# Προσομοιώσεις ab initio και Μοριακή Δυναμικής σε νανοδομές: φαινόμενα ατομικής κλίμακας.

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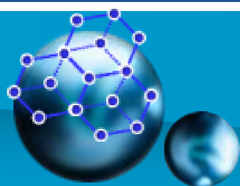


# Outline

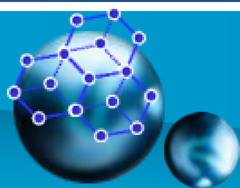
Methodology

1. Edge and screw dislocations of GaN=> Thermal Cond.

2. GaN nanoclusters formation in a-$SiO_2$ matrix

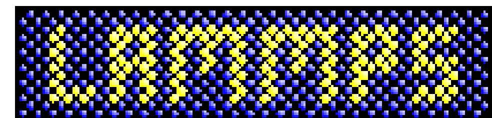
3. Defects in novel 2D materials-ARSENENE

4. Ab initio investigation of the AlN:Er system



# Methodology

## ***Molecular dynamics-Interatomic potentials***




- LAMMPS MD simulator
- Bond-order many body Tersoff-Brenner interatomic potentials
- Embedded-atom method interatomic potentials

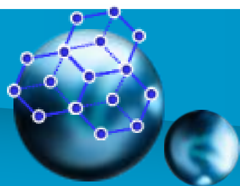
## ***ab-initio* methods**

- Abinit code with modified Troullier-Martins pseudopotentials
- VASP code with Projector Augmented Wave pseudopotentials.
- AIMPRO code uses Hartwigsen-Goedecker-Hutter pseudopotentials and a Gaussian basis set to describe the Kohn-Sham wave functions of the valence electrons.

abinit

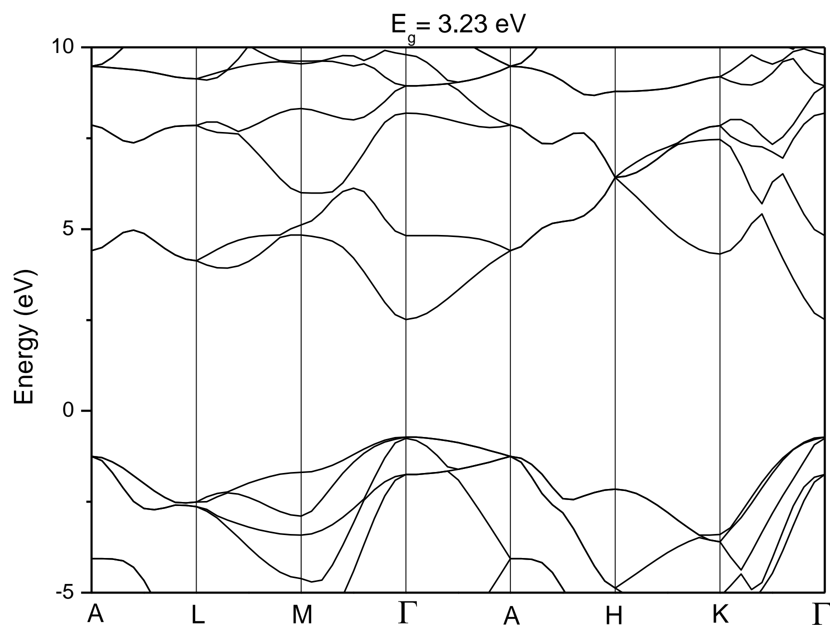
VASP b-initio ackage imulation ienna

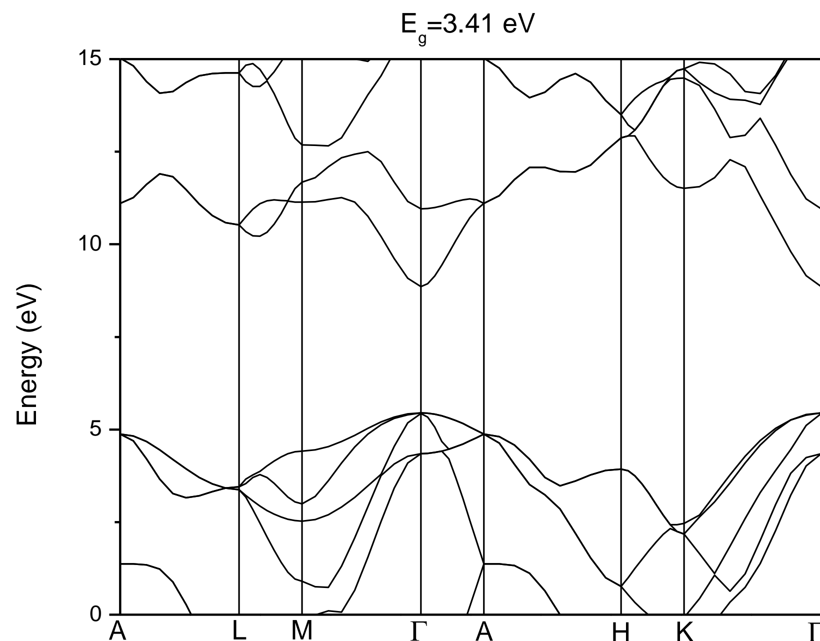
AIMPRO.abinitio

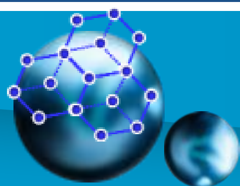


# Bulk Calculation

| | GaN | | |
|---|---|---|---|
| | | | |
| | ABINIT modified Troullier-Martins | AIMPRO modified HGH | AIMPRO HGH NLCC |
| a | 3.226 | 3.073 | 3.157 |
| c | 5.236 | 5.005 | 5.15 |
| c/a | 1.6231 | 1.6287 | 1.6313 |
| Bandgap (eV) | 3.23 | 3.41 | 2.58 |

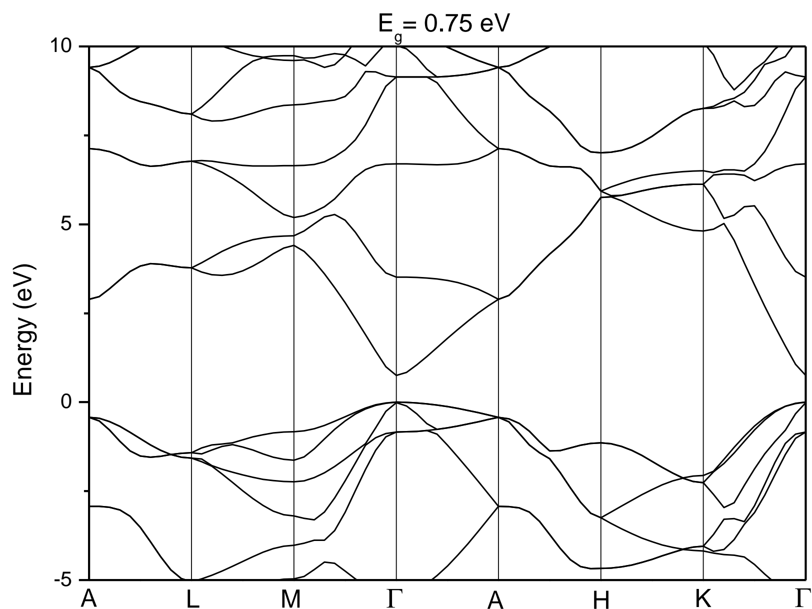


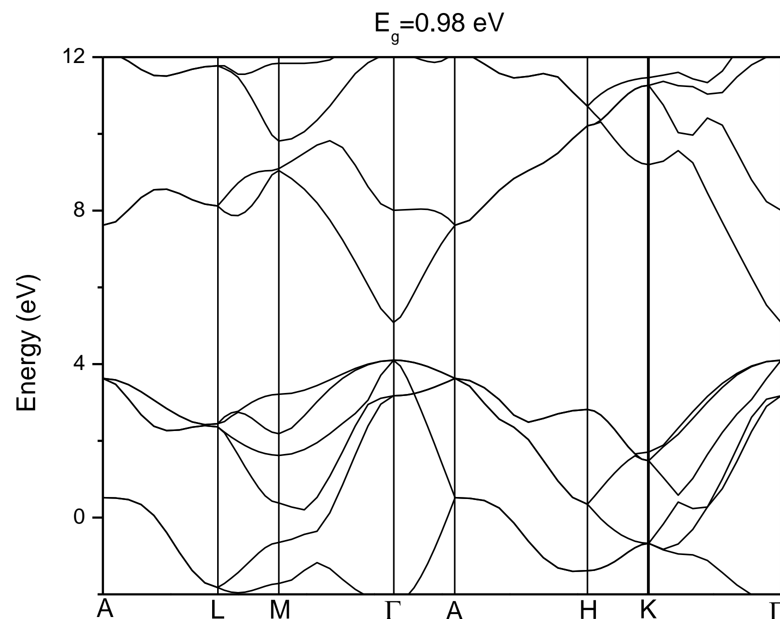



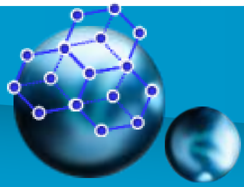


# Bulk Calculation

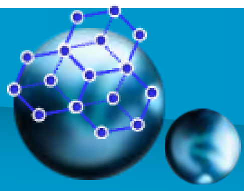
| | InN | | |
|---|---|---|---|
| | | | |
| | ABINIT modified Troullier-Martins | AIMPRO modified HGH | AIMPRO HGH NLCC |
| a | 3.554 | 3.406 | 3.544 |
| c | 5.737 | 5.514 | 5.721 |
| c/a | 1.6142 | 1.6189 | 1.6143 |
| Bandgap (eV) | 0.75 | 0.98 | 0.02 |





# PART I:
# The influence of edge and screw dislocations of wurtzite GaN on the thermal conductivity



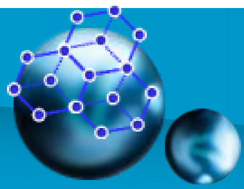
# Dislocations and thermal properties

➢ **Dislocations and GaN:**

- ❖ Phonon scattering processes due to dislocations (Holland model)
- ❖ Phonon relaxation time related to the Burgers vector (scattering direction and orientation of the dislocation: perpendicular and in random orientation)
- ❖ "Thermal Transport along (screw) dislocation line in Silicon Carbide" (10-25% reduction)
- ❖ "Atomic simulation of the size and orientation dependences of TC in GaN nanowires"

**Applications**

- ❖ Design materials of high-temperature electronics and thermoelectric applications
- ❖ Few materials exhibit high thermal conductivity at reduced dimensions, GaN is one of them
- ❖ GaN: next generation of high frequency and high power transistors
- ❖ GaN: capable of operating in high temperatures
- ❖ GaN: optoelectronics and photonic devices (desire high TC)



# Equilibrium Molecular Dynamics:

- **LAMMPS code,  EMD method**

➢ Green-Kubo formula for the autocorrelation function of the heat flux in z-direction

➢ Initial structures are relaxed with the conjugate gradient energy minimization algorithm

➢ EMD: repeat simulation set-up for each system 10 times

➢ Obtain thermalisation NVT (T=300K) for 200 ps,

equilibration NVE in 2 ns,

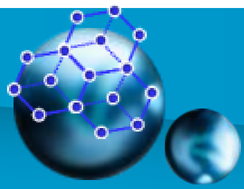
then averaging NVE for  4-5 ns

➢ Periodic boundary conditions in the all directions

➢ Interatomic potential reproduce well the bulk TC 160 W/mK

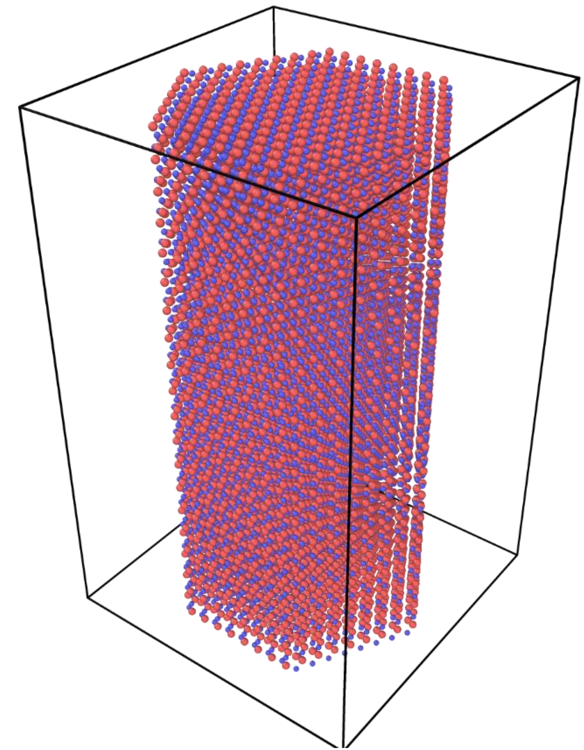
Stillinger-Weber, PRB **31**, 5262 (1985)

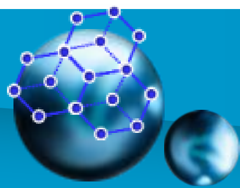
➢ Simulation box: 6nm x 6nm x 10nm (1nm empty space)



# Modelling nanowires I:

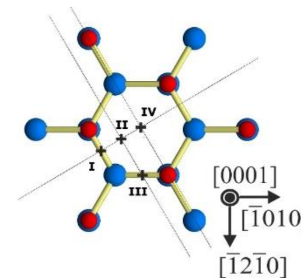
- Pristine nanowires with different cross sections
- Square cross-section for the study of dislocations with cross-section 4nmx4nm, length 10nm
- NWs with dislocations
- 3 types of "perfect "edge dislocations (4, 5/7, 8) and
- 2 of screw "perfect" dislocations (S6,D6)
- "perfect" dislocation b=1 (a or c)
- Lattice constants a = b = 3.189 Å, c = 5.214 Å

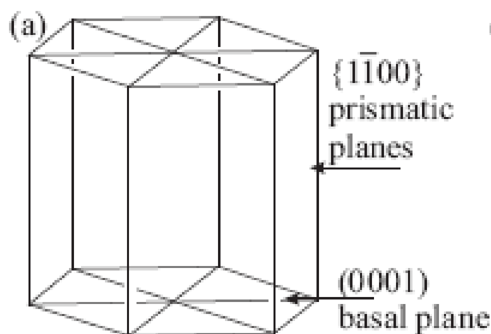


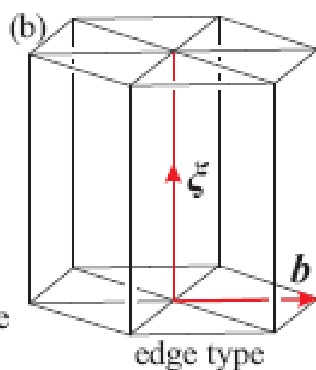


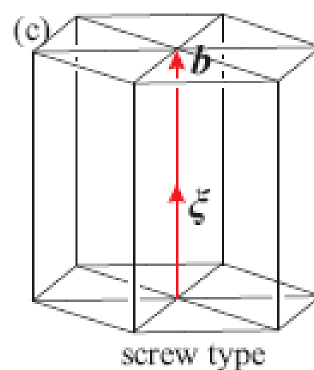
# Modelling nanowires II:

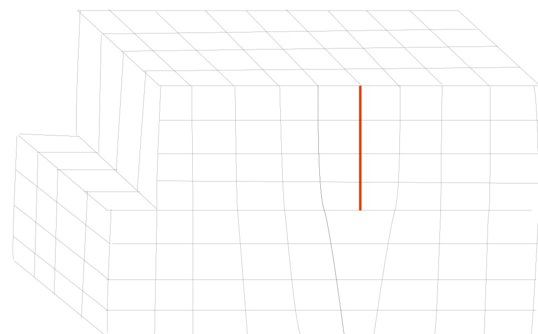
| Three types of dislocations | | l=[0001] | l=[11-20] | Line-direction |
|---|---|---|---|---|
| a-type | **b**=1/3<11-20> | edge | screw, mixed(60°) | |
| c- type | **b**=[0001] | screw | edge | |
| (a+c)-type | **b**=1/3<11-23> | mixed | mixed | |

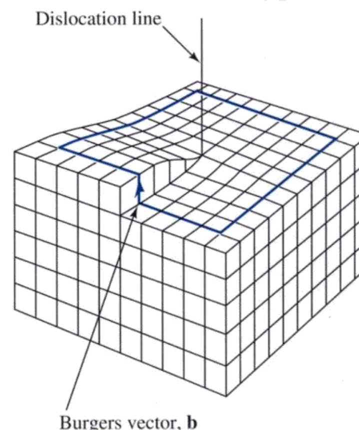


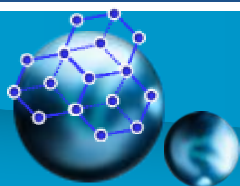



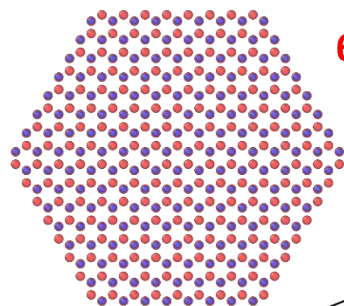



- **90% of dislocations in III-V has line-direction the [0001],**
- **We model this dislocation line**
- **Edge: ξ perpendicular b,**
- **Screw: ξ // b**



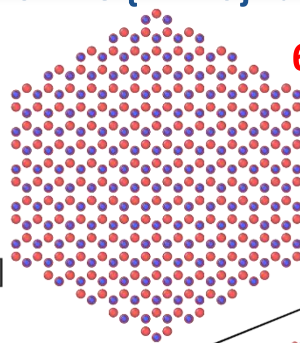
# I. GaN NWs with different orientations of the facets and cross-sections

Nanowire {10-10} facets



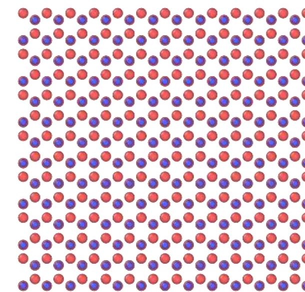
66±6 W/mK

Nanowire {11-20} facets

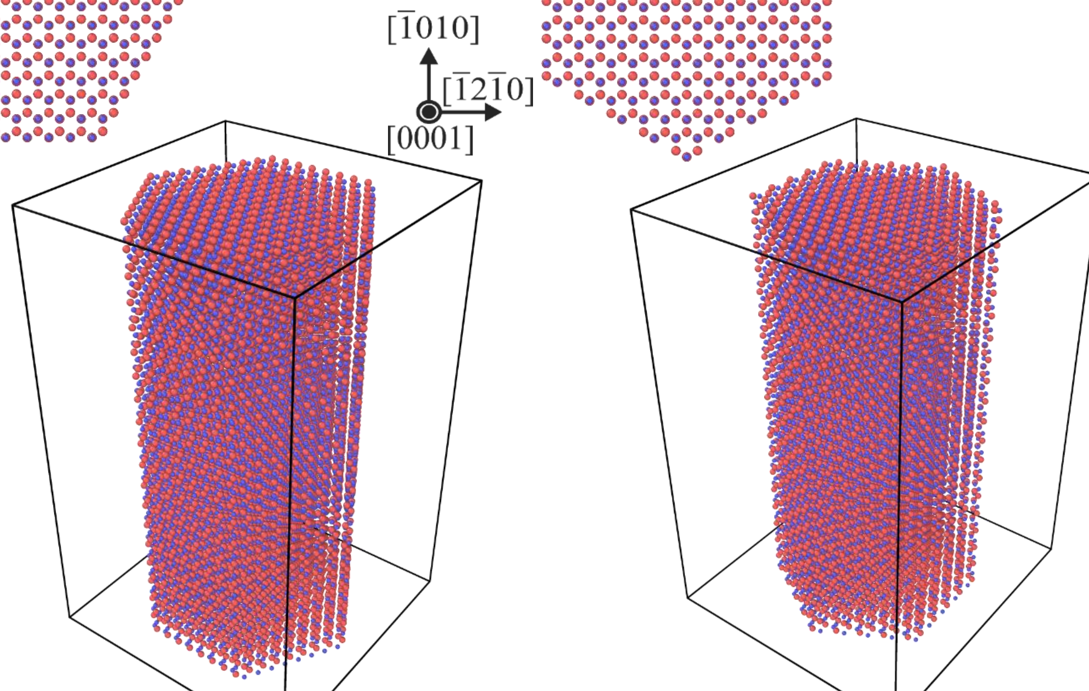


69±6 W/mK

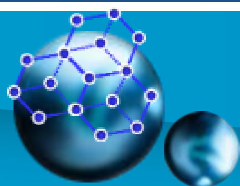
Nanowire {11-20} and {10-10} facets



49±3 W/mK

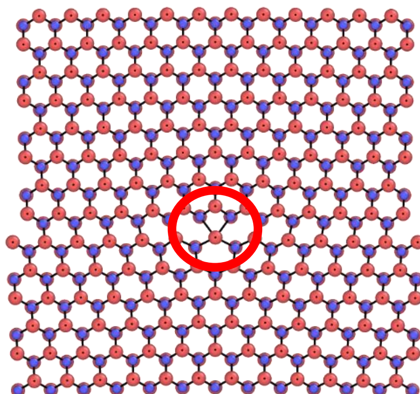



- Better relaxed free surfaces for the square cross-sections
- Better accommodation of strain of dislocations (avoid numerous edges between facets)



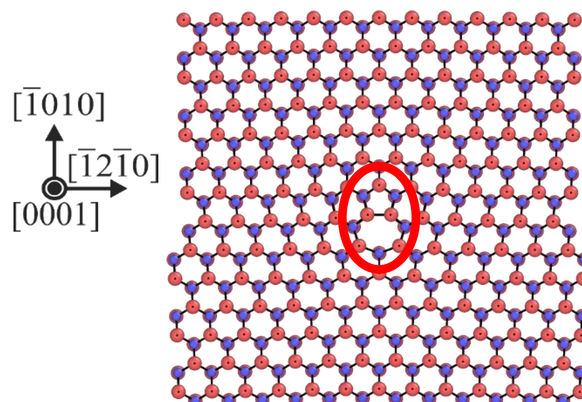
# II. GaN with edge dislocations: 4, 5-7, 8

a-edge dislocation:
OVER-coordinated atomic column
4-atom ring configuration



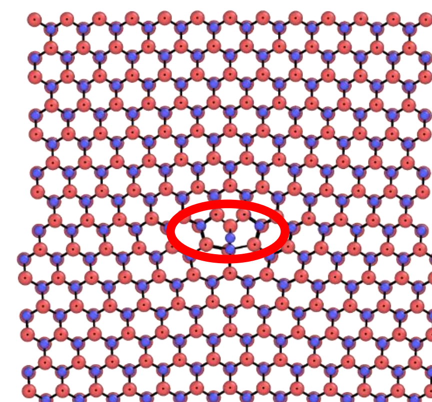
**Edge4: 38±4 W/mK**

a-edge dislocation
Formation of Ga-Ga and N–N "wrong" bonds
5/7-atom rings configuration




**Edge5/7: 42±5 W/mK**

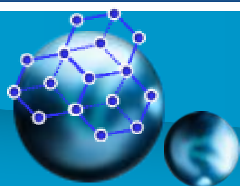
a-edge dislocation
LOW-coordinated atomic column
8-atom ring configuration



**Edge8: 51±4 W/mK**

**TC_Edge4 < TC_Edge5/7 < TC_Edge8 ~ TC_NWs without dislocations**
**Explanation with the bonds**
Edge4: all bonds are covalent, high stress
Edge5/7: wrong bonds, metallic bonds (Ga-Ga, N-N), less stress
Edge8: presence of dangling bonds, less stress

- **Impact of dangling and metallic bonds on TC**
- **Impact of stress on TC**

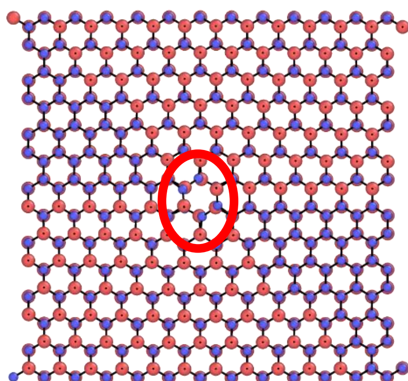


# III. GaN with screw dislocations: S6, D6

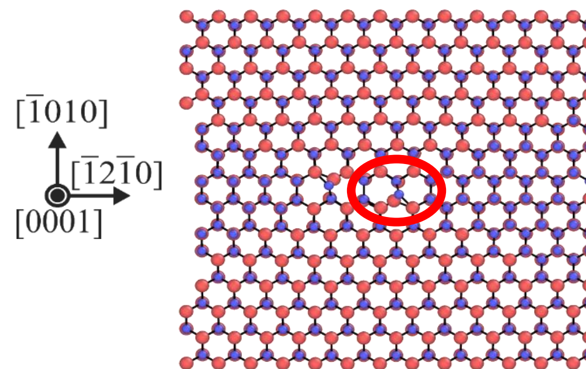
c-screw dislocation:
Single six-atom ring

c-screw dislocation
Double six-atom ring: two fully coordinated six atom rings with Ga-Ga and N-N “wrong” bonds
Double six-atom ring

[$\bar{1}010$]
[$\bar{1}2\bar{1}0$]
[0001]

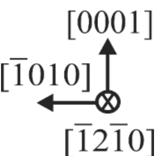


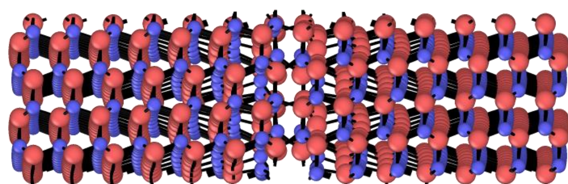
[$\bar{1}010$]
[$\bar{1}2\bar{1}0$]
[0001]

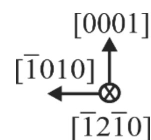


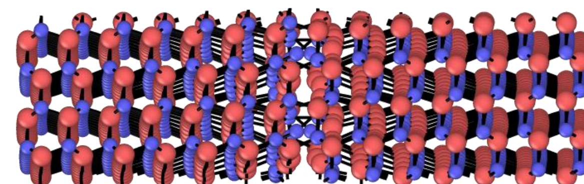
**ScrewS6: 20±1 W/mK**

**ScrewD6: 28±2 W/m**

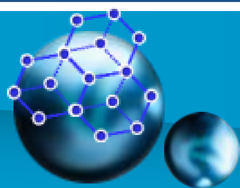


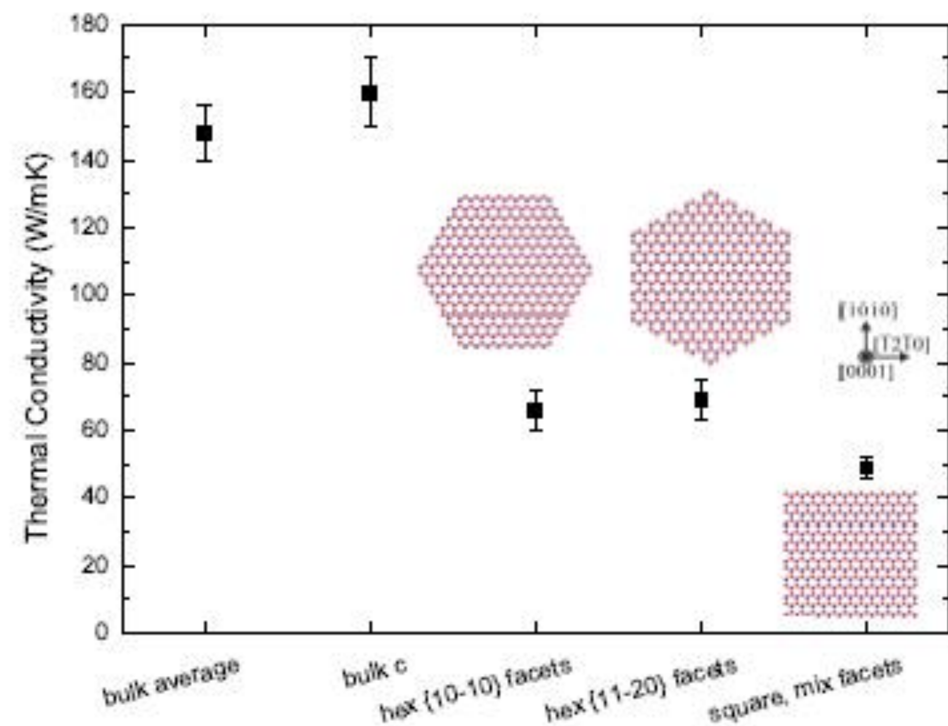


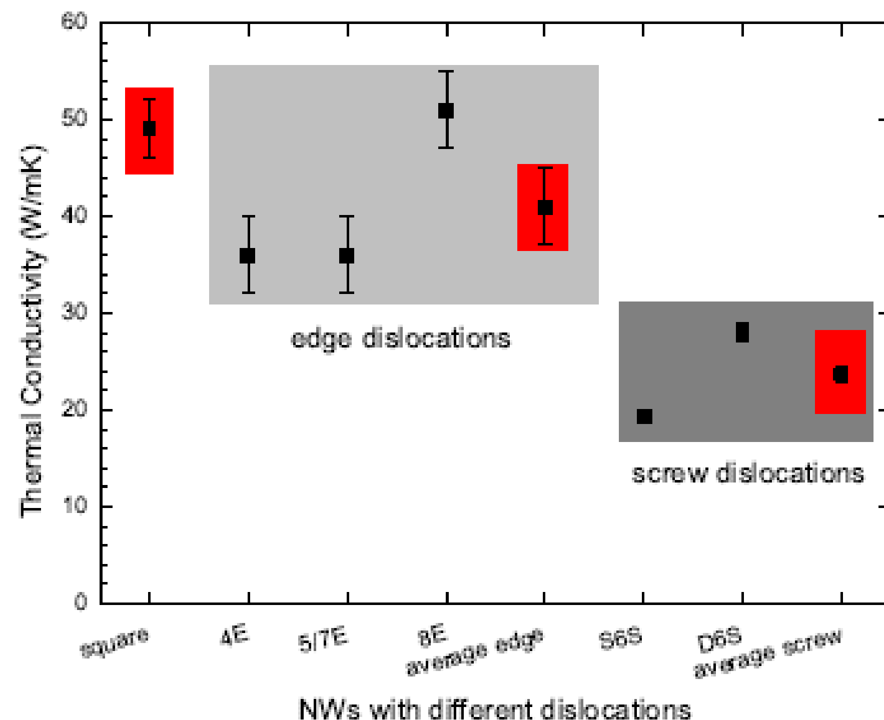



**TC_ScrewS6 < TC_ScrewD6**
**Explanation with the bonds**
ScrewS6: all bonds are covalent, high stress
ScrewD6: wrong bonds, metallic bonds (Ga-Ga, N-N), less stress



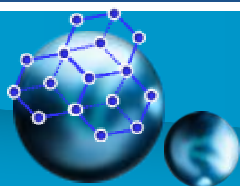
# IV. Screw .vs. Edge dislocations




Thermal conductivity calculated with the EMD method for the bulk GaN (all directions and c-direction), and for GaN nanowires with different external free surfaces facets and cross-section shapes.

Thermal conductivity for pristine nanowires and nanowires containing difference types of dislocations. There are three sub-types of edge dislocations and two sub-types of screw dislocations.



# IV. Edge .vs. Screw dislocations

$$\sigma_{xz} = \sigma_{zx} = \sigma_{yz} = \sigma_{zy} = 0$$

$$\sigma_{xx} = -\frac{Gb}{2\pi(1-\nu)} y \frac{3x^2 + y^2}{(x^2+y^2)^2}$$

$$\sigma_{yy} = \frac{Gb}{2\pi(1-\nu)} y \frac{x^2 - y^2}{(x^2+y^2)^2}$$

$$\sigma_{xy} = \sigma_{yx} = \frac{Gb}{2\pi(1-\nu)} x \frac{x^2 - y^2}{(x^2+y^2)^2}$$

σxx 8 GPa -8 GPa 200 Å

σyy 7.5 GPa -7.5 GPa 200 Å

σxy 7.5 GPa -7.5 GPa 200 Å

a.

σxz 7.9 GPa -7.9 GPa 200 Å

σyz 7.9 GPa -7.9 GPa 200 Å

σθz 1 GPa 0 GPa 200 Å

b.

$$\sigma_{xx} = \sigma_{yy} = \sigma_{zz} = \sigma_{xy} = \sigma_{yx} = 0$$

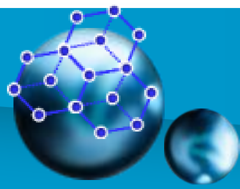
$$_{xz} = \sigma_{zx} = -\frac{Gb}{2\pi}\frac{\sin\theta}{r} = -\frac{Gb}{2\pi}\frac{y}{x^2+y^2}$$

$$\sigma_{yz} = \sigma_{zy} = \frac{Gb}{2\pi}\frac{\cos\theta}{r} = \frac{Gb}{2\pi}\frac{x}{x^2+y^2}$$

Taking into account that in cylindrical polar coordinates:

$$\sigma_{\theta z} = -\sigma_{xz}\sin\theta + \sigma_{yz}\cos\theta$$

$$\sigma_{\theta z} = \sigma_{z\theta} = \frac{Gb}{2\pi r}$$



# IV. Screw .vs. Edge dislocations

| | TC(W/mK) |
|---|---|
| Bulk GaN | 160±5 |
| GaN NW | **49±3** |
| GaN NW Edge4 | 38±4 |
| GaN NW Edge5/7 | 42±5 |
| GaN NW Edge8 | 51±4 |
| GaN NW ScrewS6 | **20±2** |
| GaN NW ScrewD6 | 28±1 |

**Average 44 W/mK 0-22% reduction** (Edge)

**Average 24 W/mK 43-60% reduction** (Screw)

Using linear elasticity theory,
the strain energy of a dislocations is:

$$E_{total}=E_{elastic}+E_{core}$$

with

$$E_{elastic}=A\ln(R/r_0)$$

$$A=Kb^2/4\pi$$

(K:energy factor, b: Burgers vector)

$$K_{edge}=C_{11}^2-C_{12}^2/2C_{11}$$

$$K_{screw}=C_{44}$$

Finally the prelogarithmic factors for both dislocations:

$$A_{edge}=0.77eV/A,\ A_{screw}=1.38Ev/A$$

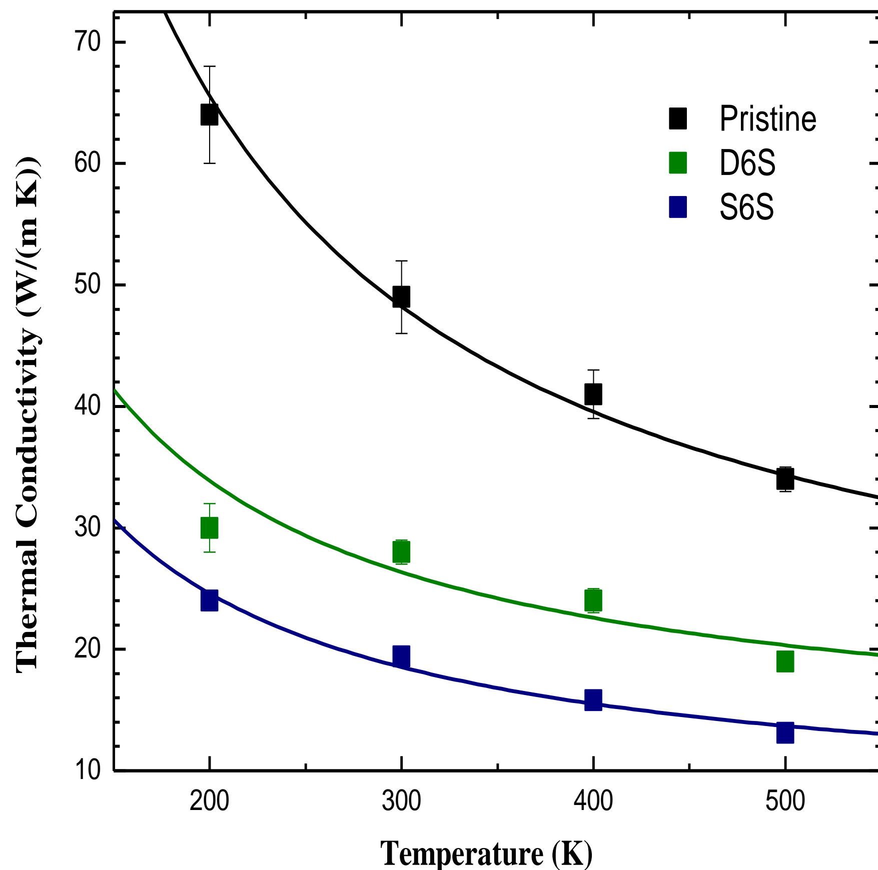
So ratio **Aedge/Ascrew = 0.53**

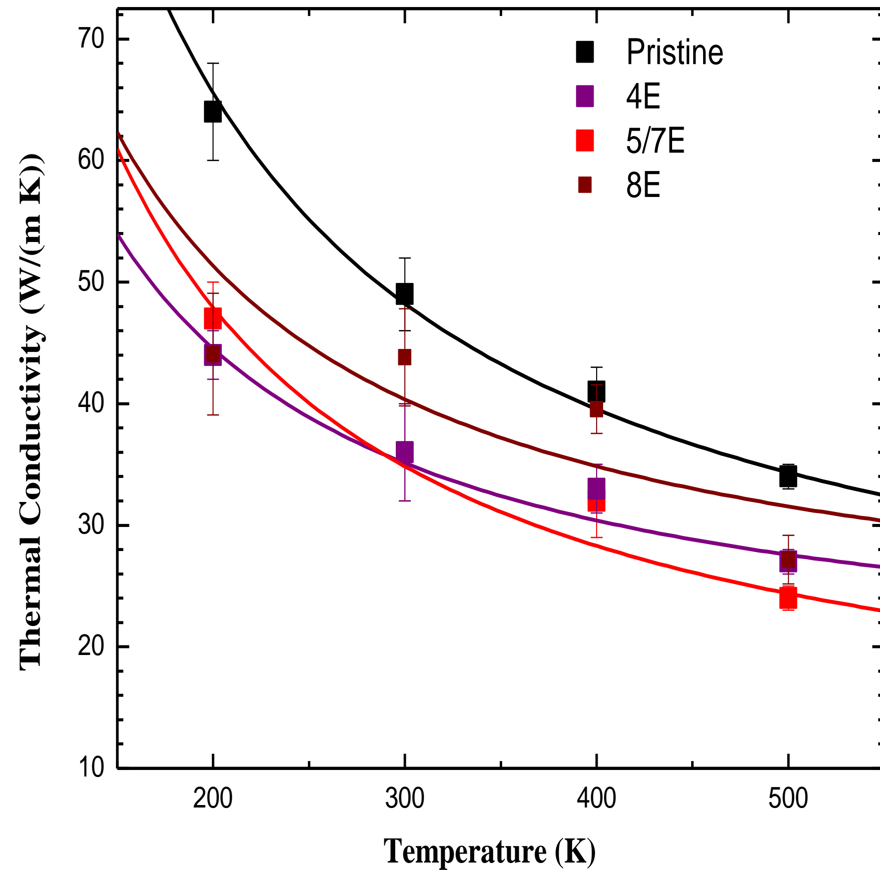
TC ratio **TCscrew/TCedge = 0.54**

➤ **The TC is inverse proportional to the elastic energy of dislocations**

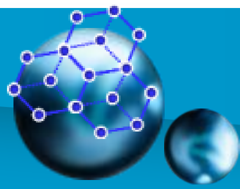
# IV. Screw .vs. Edge dislocations

$\kappa \sim T^{-1} A^{-J}$




Thermal conductivity of the pristine and the two screw (a) and three edge (b) defected nanowires as the function of the temperature. The solid lines represent the above described theoretical approach.



# 5. Summary

## ❑ Conclusions

❖ **TC is inverse proportional to the elastic energy of dislocations. The screw dislocations having higher strain energy i.e. more strained bonds hinder the thermal transport more than the edge dislocations, which have less elastic energy - less included strain.**

ratio **Aedge/Ascrew = 0.55**

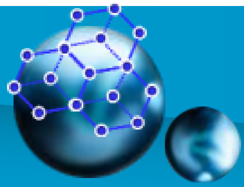
TC ratio **TCscrew/TCedge = 0.54**

❖ **The structural characteristics of the core and more specifically the coordination which characterize each individual core structure rules the corresponding J factor. Highly deformed core region => significant source of anharmonic phonon-phonon scattering** Y. Ni, S. Xiong, S. Volz, T. Dumitrica PRL **113**, 124301 (2014)

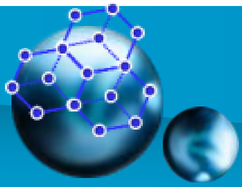
$$\kappa \sim T^{-1} A^{-J}$$

❖ **TC of screw dislocations < TC of edge dislocations < TC pristine**

**50% reduction** **10% reduction**

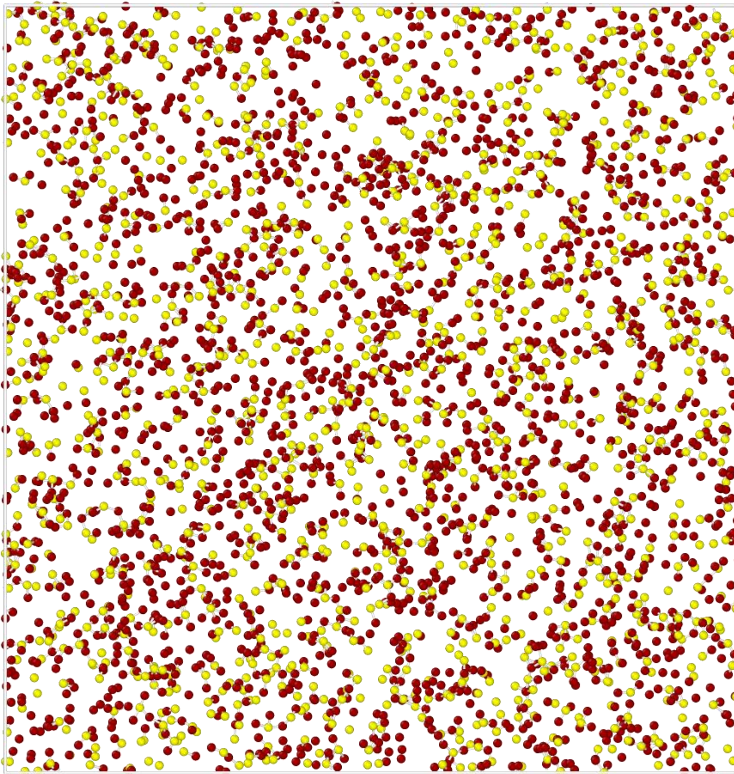


# PART II:
# GaN nanoclusters formation in amorphous $SiO_2$ matrix



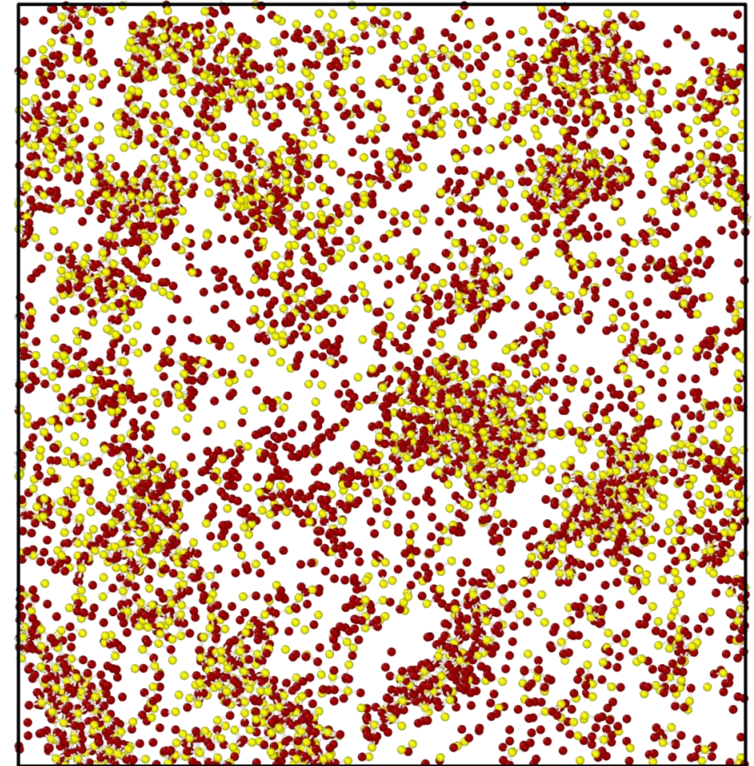
# Cluster formation

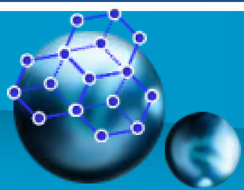
**1300K: $SiO_2$ matrix atoms removed, time =4ns**



For the same concentration of Vacancies

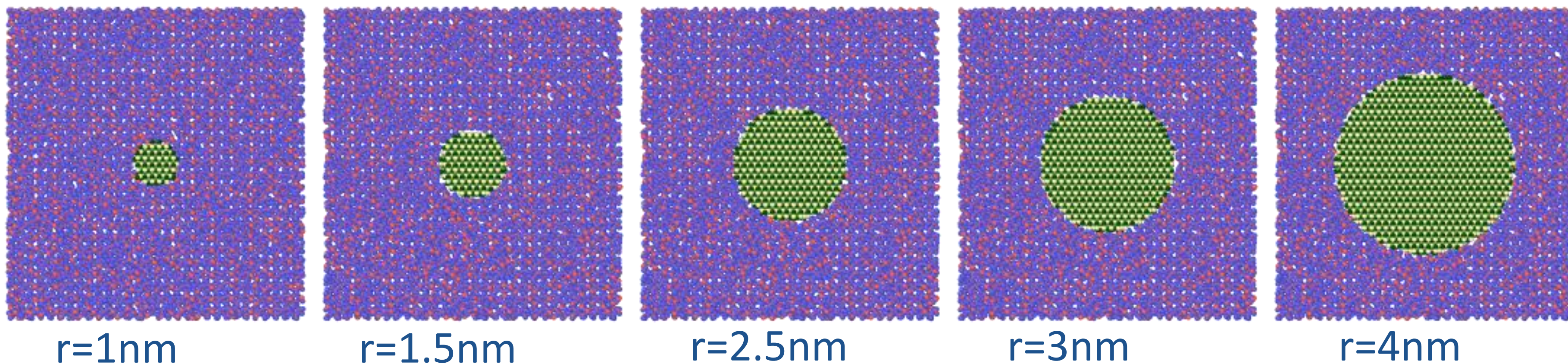
**1400K: $SiO_2$ matrix atoms removed, time = 4ns**

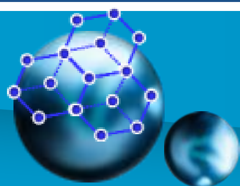




# Influence of structural properties on thermal conductivity

1. Influence of **radius** on TC
   - 5 structures were created, containing a single cluster of different radius in the center
   - Radiuses examined: 1nm, 1.5nm, 2.5nm, 3nm and 4nm





# TC results

**k - r for single clusters**

70
60
50
40
30
20
10
0

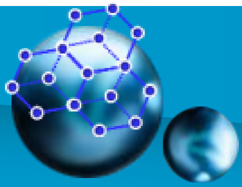
k (W/mK)

0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5

r (nm)

| Model | ExpGro1 | | |
|---|---|---|---|
| Equation | y = A1*exp(x/t1) + y0 | | |
| Reduced Chi -Sqr | 0.3684 | | |
| Adj. R-Squar | 0.9857 | | |
| | | Value | Standard Err |
| k | y0 | 0.7513 | 0.17926 |
| k | A1 | 0.0973 | 0.03341 |
| k | t1 | 0.6355 | 0.04071 |
| k | k | 1.5733 | 0.10078 |
| k | tau | 0.4405 | 0.02822 |

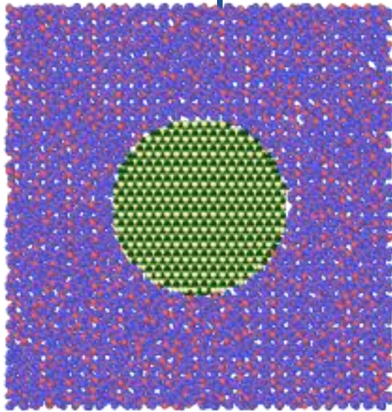
MD simulation revealed that TC is **increasing exponentially** with the increase in radius

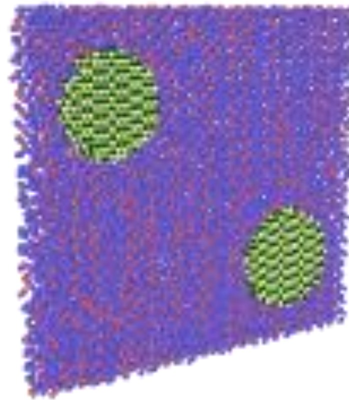


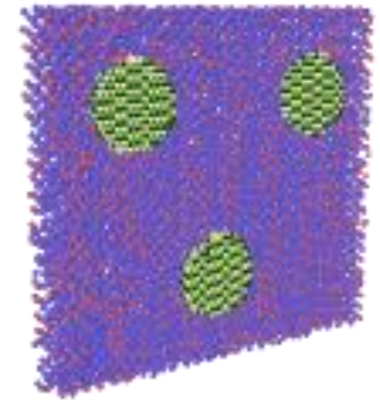
# Influence of structural properties on thermal conductivity

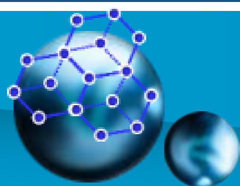
## 2. Influence of **surface** on TC

- The surface of the 3nm cluster was calculated equal to :113.097 $nm^2$
- Keeping constant the same total surface, we divided the 1 cluster to 2 and 3 smaller clusters, in specific positions.









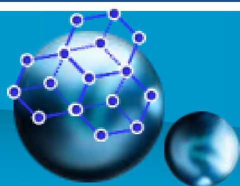
# TC results

## k - number of clusters for the same surface

k (W/mK)

Number of clusters

| Equation | y = a + b*x | | |
|---|---|---|---|
| Weight | Instrumental | | |
| Residual Sum of Squares | 0.00296 | | |
| Pearson's r | -0.999 | | |
| Adj. R-Squ | 0.9998 | | |
| | | Value | Standard E |
| k | Interce | 14.881 | 0.10358 |
| k | Slope | -4.1783 | 0.03635 |



# TC results

## k - r for the same surface

k (w/mK)

12

9

6

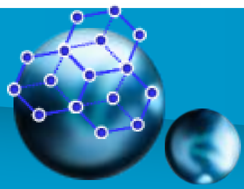
3

0

1.5 2.0 2.5 3.0 3.5

r (nm)

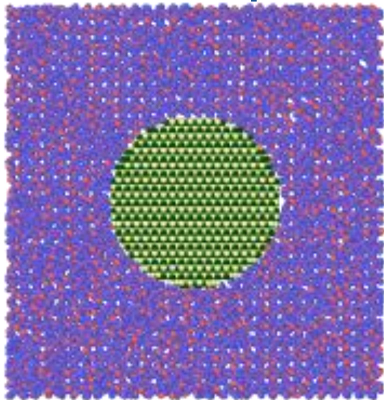
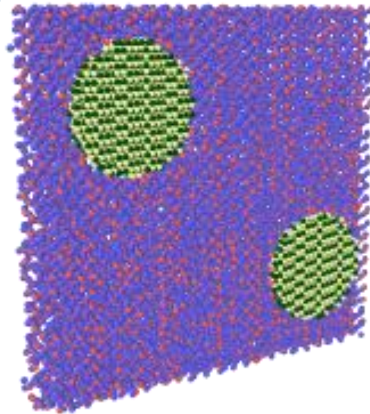
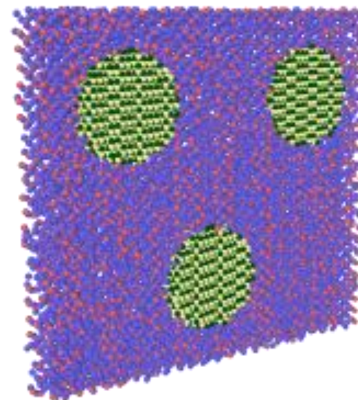
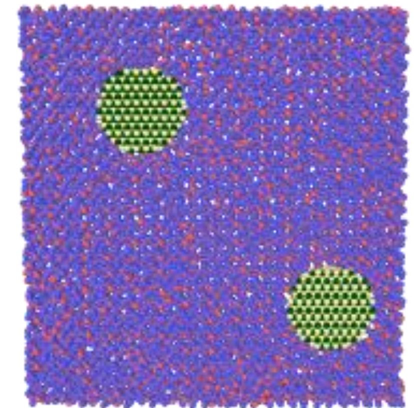
| Model | ExpGro1 | | |
|---|---|---|---|
| Equation | y = A1*exp(x/t1) + y0 | | |
| Reduced Chi-Sqr | 0 | | |
| Adj. R-Squar | 0 | | |
| | | Value | Standard Erro |
| k | y0 | 12.98403 | 0 |
| k | A1 | -90.0965 | 0 |
| k | t1 | -0.81057 | 0 |
| k | k | -1.2337 | -- |
| k | tau | -0.56184 | -- |

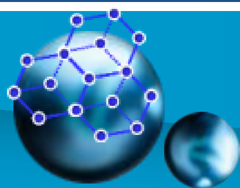


# Influence of structural properties on thermal conductivity

## How **volume** affects on TC?

- The volume of the 3nm cluster was walculated equal to: 113.1 $nm^3$
- Keeping constant the cluster's total volume, we divided 1 cluster to 2, 3 and 4 smaller clusters, in specific positions



# TC results

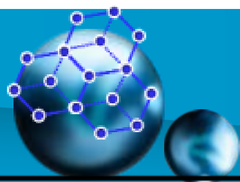
k - r same volume

k (w/mK)

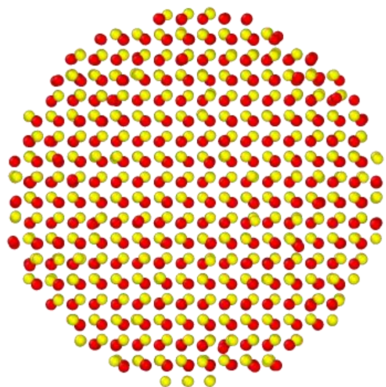
30
25
20
15
10
5
0

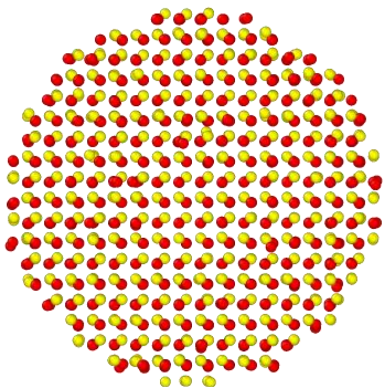
1.8 2.1 2.4 2.7 3.0

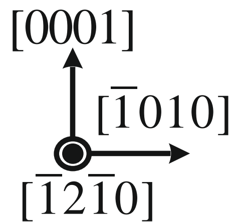
r (nm)

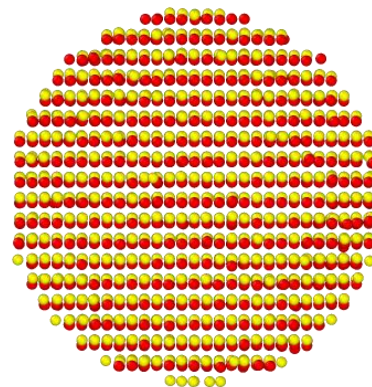


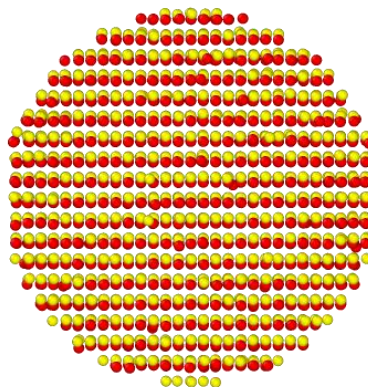
# TC results

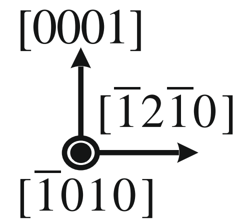


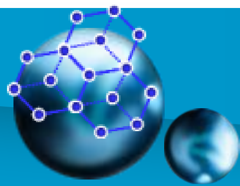




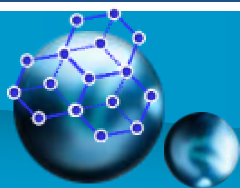







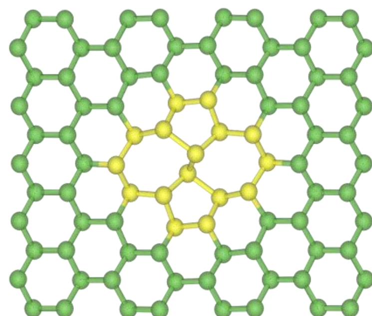


# PART III:
# Defects in novel 2D materials-ARSENENE

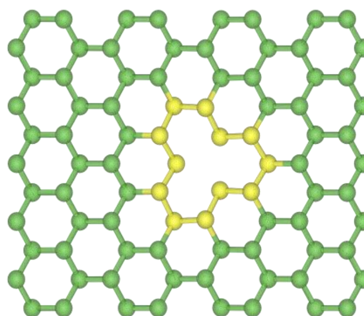


# Structural & Energetic properties of defective buckled arsenene

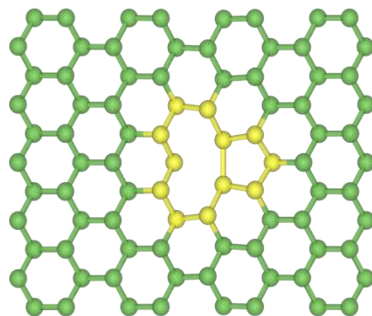
SW, $E_{for}$= 1.22eV



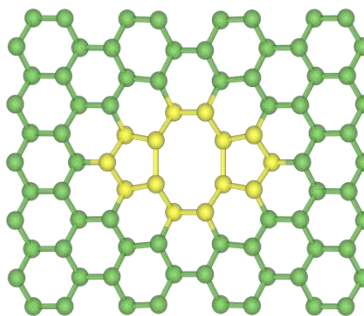
SV, $E_{for}$= 2.22eV



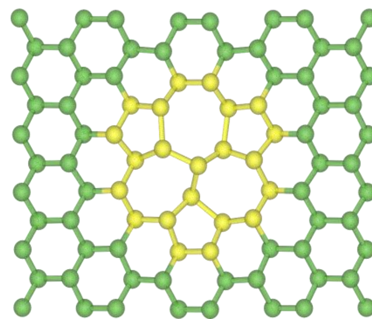
SV-59, $E_{for}$= 2.01eV



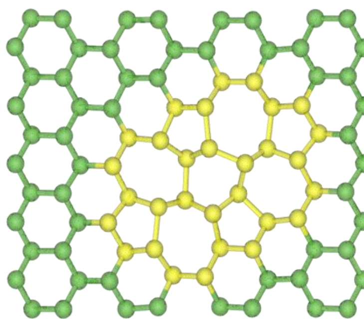
DV-585, $E_{for}$= 2.27eV

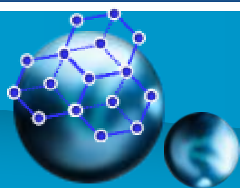


DV-555-777, $E_{for}$= 2.26eV

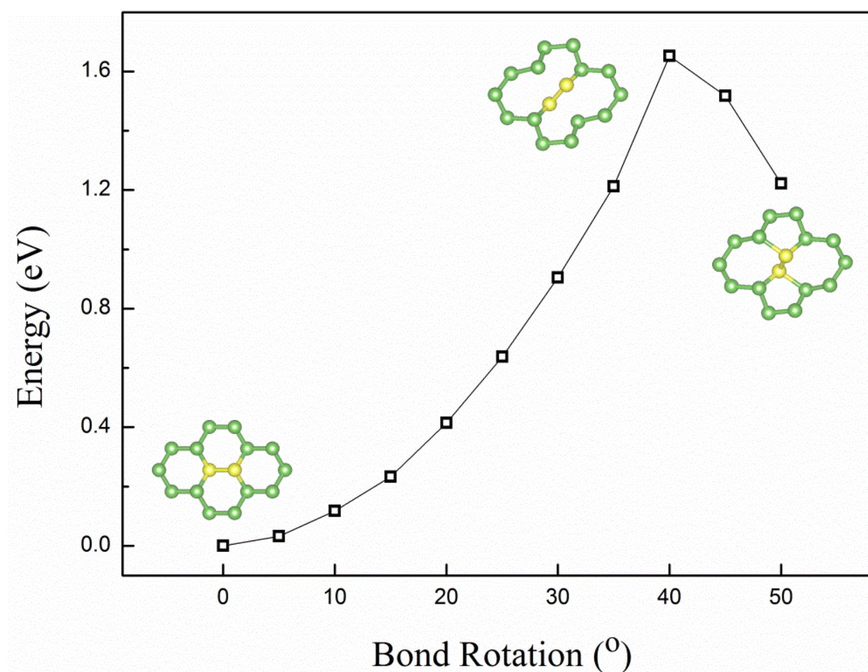


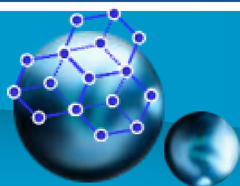
DV-5555-6-7777, $E_{for}$= 2.81eV





# Energetics of SW defect creation in buckled arsenene





# Electronic properties of defective buckled arsenene

Pristine

$E_g$=1.59 eV

SW

SV

SV-59

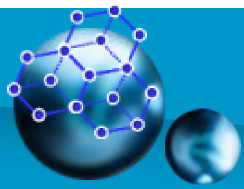
DV-585

DV-555-777

DV-5555-6-7777

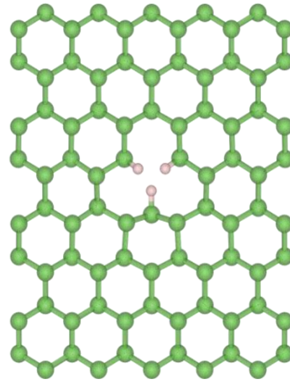
$E-E_F$ (eV)

Γ M K Γ

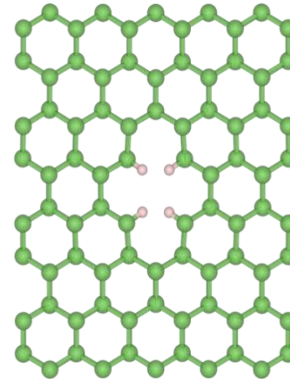


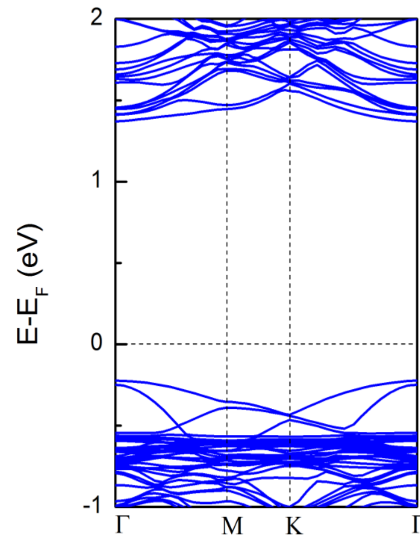
# H-passivated defective buckled arsenene

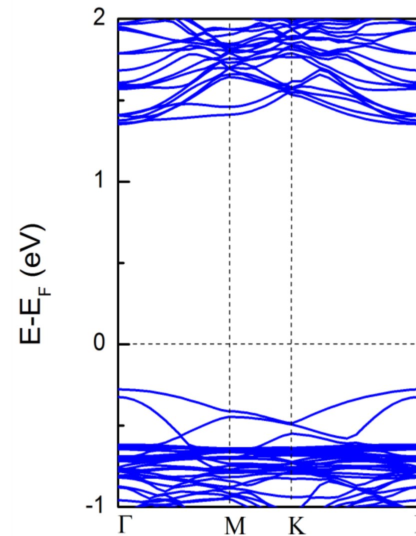
SV-3H, $E_{for}$=0.97 eV

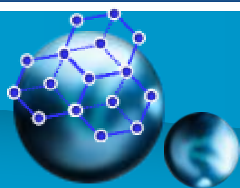


DV-4H, $E_{for}$=1.11 eV



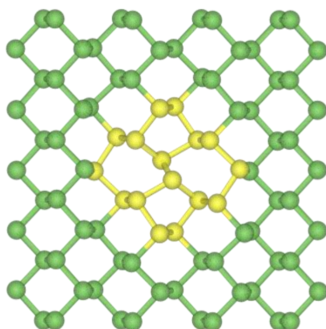


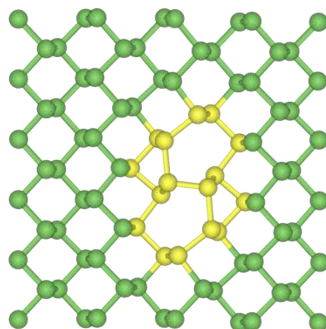


# Structural & Energetic properties of defective puckered arsenene

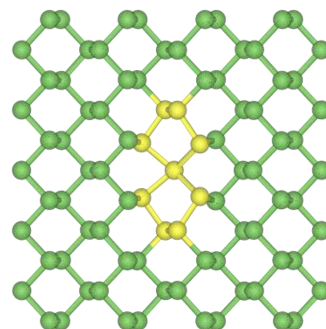
SW-1, Efor=0.68 eV



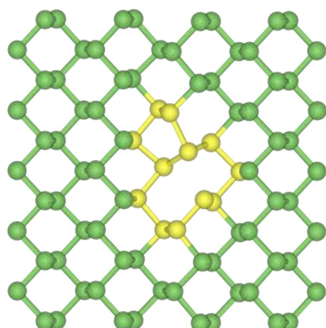
SW-2, Efor=1.18 eV



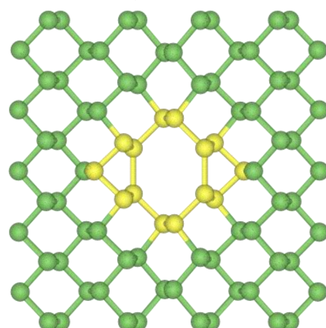
SV-55-66, Efor=1.46 eV



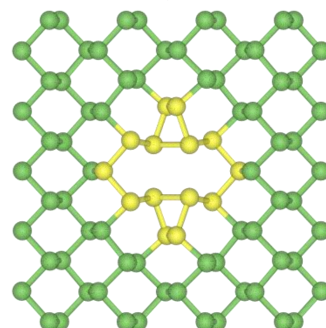
SV-59, Efor=1.24 eV



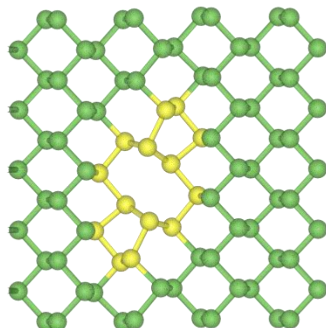
DV-585-1, Efor=2.42 eV



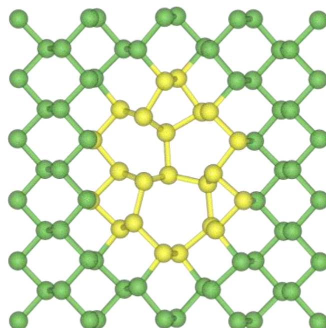
DV-4-10-4, Efor=1.24 eV

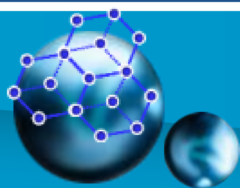


DV-585-2, Efor=1.01 eV

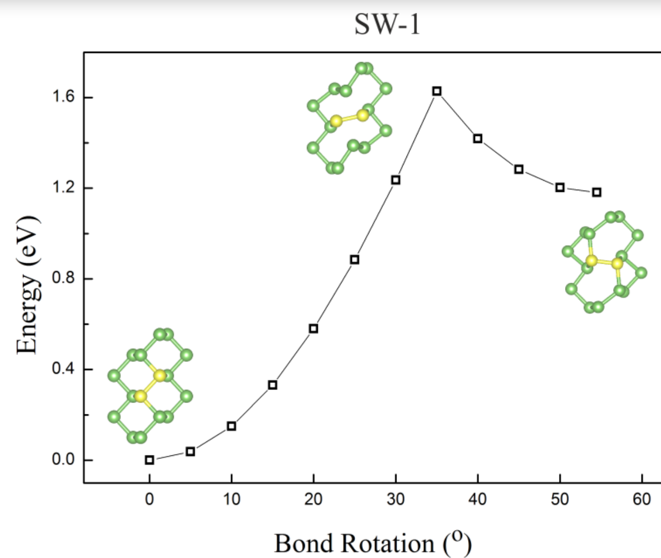


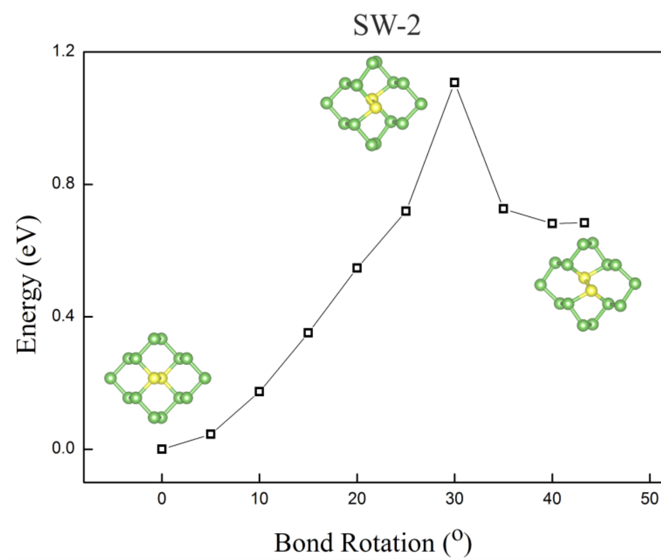
DV-555-777, Efor=1.90 eV

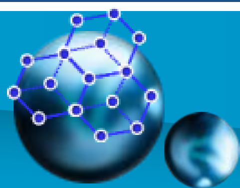




# Energetics of SW defects creation in puckered arsenene





# Electronic properties of defective puckered arsenene

Pristine | SW-1 | SW-2

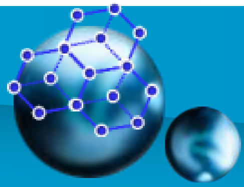
SV-55-66 | SV-59 | DV-585-1

DV-4104 | DV-585-2 | DV-555-777

$E-E_F$ (eV)

$E_g$=0.78 eV

Γ X S Y Γ



# PART IV:
# Ab initio investigation of the AlN:Er system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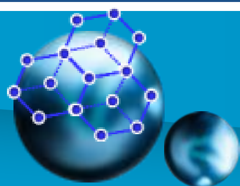
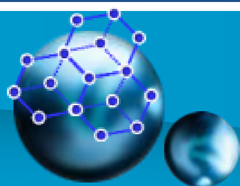
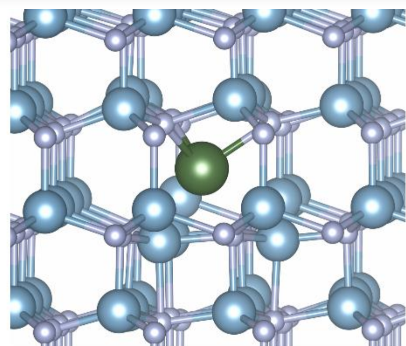


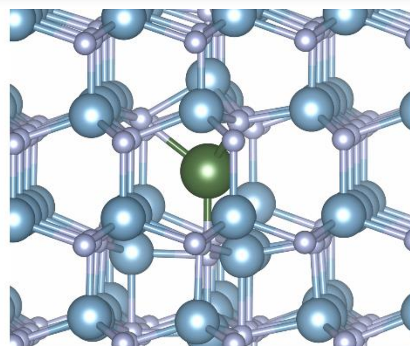
# DFT+U for RE nitrides

The spin-resolved bandstructures of (a)-(b) rocksalt ErN and (c)-(d) AlN:$Er_{Al}$ for $U_{eff}$=8.6 eV. The Fermi level is at 0 eV.

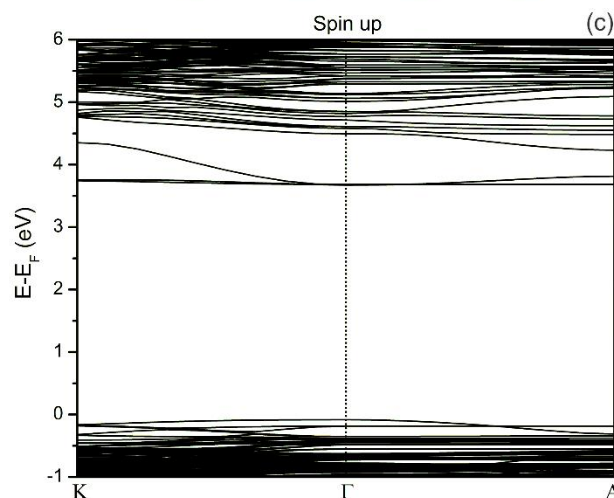
# Octahedral - Tetrahedral

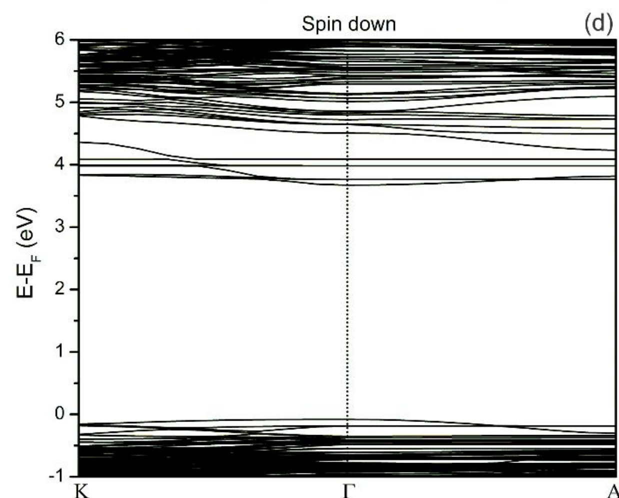




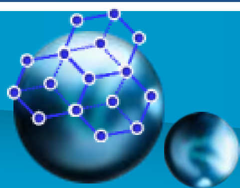




| Charge state | $Er_{i,O}$ | $Er_{i,T}$ |
|---|---|---|
| **0** | 11.92 | 14.14 |
| **+1** | 8.31 | 10.22 |
| **+2** | 4.33 | 6.77 |
| **+3** | 0.62 | 3.86 |

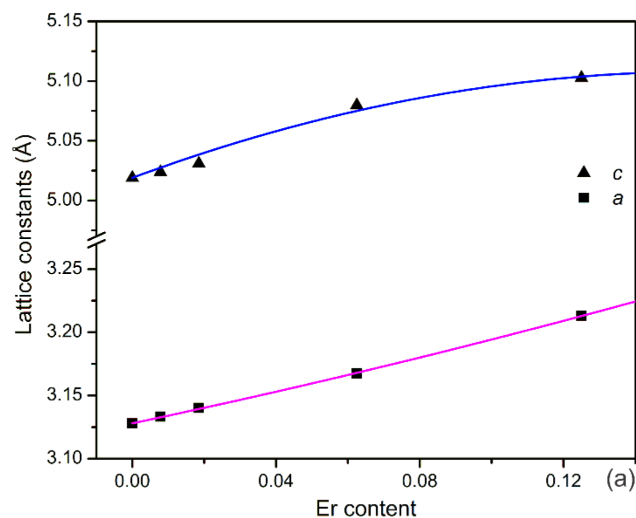


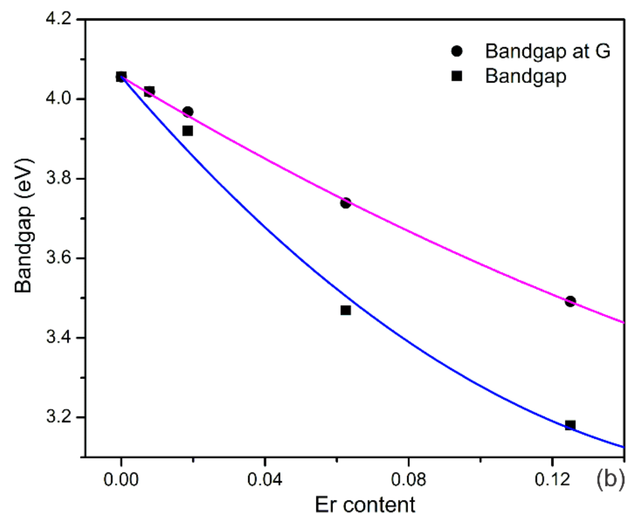



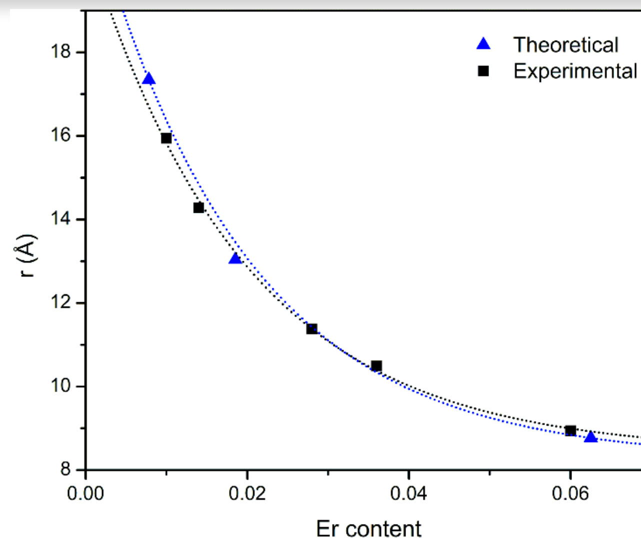

The (a) $Er_{i,O}$ and (b) $Er_{i,T}$ localizations in the AlN wurtzite structure after the relaxations for a +3 charge state. Small silver spheres represent N atoms, big blue spheres Al atoms, and the biggest green spheres correspond to Er atoms. (c) and (d) The spin-resolved bandstructure of AlN:$Er_{i,O}$. The defect charge is +3.



# Structural analysis

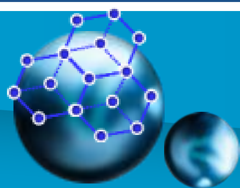


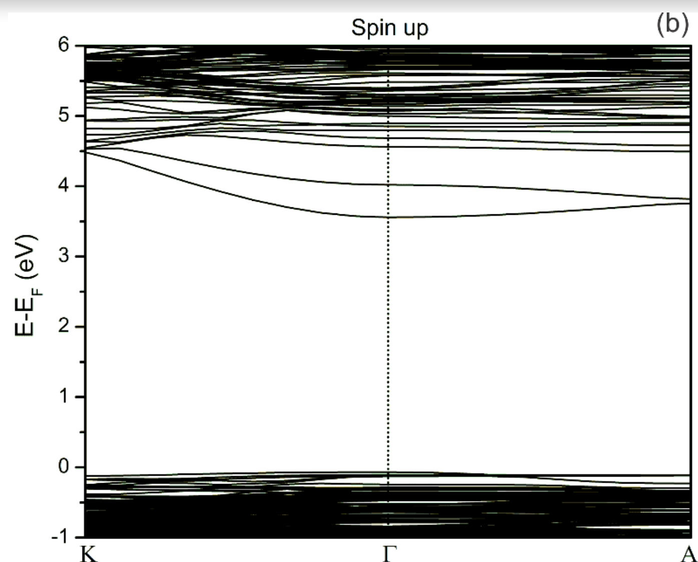



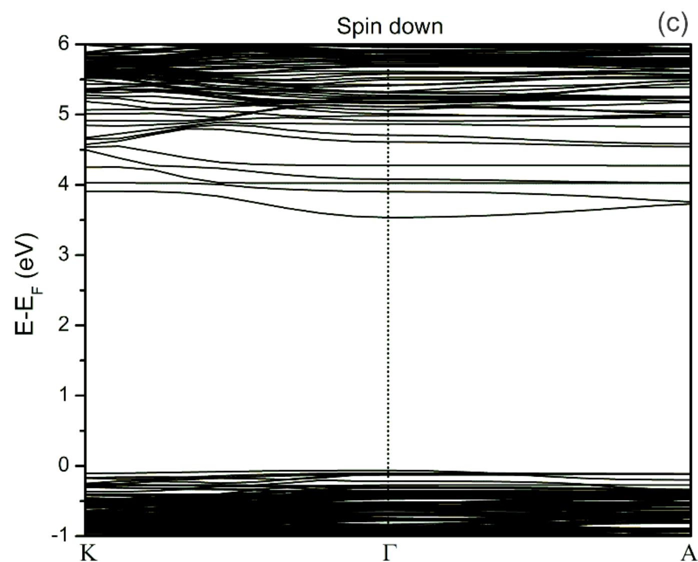

The average distance *r* between two Er atoms calculated using experimental and theoretical results as a function of the Er content. The corresponding dotted curves are exponential decay fits on the two sets of data.

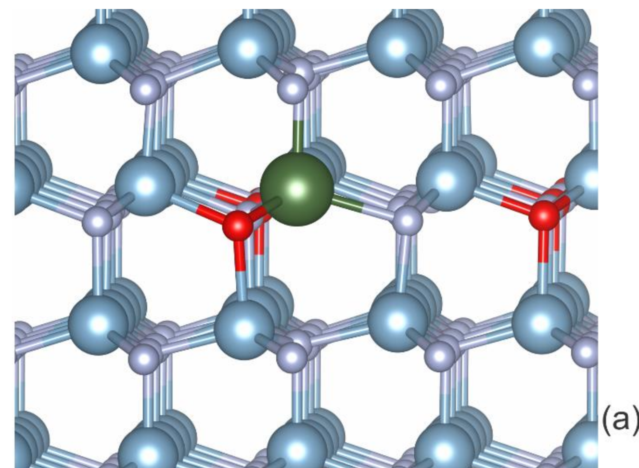
(a) The *a* (rectangles) and *c* (triangles) lattice constants of the $Er_xAl_{1-x}N$ alloys as a function of the Er content and (b) the bandgaps of the $Er_xAl_{1-x}N$ alloys as a function of the Er content. The blue and magenta curves are a second order polynomial fit according to the quadratic Vegard's law.



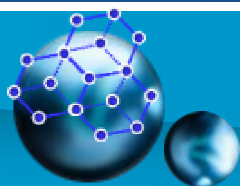
# $Er_xAl_{1-x}N_yO_{1-y}$




(a) The preferable configuration for $Er_{0.01}Al_{0.99}N_{0.94}O_{0.06}$. Small silver spheres represent N atoms, small red spheres O atoms, big blue spheres Al atoms, and the biggest green spheres correspond to Er atoms. (b)-(c) the corresponding spin-resolved bandstructures. A charge of +1 per O atom is considered.



# Collaborators

## PART I: The influence of edge and screw dislocations of wurtzite GaN on the thermal conductivity

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## PART II: GaN nanoclusters formation in amorphous $SiO_2$ matrix

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## PART Iii: Defects in novel 2D materials-ARSENENE

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## PART IV: Ab initio investigation of the AlN:Er system

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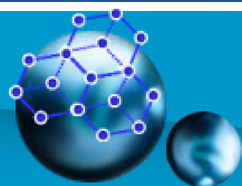

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*Thank you for your attention*