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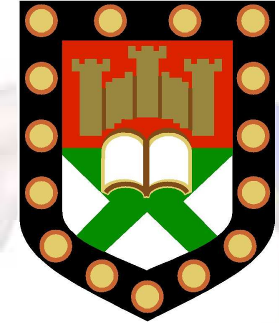

Rare earths in GaN

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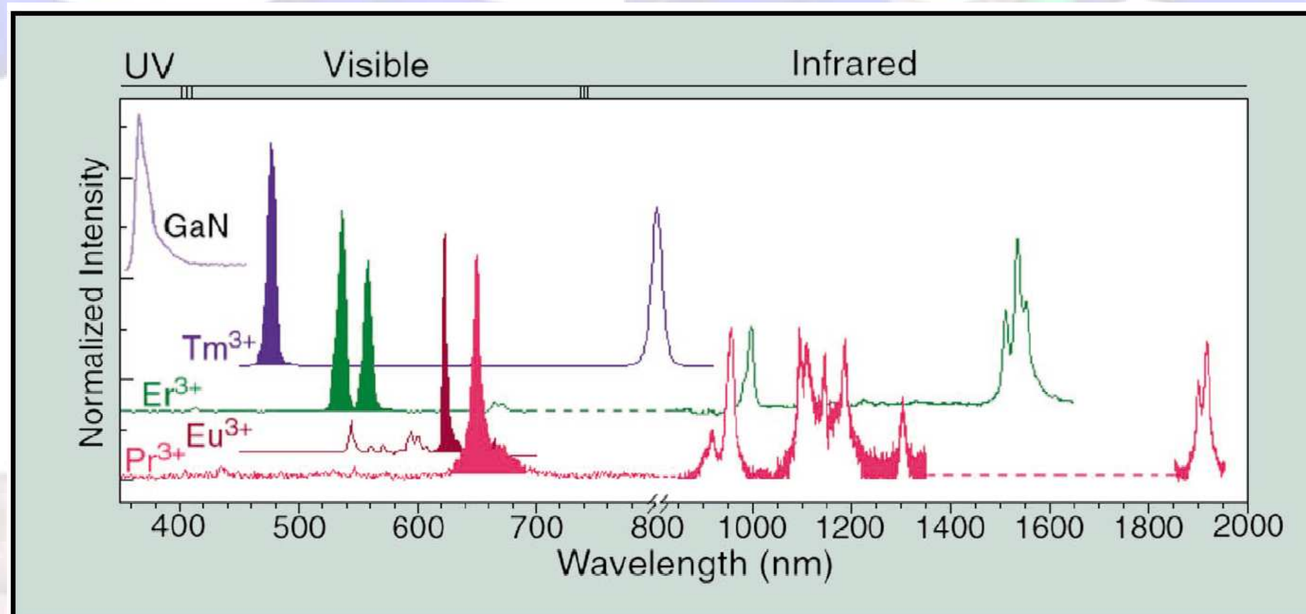
Why rare earths in GaN ?

Rare earths intra f transitions are weakly dependant of the matrix
→ Using different R.E. allows to get the primary visible colors
→ Er has an emission at 154 µm
→GaN:R.E. emission can still be strong at room temperature



Eu: Red
Er: Green (+IR)
Tm: Blue

Emission spectrum of different rare earthes (R.E.) in GaN
(A.J. Steckl et al. Compound Semiconductor 2000 *6(1)* 48)

Computational method

AIMPRO DFT package.

→ periodic density functional theory calculations
→ LDA approach
→ local Gaussian basis set
→ Monkhorst-Pack k-point sampling mesh (MP2 and MP4)
→ Hartwigsen-Goedecker-Hutter (HGH) pseudopotentials
→ unit cell: 72 atoms

Erbium f shell is kept frozen inside the core in R.E.$^{3+}$ structure

Pseudopotential validation

Rare earth nitride Nitride

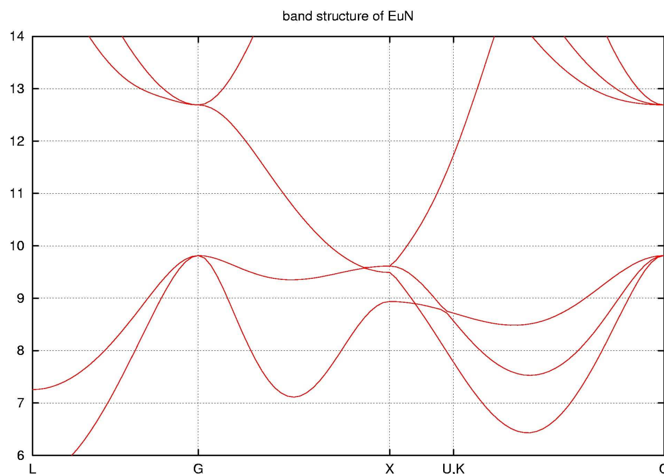
	EuN	ErN	TmN
Lattice parameter (exp.)	4.91 Å (5.01 Å)	4.74 Å (4.84 Å)	4.70 Å (4.81 Å)
Bulk modulus	179 GPa	195 GPa	201 GPa

Lattice error: ≈2%

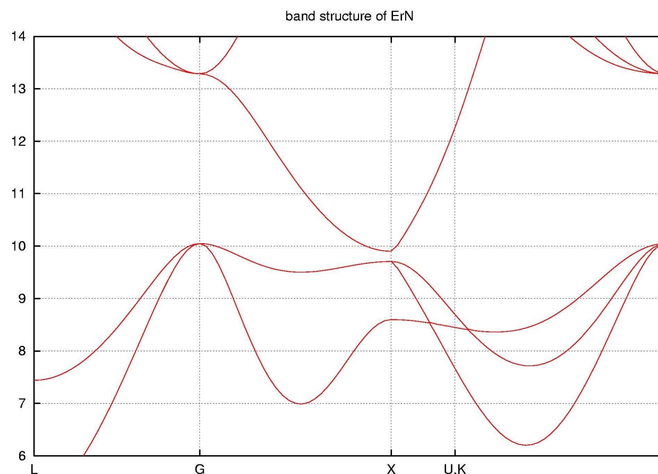
Band structure

Equivalent to previous calculations

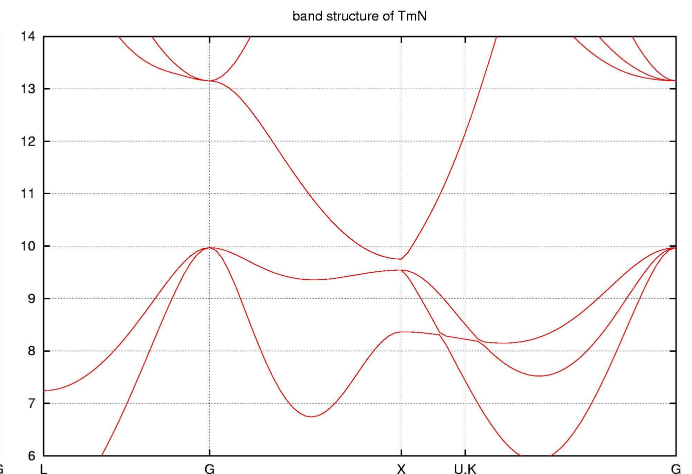
Eu > Er > Tm



EuN



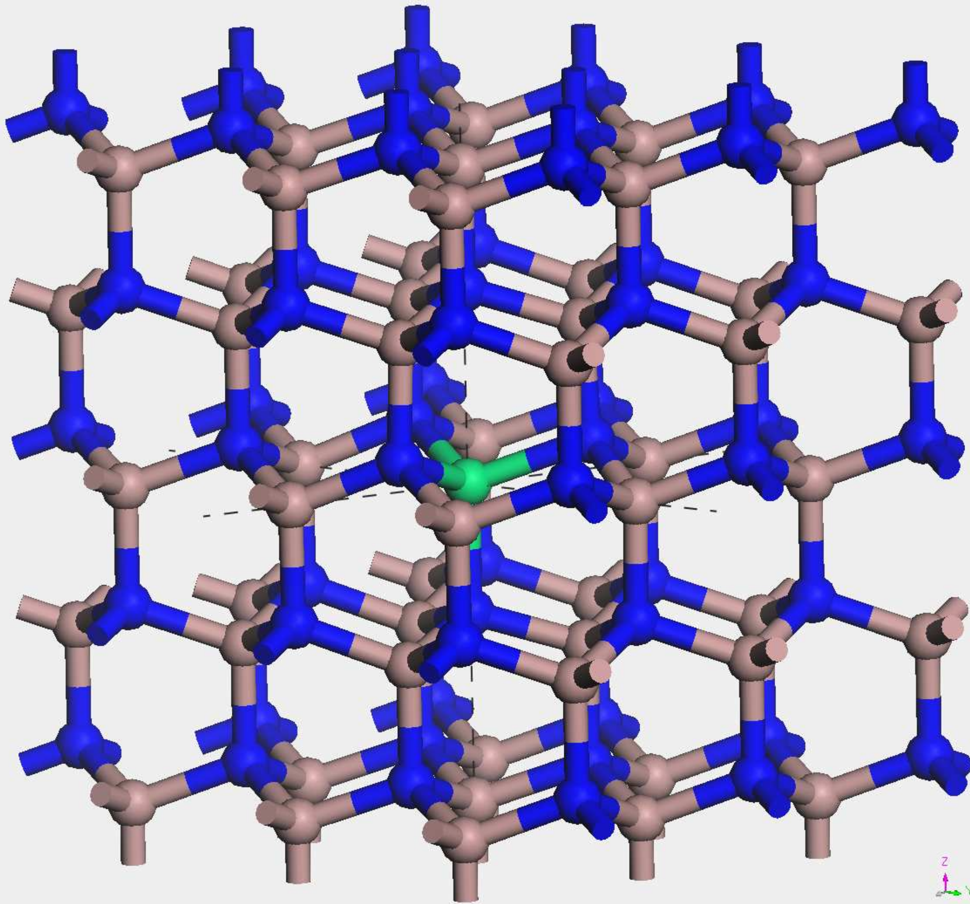
ErN



TmN

→The nitride phase of the rare earths are metallic, semi-metallic or very low gap semiconductors: quench the luminescence

Rare earths in GaN: substitutional Ga site



Er, Eu and Tm in Ga substitutional sites.

- the local symmetry is C_{3v}

-compressive strain of the GaN lattice around the R.E.

  - Er,Tm strain is 9%
  - Eu strain is 12 %

Geometry of the R.E. substitutional site

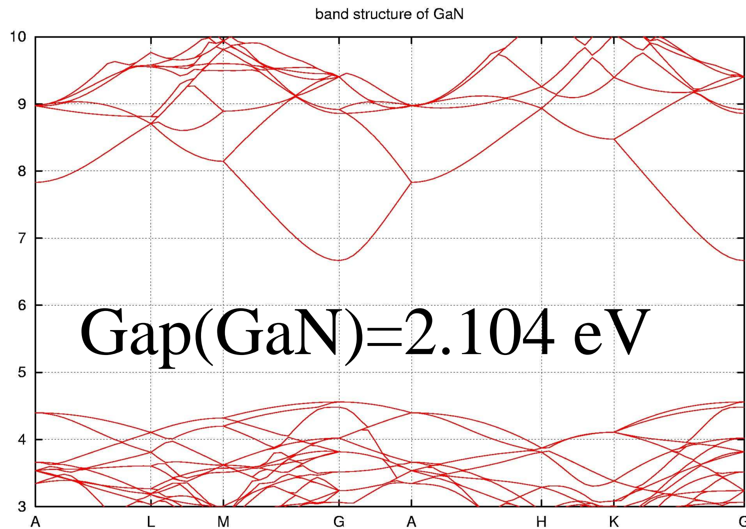
GaN:X	X-N_1 (3 bonds)	X-N_2 (1 bond)	X-Ga_1 (9 bonds)	X-Ga_2 (3 bonds)
GaN:Eu (exp.)	2.18 Å	2.22 Å	3.23 Å	3.27 Å
	(2.26 Å)[1]		(3.32 Å)[1]	
GaN:Er (exp.)	2.13 Å	2.16 Å	3.22 Å	3.26 Å
	(2.17 Å)[2]		(3.26 Å)[2]	
GaN:Tm	2.12 Å	2.15 Å	3.22 Å	3.25 Å

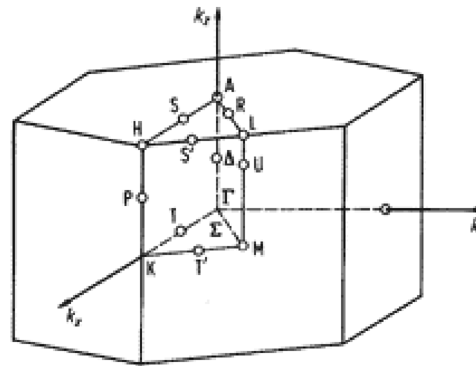
1. S. Morishima et al. internet publication…
2. Citrin et al. 2000 Appl. Phys. Lett. vol *76* p2865

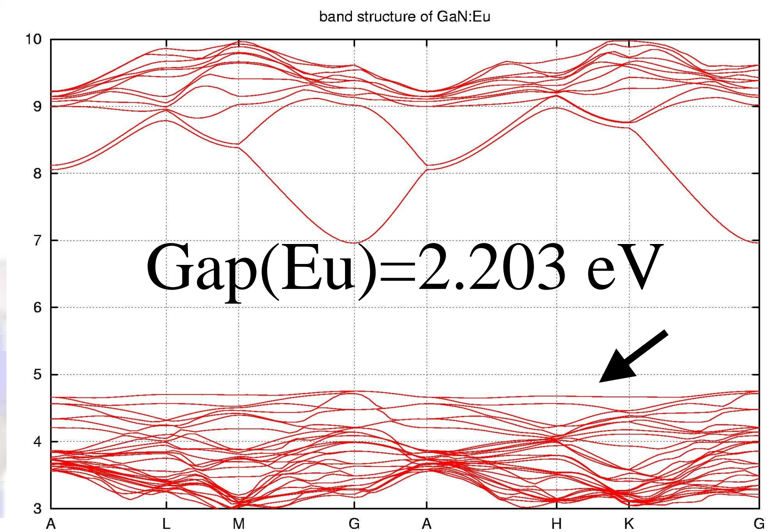
Tm < Er < Eu

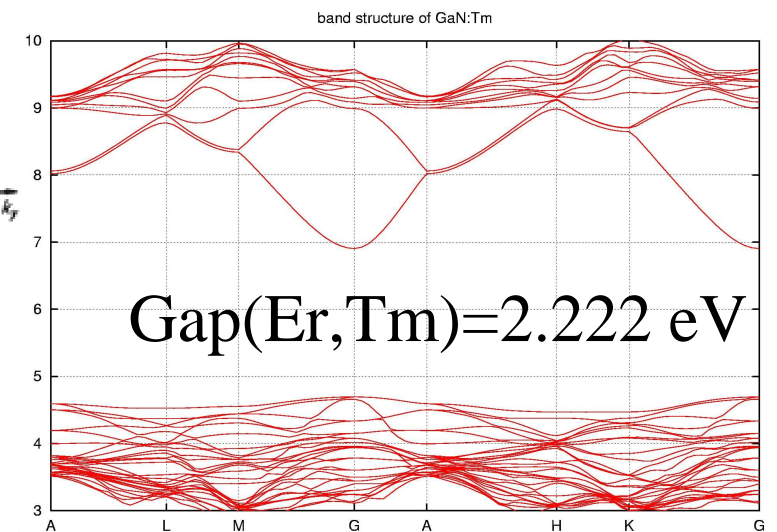
→Good agreement between the calculations and the EXAFS results
→Very short R.E.- N bond (0.2 Å shorter than in the R.E. Nitride)

Electronic properties of R.E. in Ga site







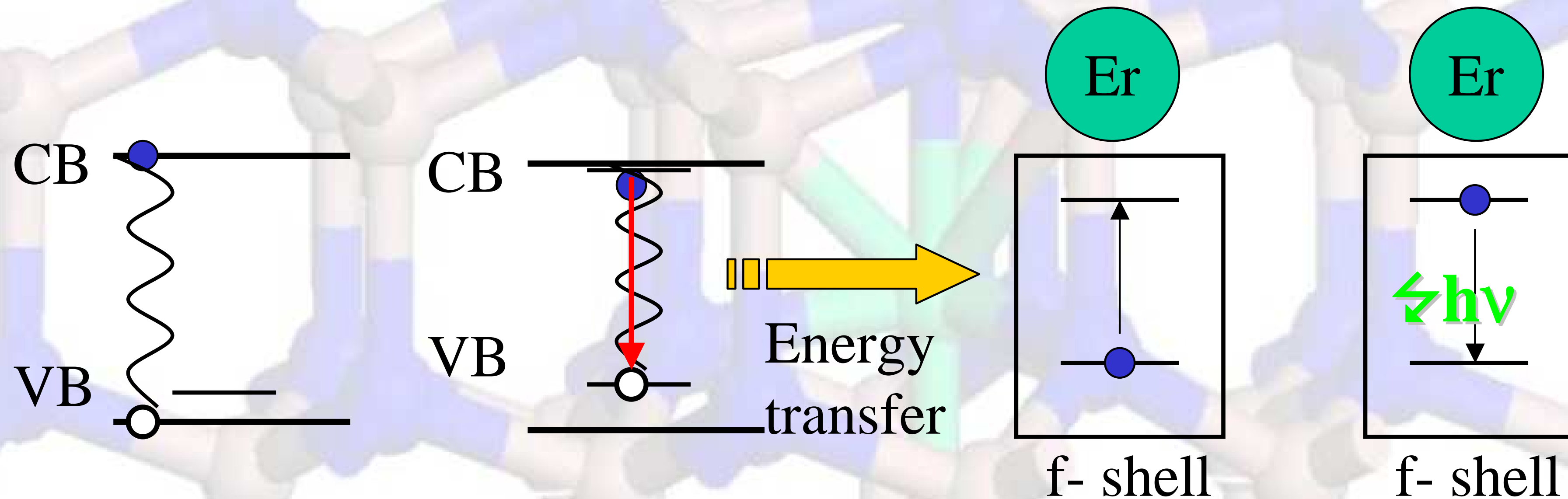


→ The effect of the R.E. in the Ga site is weak :

- small increase of the gap (DFT) by 0.1 eV
- the band structure only a little modified: level around at Fermi level (see around H)

→ very shallow donor above the VB?

Rare earth luminescence in semiconductors

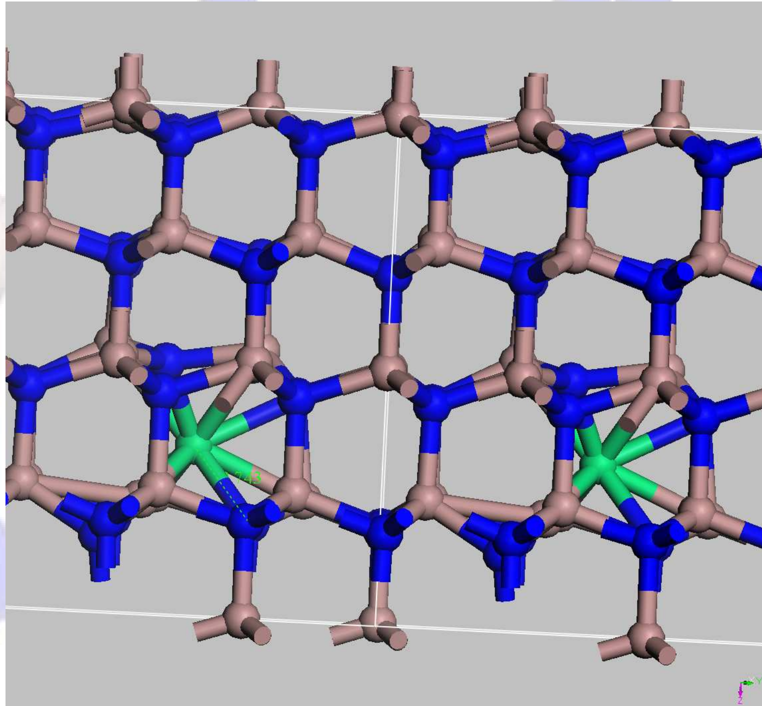


-Rare earth induced shallow donor level

→ exciton trap

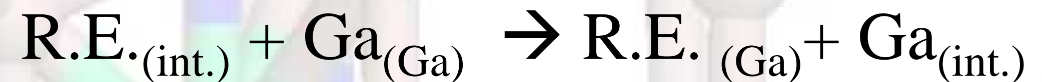
→ low energy trap : high quenching with temperature increase

R.E. in interstitial defects



Low local symmetry: C_{1h}

The R.E. atom tends to displace a Ga



$R.E._{(int.)} + Ga_{(Ga)} \rightarrow R.E._{(Ga)} + Ga_{(int.)}$

ΔE (Eu) = -900 meV

ΔE (Er) = -640 meV

ΔE (Tm) = -630 meV

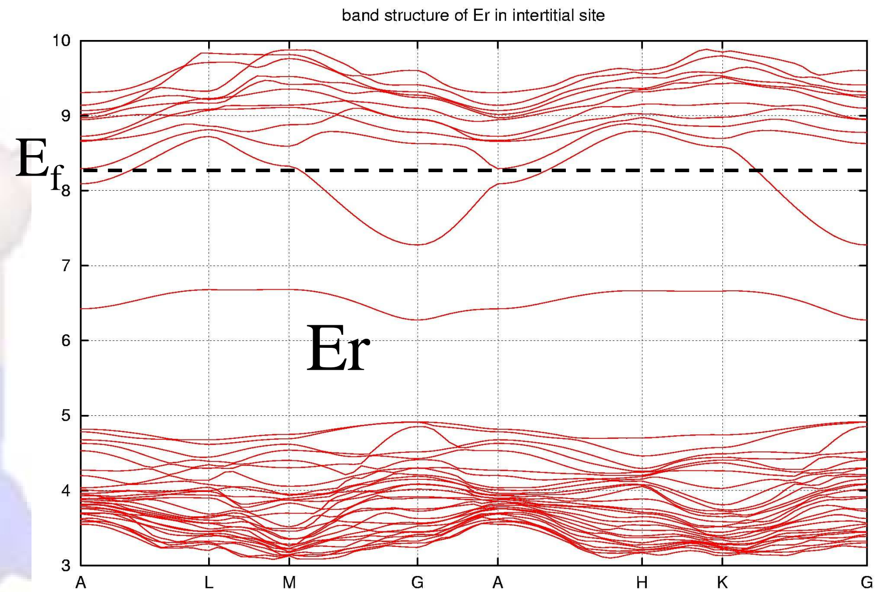
Exothermic reaction

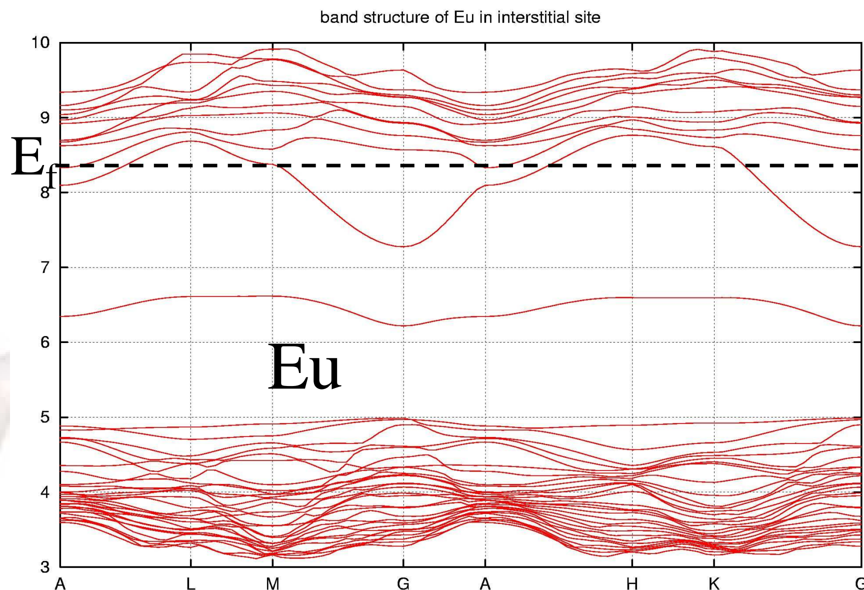
(Å)	$X-N_1$	$X-N_2(2)$	$X-N_3$ (2)	$X-Ga_1$	$X-Ga_2$ (2)	$X-Ga_3$ (2)
Eu	2.16	2.33	2.40	2.42	2.57	2.72
Er	2.11	2.29	2.35	2.38	2.54	2.70
Tm	2.10	2.28	2.35	2.37	2.54	2.69

→ R.E. atoms tend to be in substitutional Ga site in GaN

→ but interstitial structure gives a mid-gap level

Electronic properties of R.E. in interstitial sites





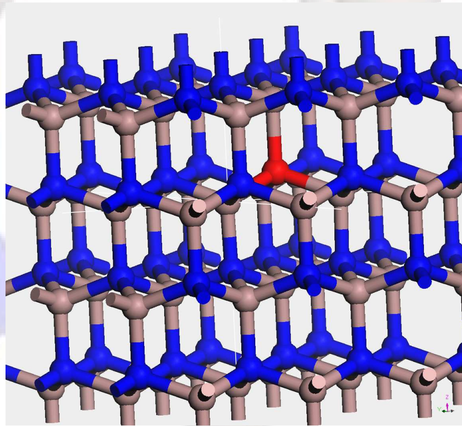
→ n type
→ the gap is mostly unchanged
→ shallow effective mass donor level
→ interstitial structure present mid-gap donor

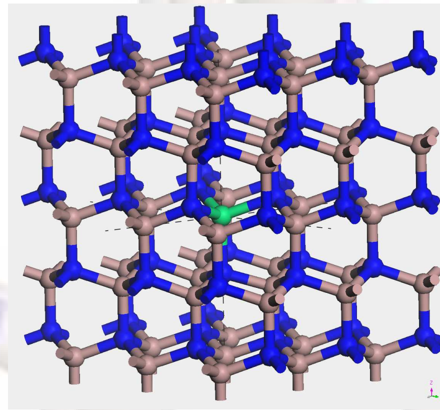
Candidate for the deep defect related with low quenching ?

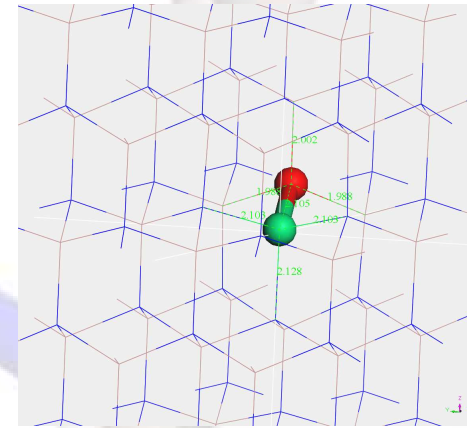
Interaction of Er with O in GaN

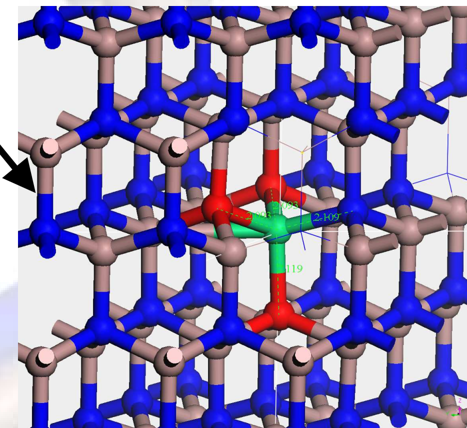
Study of O in N site and Er in Ga site

O-R.E. bonds are the only ones stronger than N- R.E.



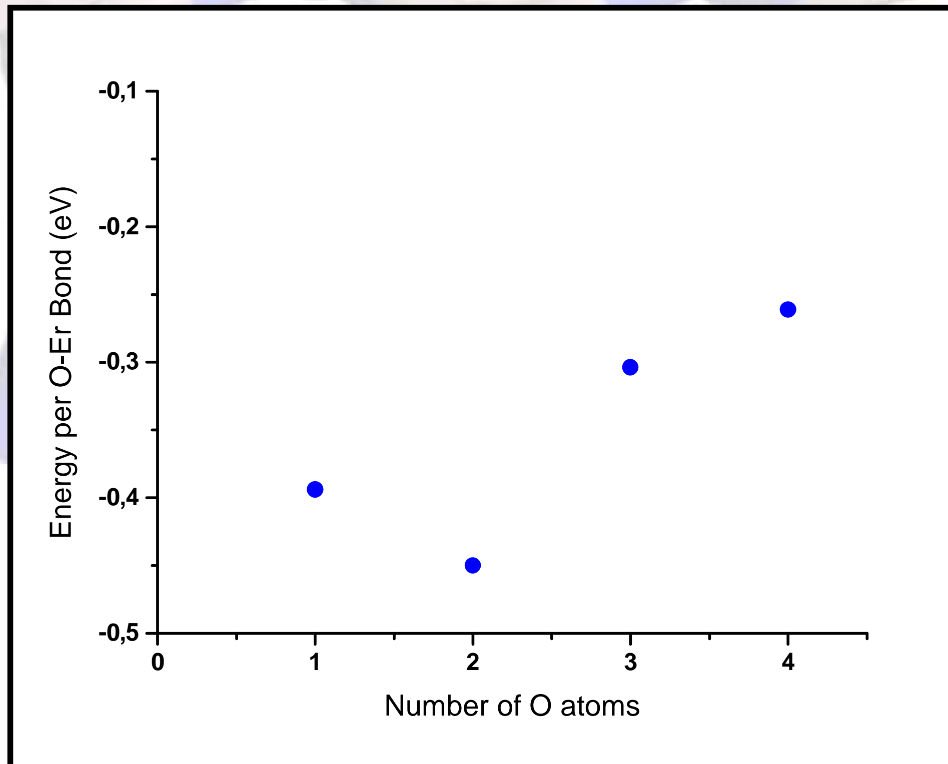






Structure
ErO
Er-O: 2.11 Å, Er-N: 2.11 Å
ErO_3
Er-O: 2.10 Å, Er-N: 2.11 Å

Formation of the ErO_x clusters



The Er-O bond formation is much weaker than in Si:

- in Si, Er-O ≈ 3 eV
- in GaN, Er-O ≈ 0.4 eV

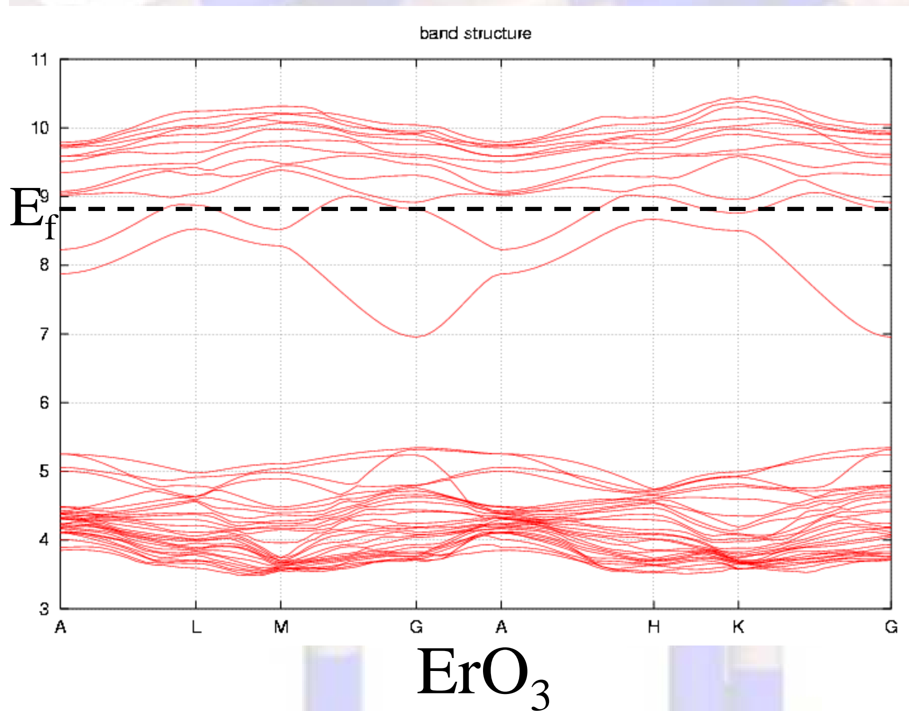
→Er-N bond is already very strong

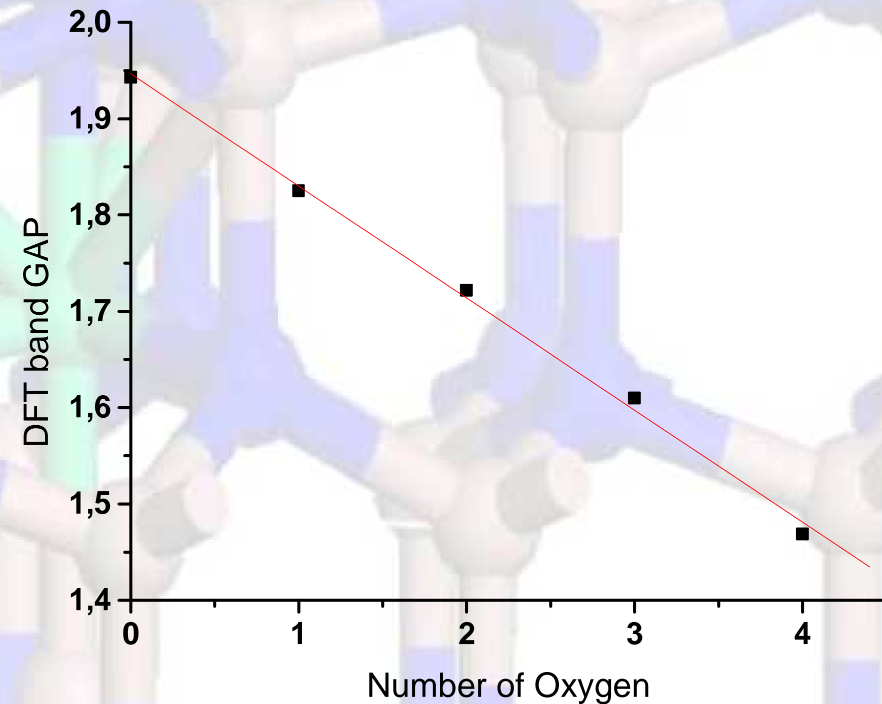
ErO_2 are favoured structures

→ The ErO_x formation is going to be sensitive to the annealing temperature

→ ErO_2 clusters are expected to form in GaN

Electronic structure of ErOx in GaN





-O in GaN is a n type dopant:

-Linear decrease of the band gap with the amount of O

-Shallow to deep level in the band gap

(ErO_2 shows a gap decrease of 0.2 eV)

Conclusion of R.E. in GaN

R.E. in a Ga site weakly modify the structure of GaN:

→ R.E. tends to be in a Ga site.

→ Er (in Ga site) doesn't modify the GaN structure much

→ limited stress caused by R.E. (only 12% strain in the R.E.-N)

R.E.are easily incorporated in GaN

R.E. in interstitial site induce mid-gap levels

The affinity of Er for O is weak in GaN

→ Er – O interaction exists in GaN

ErO_x structures are expected in GaN

The theoretical calculations seem to reproduce well the behaviour of R.E. in GaN.

Perspective: R.E. interaction with vacancies and C.