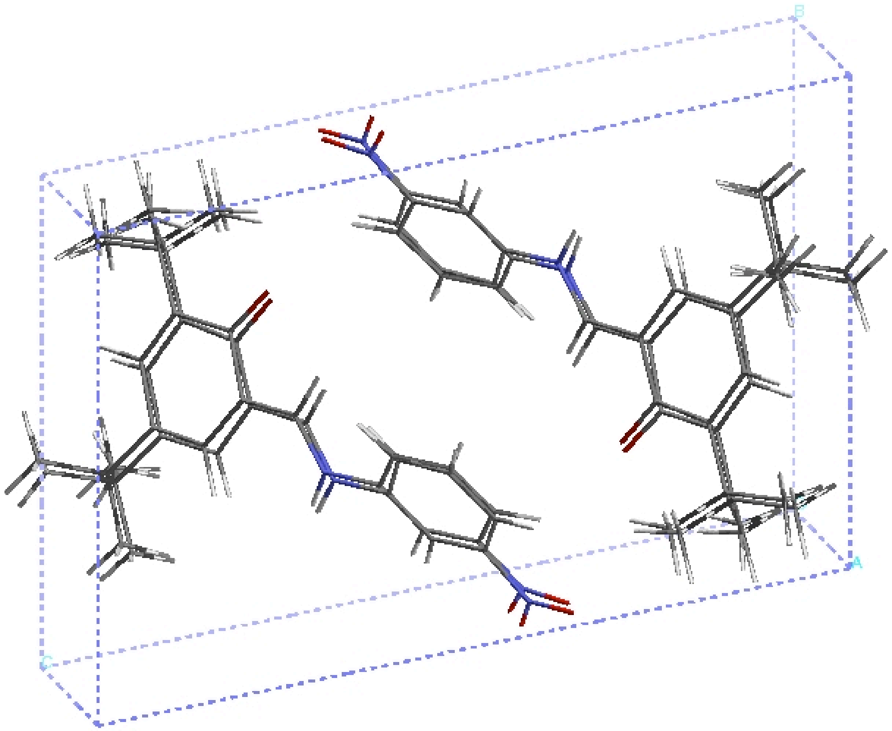
Geometry Optimization

Superposed draw of X-ray structure and optimized structure

Enol

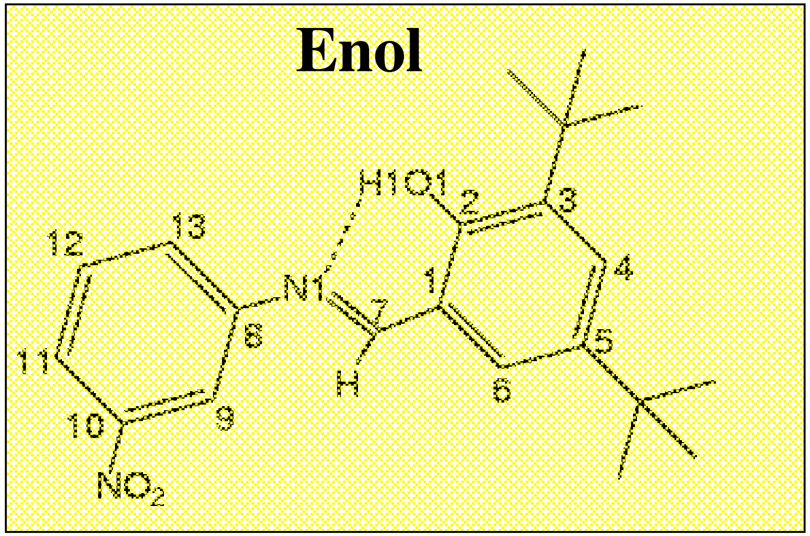


Trans-Keto



(a)

Enol



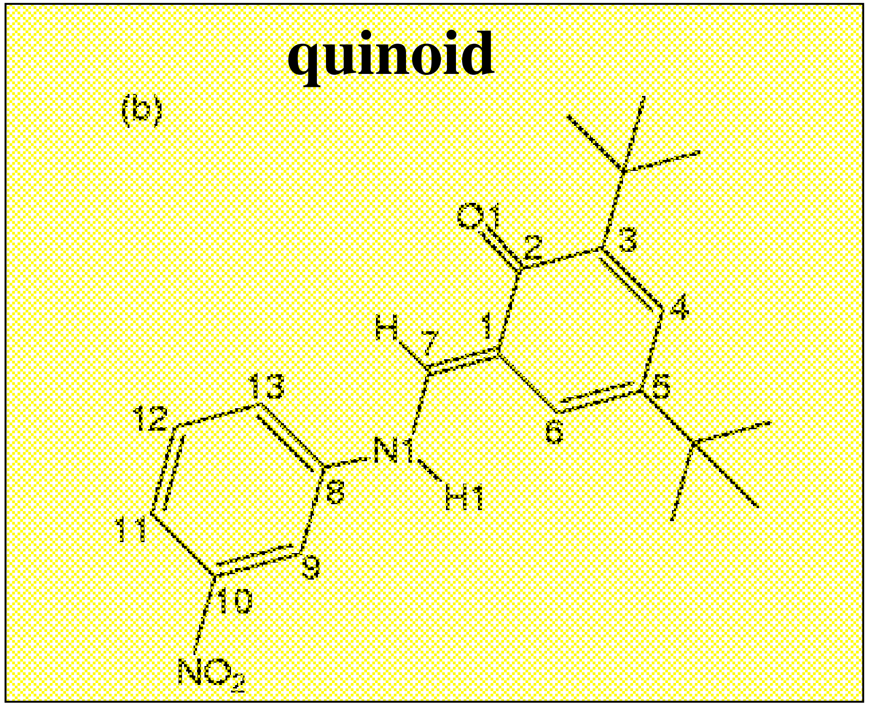
↗

Calc. geometry

↙

quinoid

(b)

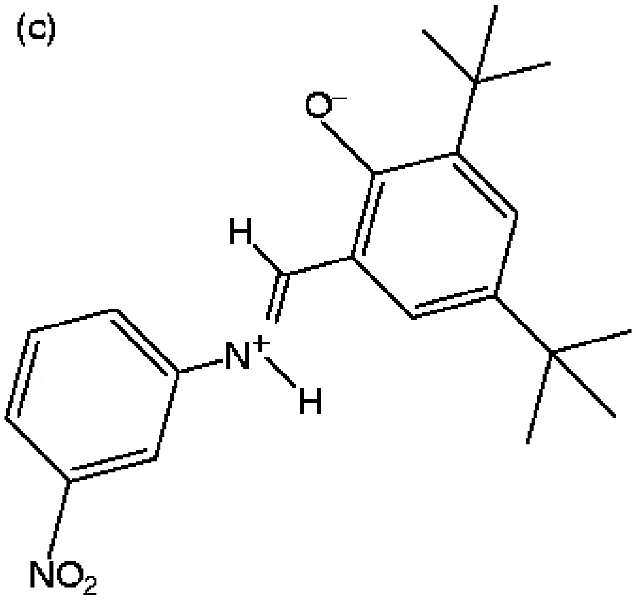


→

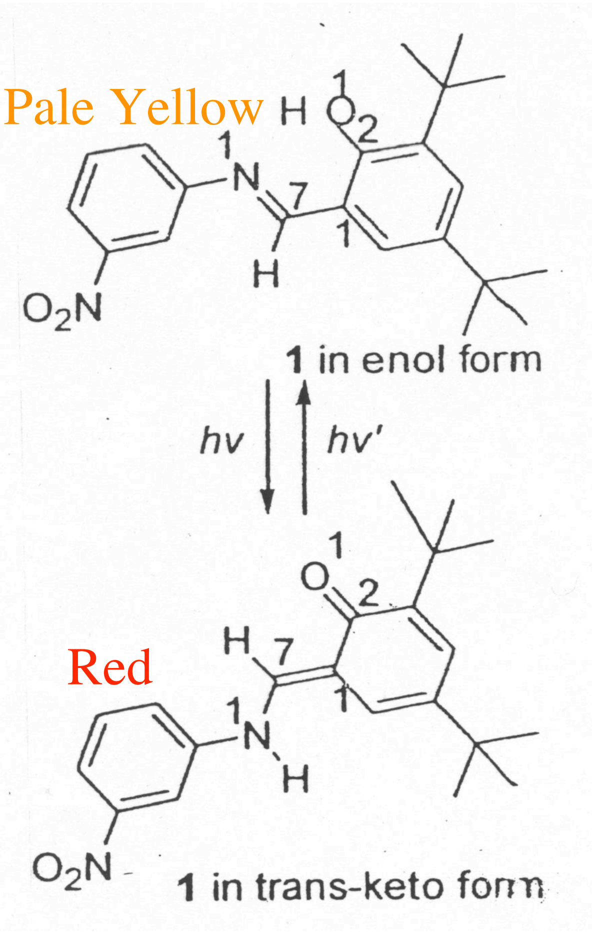
←

zwitterion

(c)



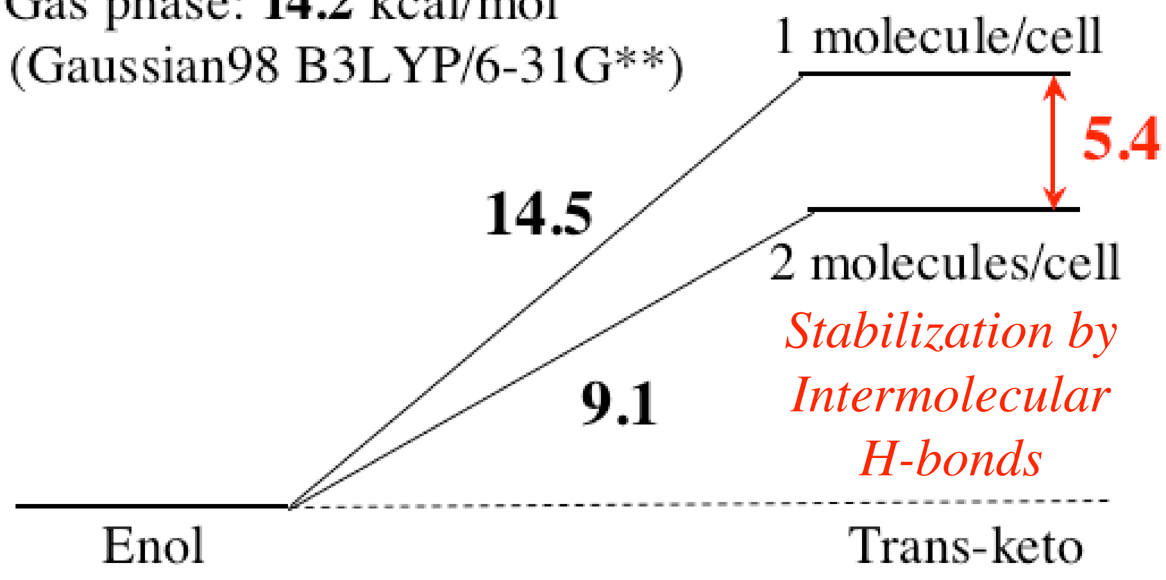
Our work on photochromic Salicylideneaniline molecular crystals



J. Harada et al.
JACS (1999) 121 5809

Energetics (unit: kcal/mol)

c.f. Gas phase: **14.2** kcal/mol
(Gaussian98 B3LYP/6-31G**)

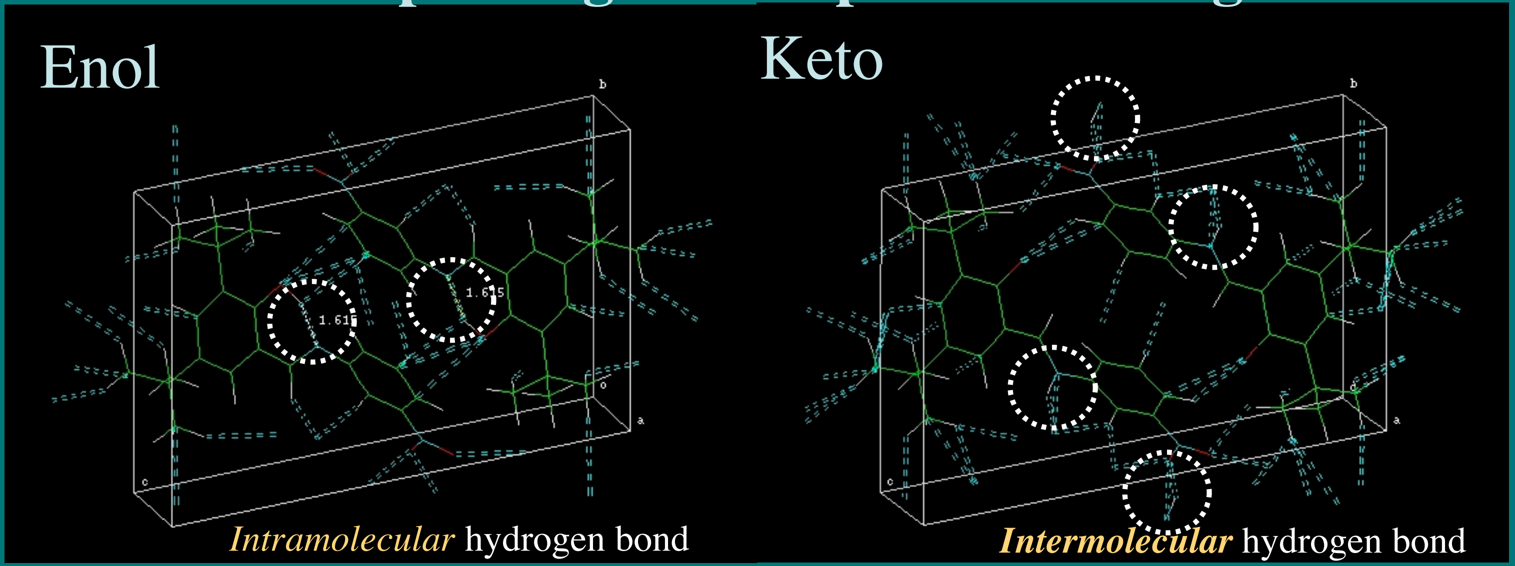


Stabilization by Intermolecular H-bonds

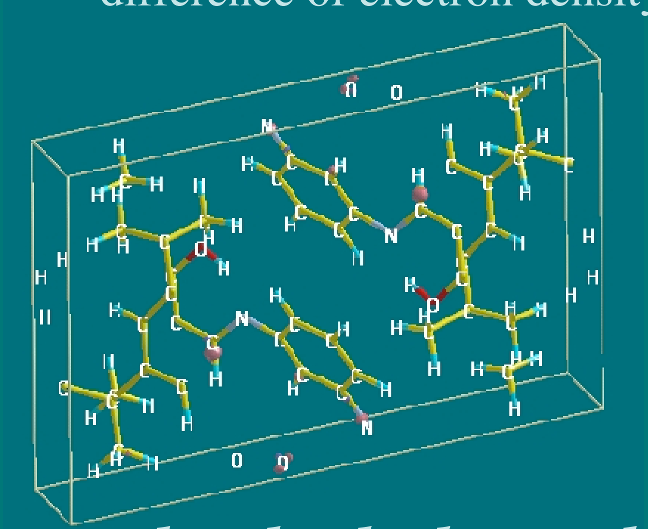
NB: extraordinary life-time of this trans-keto form
in crystalline phase (life depends on with/without -NO_2)

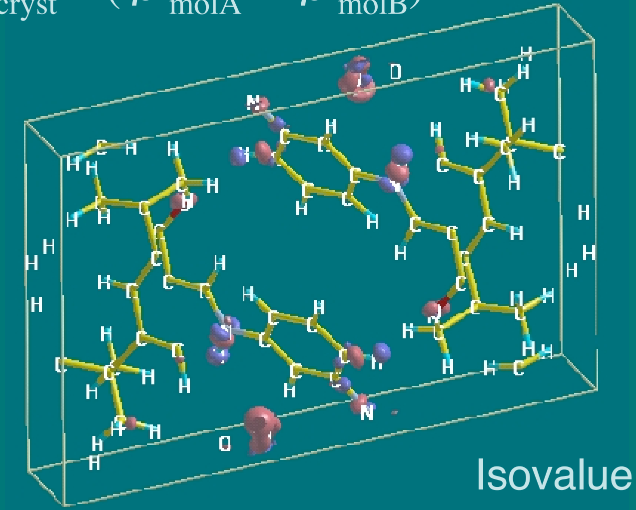
M. Mikami & S. Nakamura, PRB69, 134205 (2004)

The effect of “packing” can explain the energetics ? YES !



difference of electron density : $\rho_{\mathrm{cryst}} - (\rho_{\mathrm{molA}} + \rho_{\mathrm{molB}})$





Isovalue = 0.003a.u.

Intermolecular hydrogen bonds are strengthened in the Keto-form.

M. Mikami & S. Nakamura PRB69, 134205 (2004)

Evaluation of optical dielectric permittivity tensors

Density Functional Perturbation Theory (owing to ABINIT code)

Enol-type

$$\begin{pmatrix} 2.710 & 0.048 & -0.541 \\ 0.048 & 2.690 & 0.165 \\ -0.541 & 0.165 & 2.819 \end{pmatrix}$$

Eigenvalue 2.179, 2.719, 3.321

Mean value 2.740 (n=1.655)

Keto-type

$$\begin{pmatrix} 2.889 & -0.056 & -0.671 \\ -0.056 & 2.801 & 0.323 \\ -0.671 & 0.323 & 2.985 \end{pmatrix}$$

Eigenvalue 2.204, 2.774, 3.696

Mean value 2.892 (n=1.701)

Refractive index change under photoirradiation ($\Delta n \sim 0.046$)

NB:Photonic memory using the change of refractive indices in a photochromic system
(e.g. T.Fukaminato, S.Kobatake, T.Kawai, M.Irie, Proc.Japan.Acad.77(B), 30 (2002))

M. Mikami & S. Nakamura, PRB69, 134205 (2004)

2. Summary for the 2nd part of my talk

Salicylideneaniline molecular crystals :

- energetics → analysis/evaluation of intermolecular H-bonds
  → understanding stability of trans-keto in crystalline state
- evaluation of ε / n→ powerful design tool for photomemory

Lessons gained:

- k-point sampling may not affect for RF-calculation
  if a system has a ***low-symmetry & large unit-cell***.
  NB: C_{60} fcc solid: optical dielectric permittivity
  5.64 for k=(0,0,0), 4.72 for k=(1/2,1/2,1/2), *c.f.* expt. 4.4

- VERY SLOW convergence in geometry optimization
  if an initial geometry is far from an equilibrium geometry.
  other geometry optimizers ? and/or ***initial <u>WF</u>/DEN*** ?

Thank you for your attention !

Thank you again for ABINIT !

Our publications owing to ABINIT:

TiO_2-anatase : Jpn.J.Appl.Phys., PRB
Y_2O_2S: PRB, J.Lumin.
RE_2O_3/RE_2O_2S: submited to RE'04 (J.Alloy Compd.)
Salicylideneaniline : PRB