# The physics of blue lasers, solar cells, and stop lights

**Paul Kent**

University of Cincinnati & ORNL

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Solid State Theory Group

National Renewable Energy Laboratory

Thanks to: **Alex Zunger & SST Group/Basic Sciences**

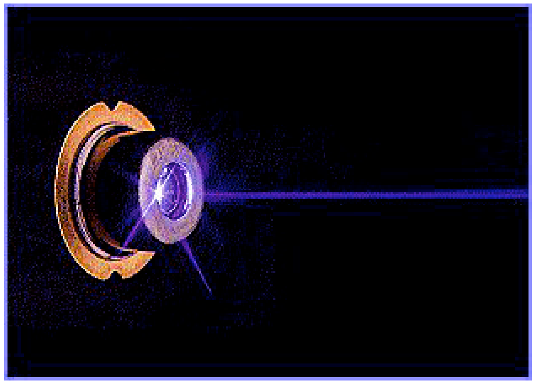
U.S. Department of Energy
Office of Science
Basic Energy Sciences
Division of Materials Sciences

# Outline

**1.** Introduction

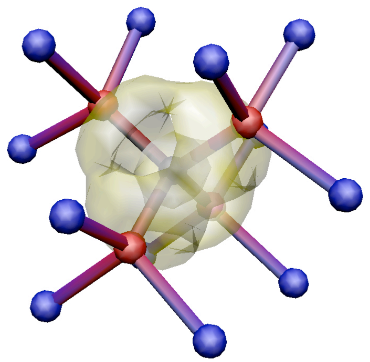
*Nitride semiconductors*

*Novel phenomena. Localized states*



**2.** How can we model these systems?

*Computational techniques*



**3.** New photovoltaic materials

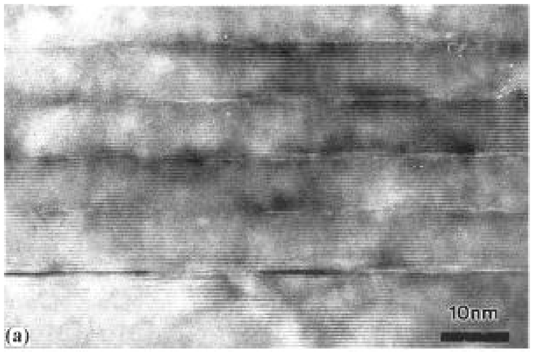
*GaAsN (and GaPN)*

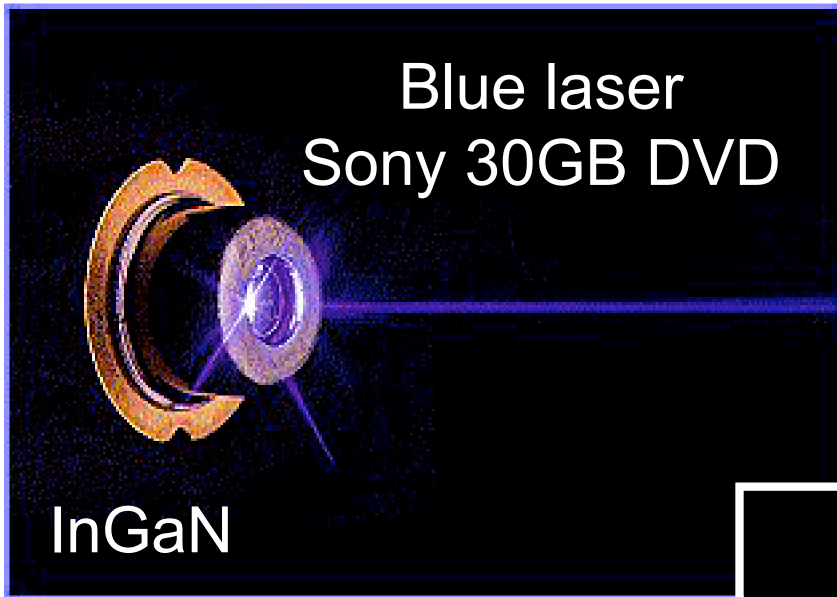
*Band gap reduction. Localized states*

**4.** Blue emitters

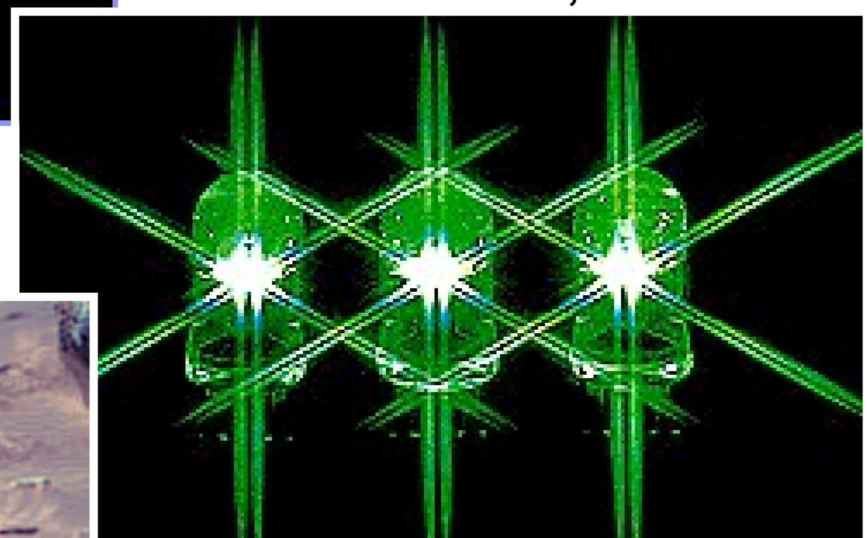
*InGaN*

*Localization at In inhomogeneities*



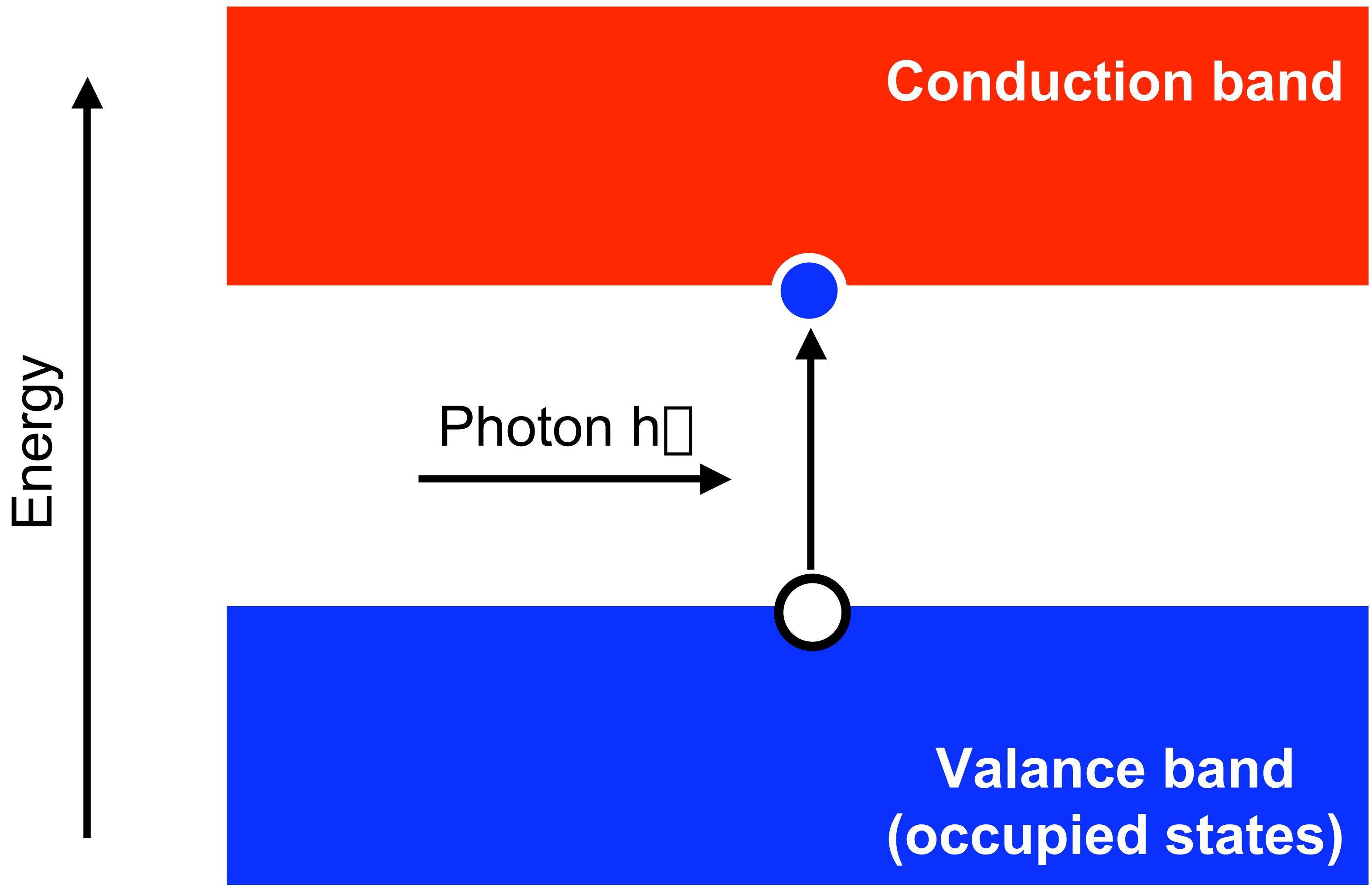



High brightness LEDs
Traffic signals. Solid state lighting?
InGaN, AlGaN…




High efficiency photovoltaics?
GaAsN

# Absorption in semiconductors



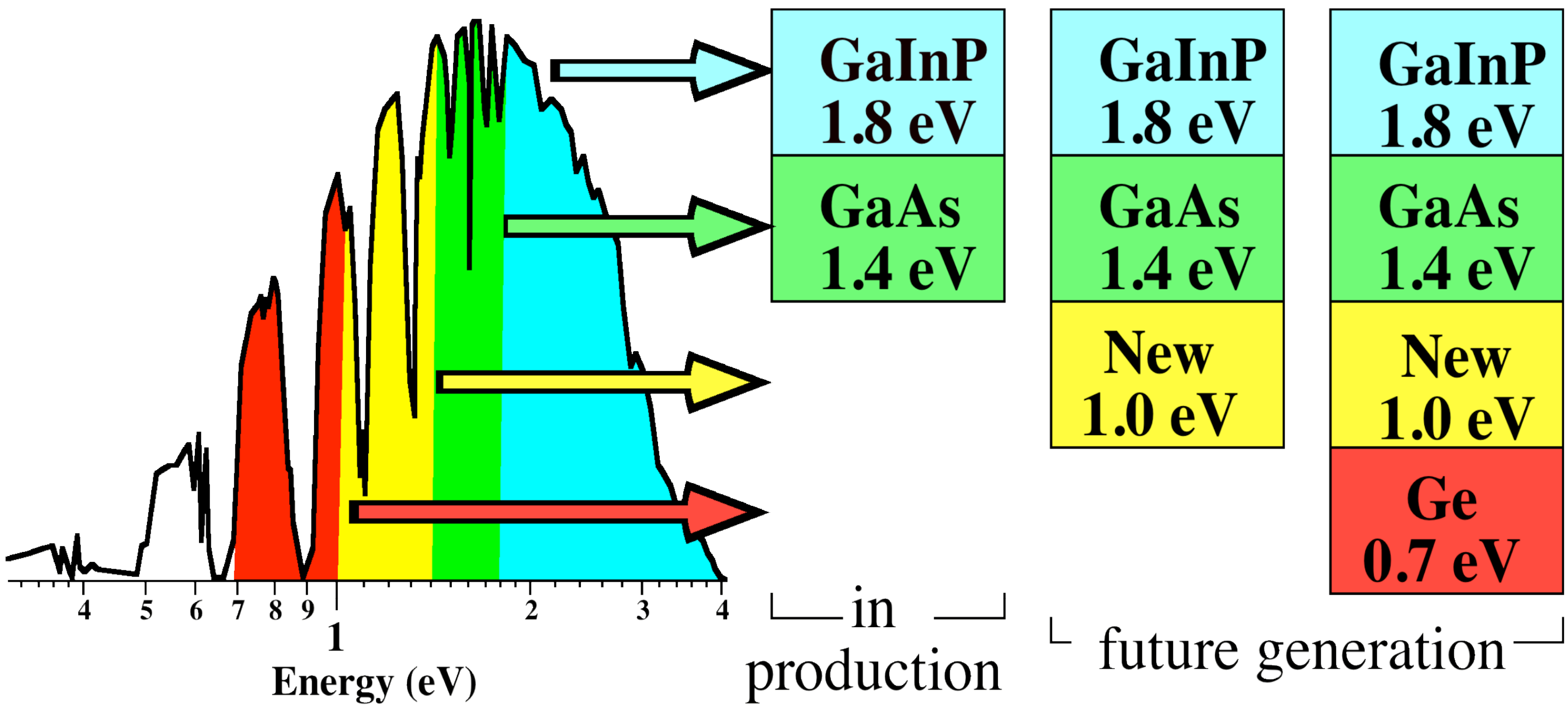
# High Efficiency Multijunction Solar Cells

- Want 1 eV material lattice-matched to GaAs

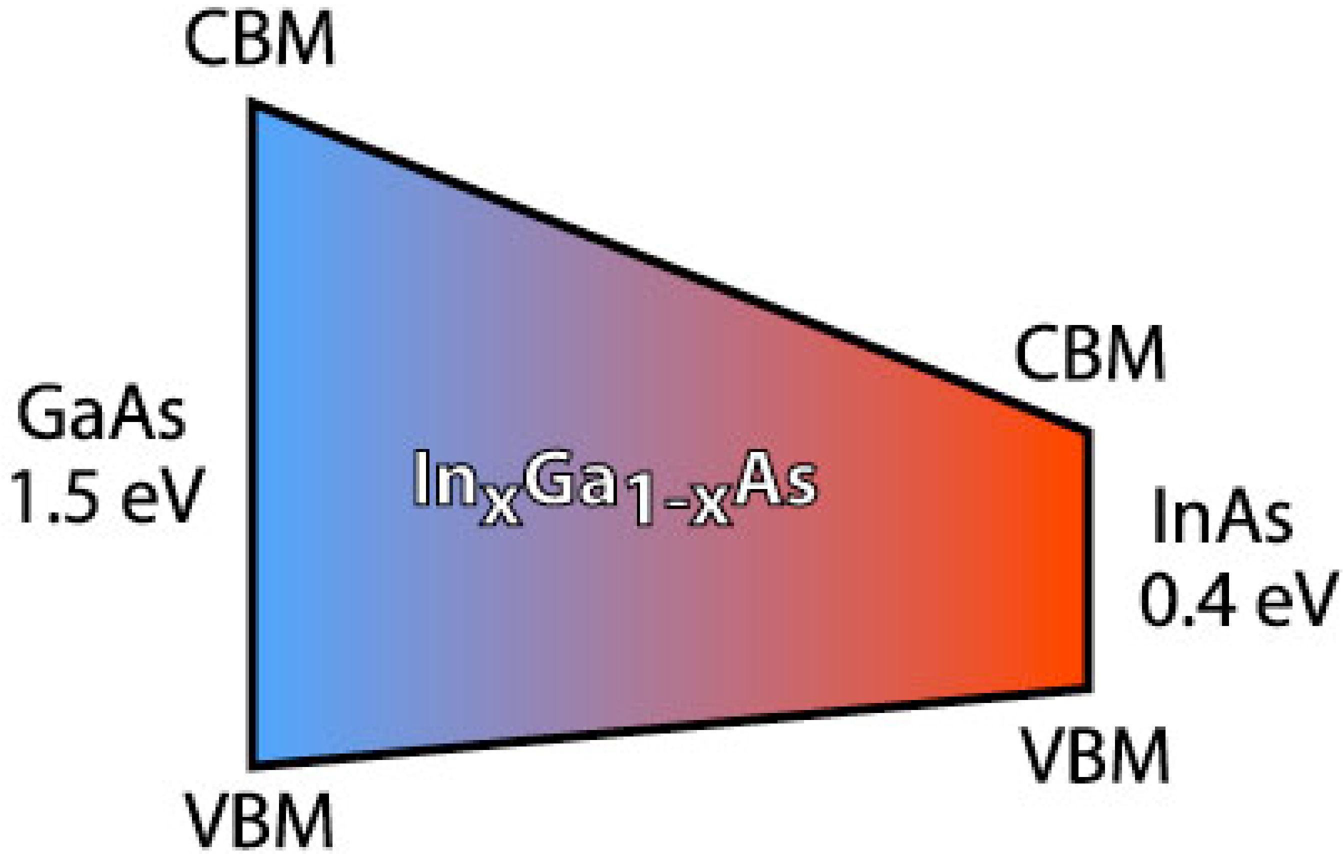
□ Try GaInNAs

Calculated efficiencies (ideal)

| | | | |
|---|---|---|---|
| 500X AM1.5D: | 36% | 47% | 52% |
| one sun AM0: | 31% | 38% | 41% |

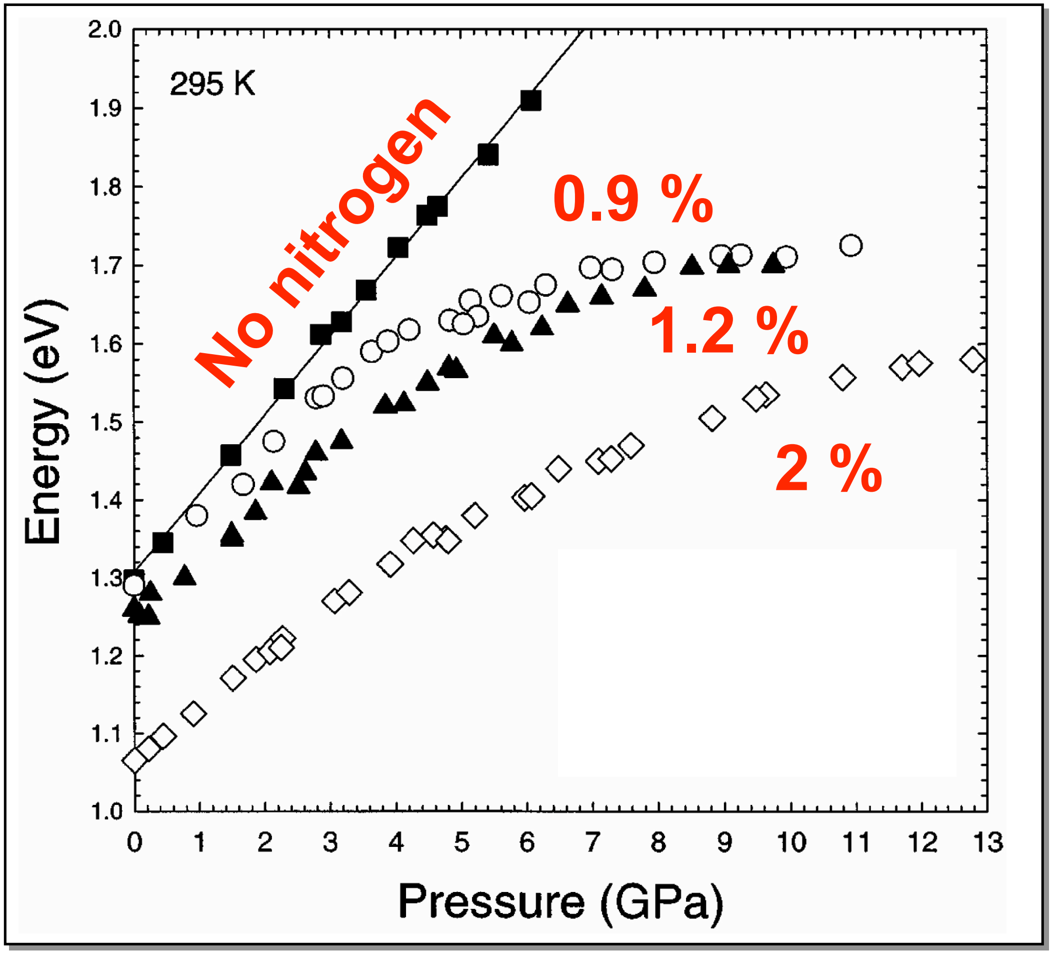


# Isostructural semiconductor alloying




**Properties approx. a linear combination of the components**

# Anomaly #1: Band gap reduction in GaAsN

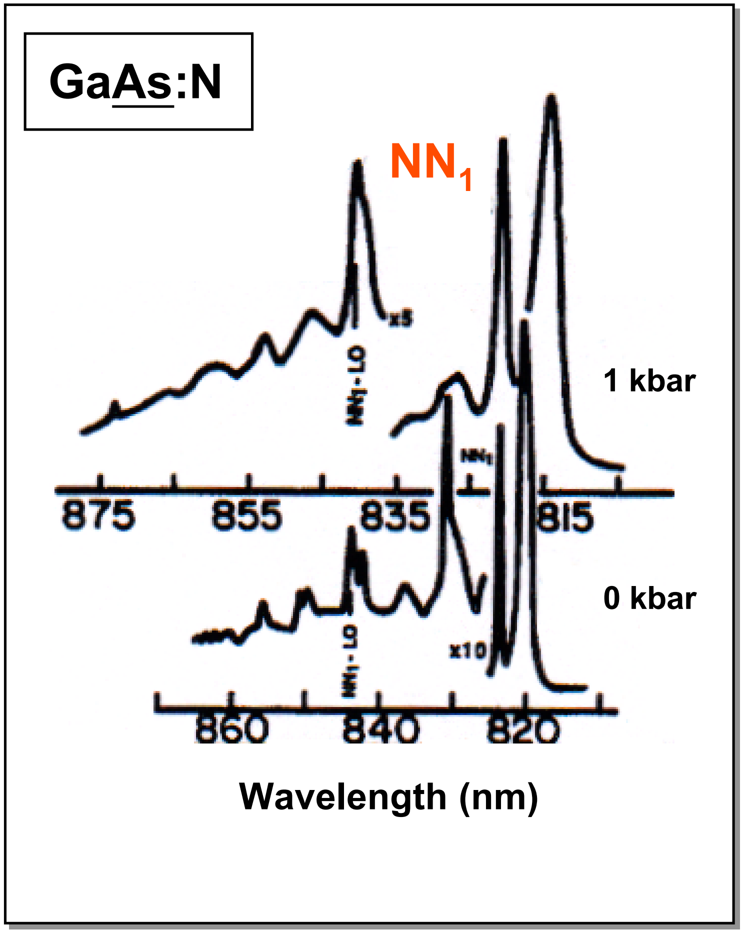



Band gaps
GaAs ~1.5 eV
GaN ~3.5 eV

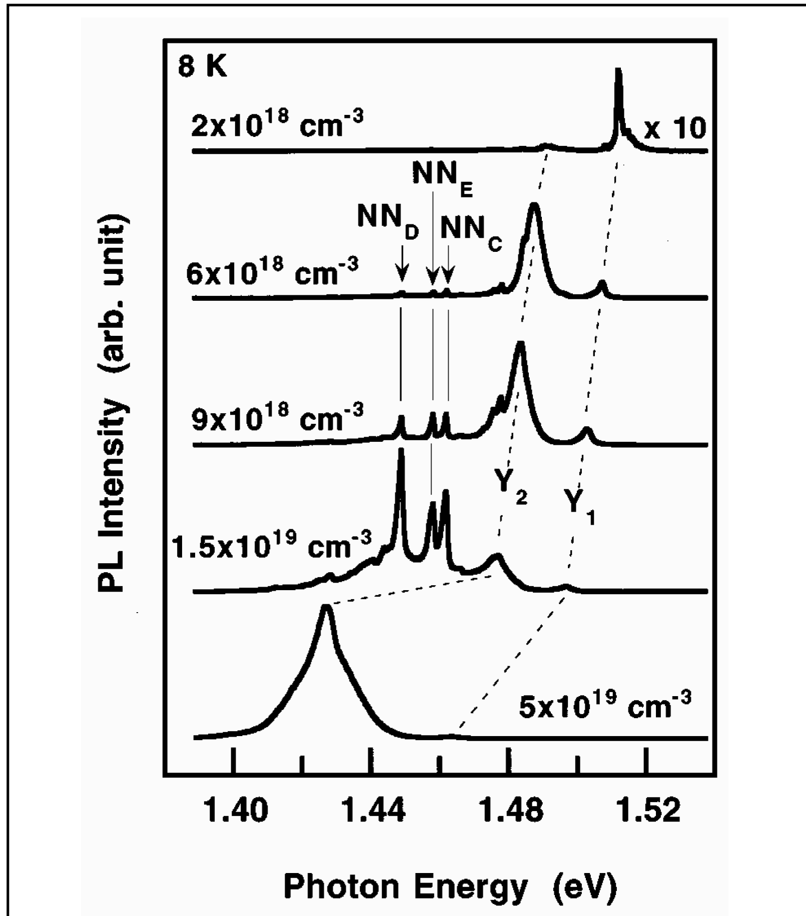
Shan *et al.* Phys. Rev. Lett. **82** 1221 (1999)

**Band gap reduced by ~120meV per % nitrogen!**

# Anomaly #2: Dilute Nitrogen in GaAs




Liu, Pistol and Samuelson. Appl. Phys. Lett. **56** 1451 (1990)




T. Makimoto *et al.* Appl. Phys. Lett. **70** 2984 (1997)

**Many sharp lines seen in emission!**

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**2.** How can we model these systems?

*Computational techniques*

**3.** New photovoltaic materials

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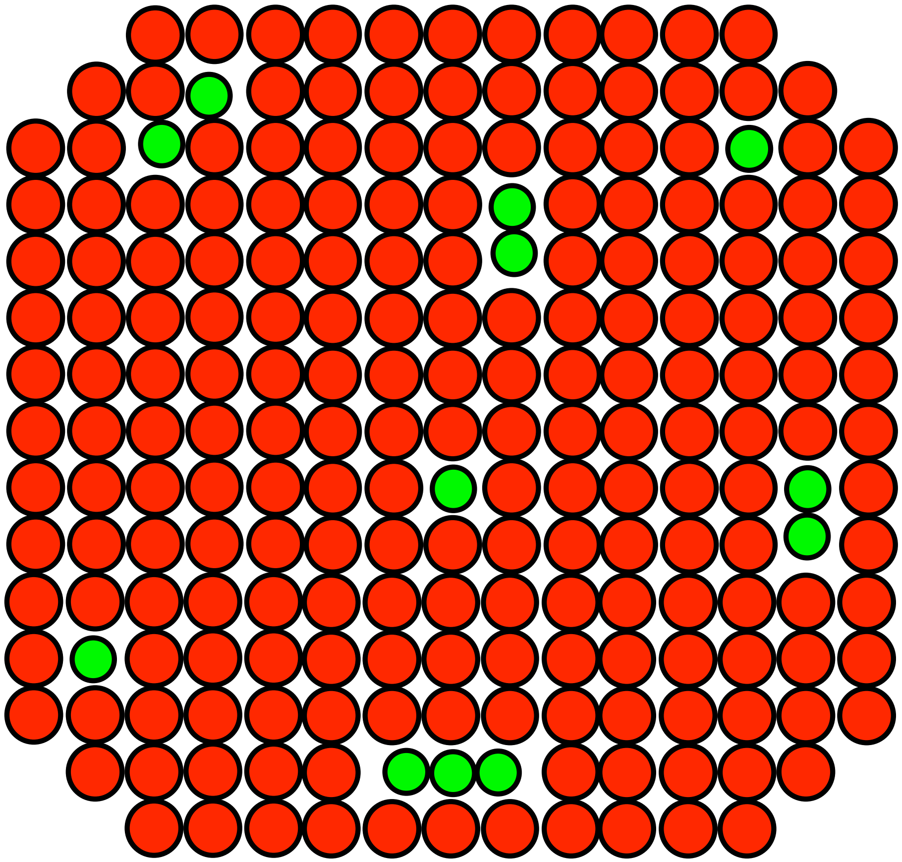
*InGaN*

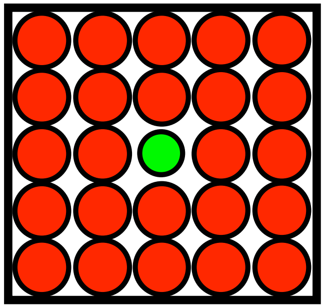
*Localization at In inhomogeneities*

# Simplified view of a semiconductor alloy



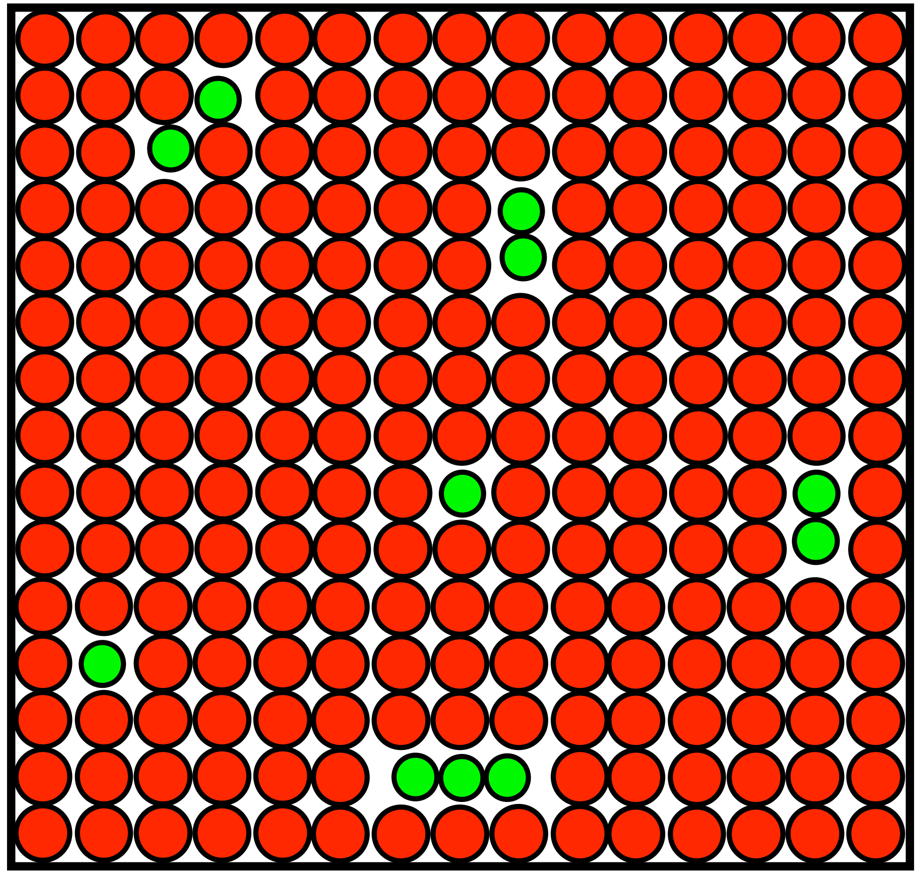
- Simulate regular lattices
- Distributions of atoms
- 10^3-10^6 atoms required
- Atomic relaxation important

# Computational Modeling of Alloys



Small Supercell Approach

Large Supercell Approach

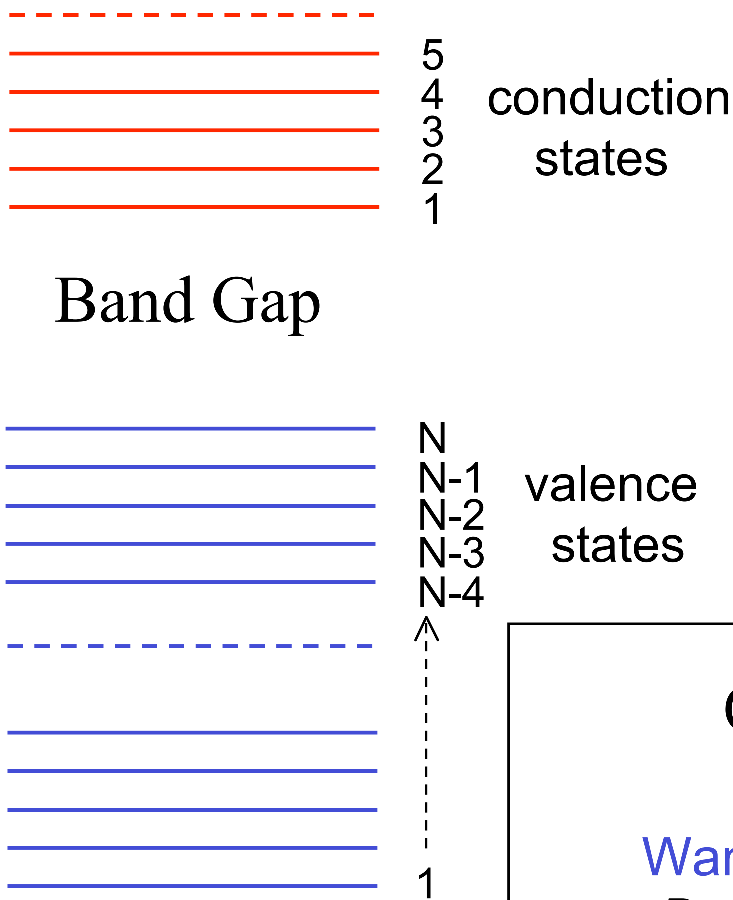


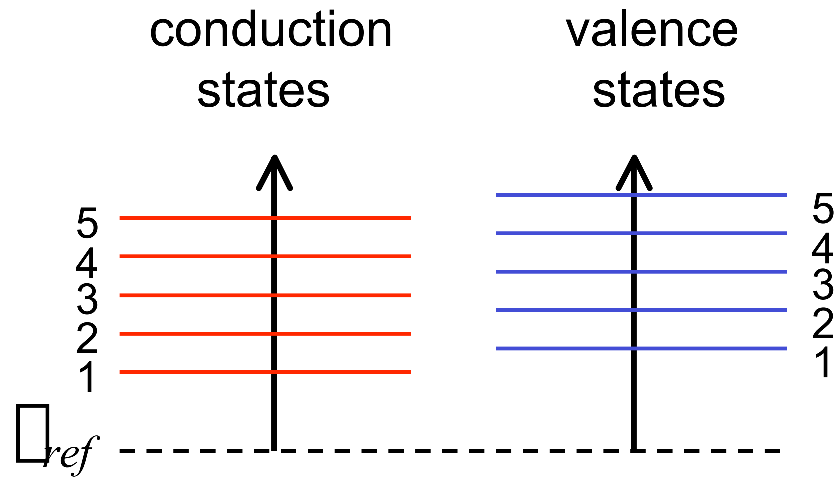
- Use large supercells (10^3-10^6 atoms) containing many nitrogens
- Statistically average properties of many random configurations
- Use Valence Force Field for structural relaxation
- Use Empirical Pseudopotential Method for wavefunctions

# Folded Spectrum Method (FSM)

$$\hat{H}\psi_i = \varepsilon\psi_i$$

$$(\hat{H} - \varepsilon_{ref})^2\psi_i = (\varepsilon - \varepsilon_{ref})^2\psi_i$$




"Fold" States

Only calculate "interesting" states around band gap

Wang & Zunger J. Chem. Phys. (1994)

*Recently: Jacobi-Javidson Tackett PRB (2002)*

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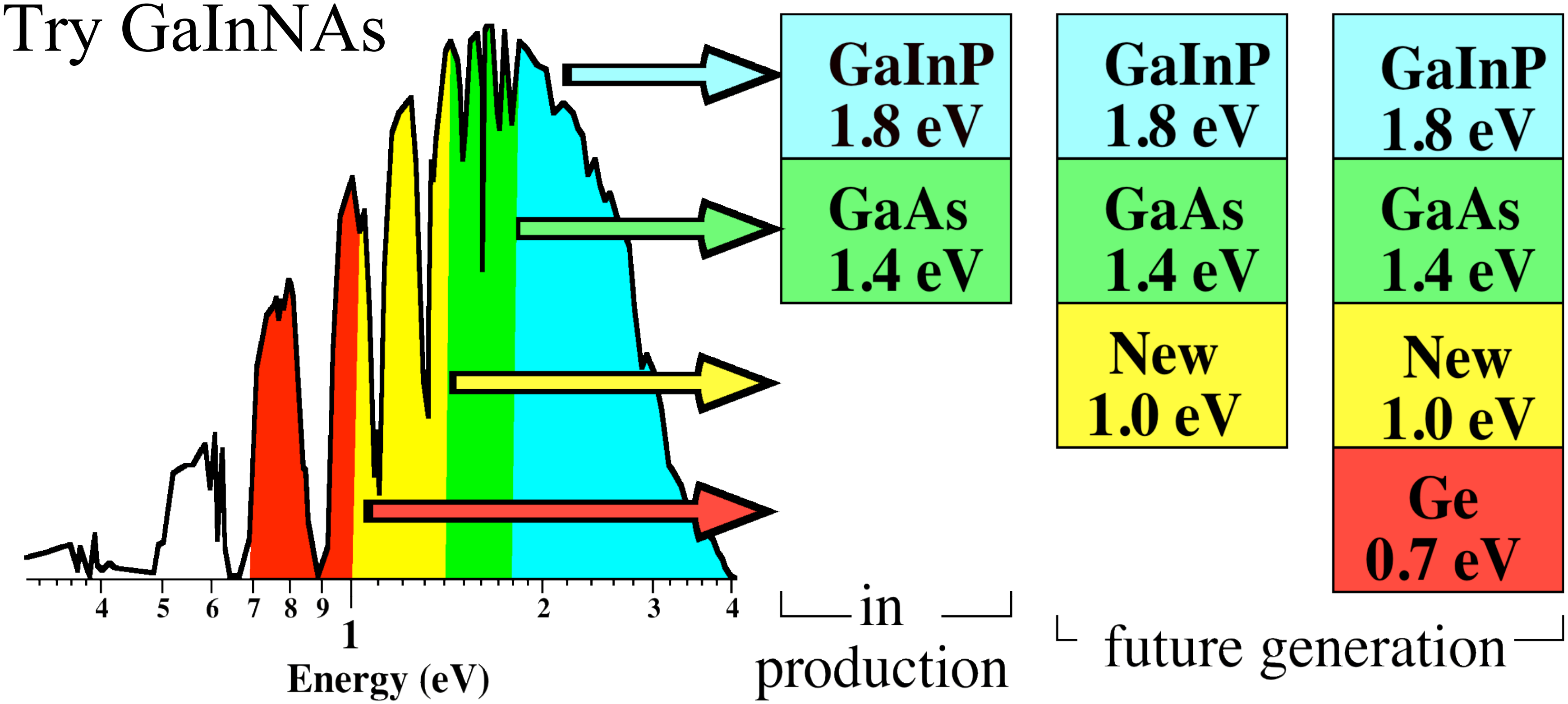


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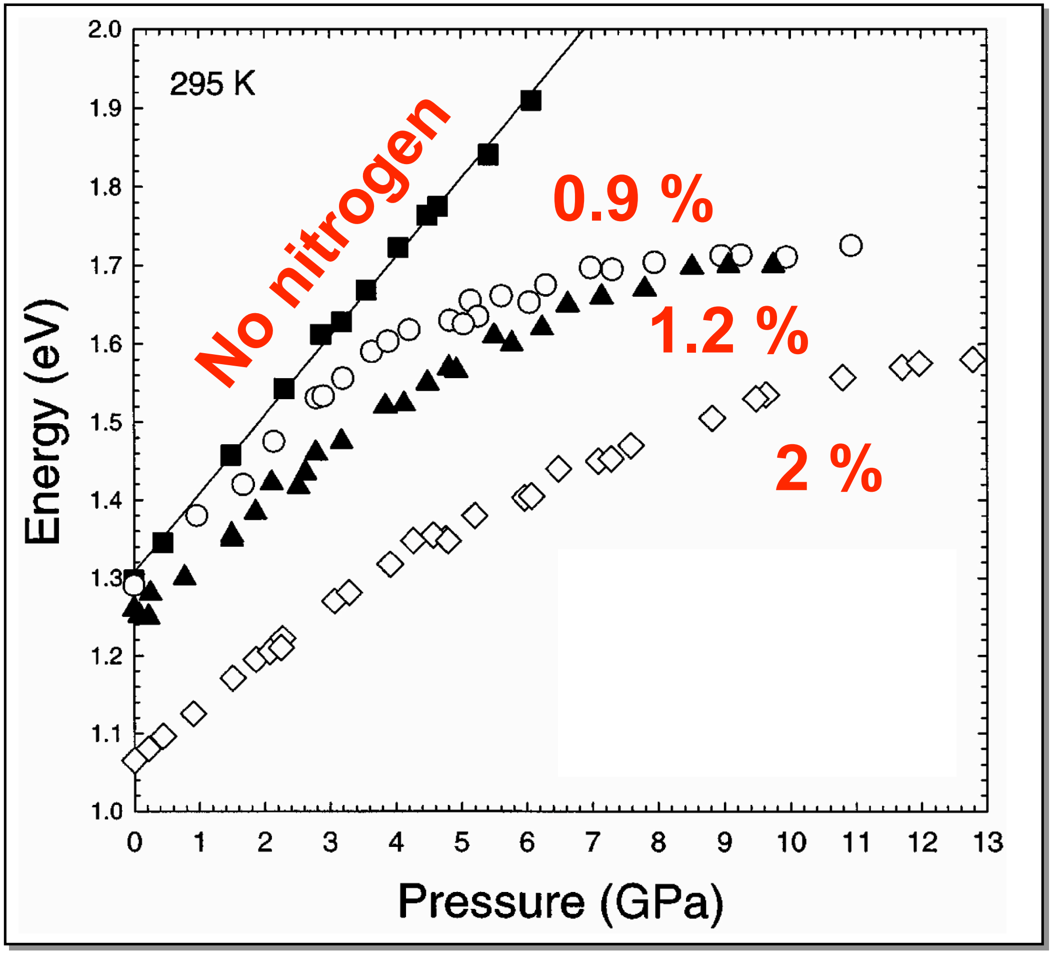
# Anomaly #1: Band gap reduction in GaAsN

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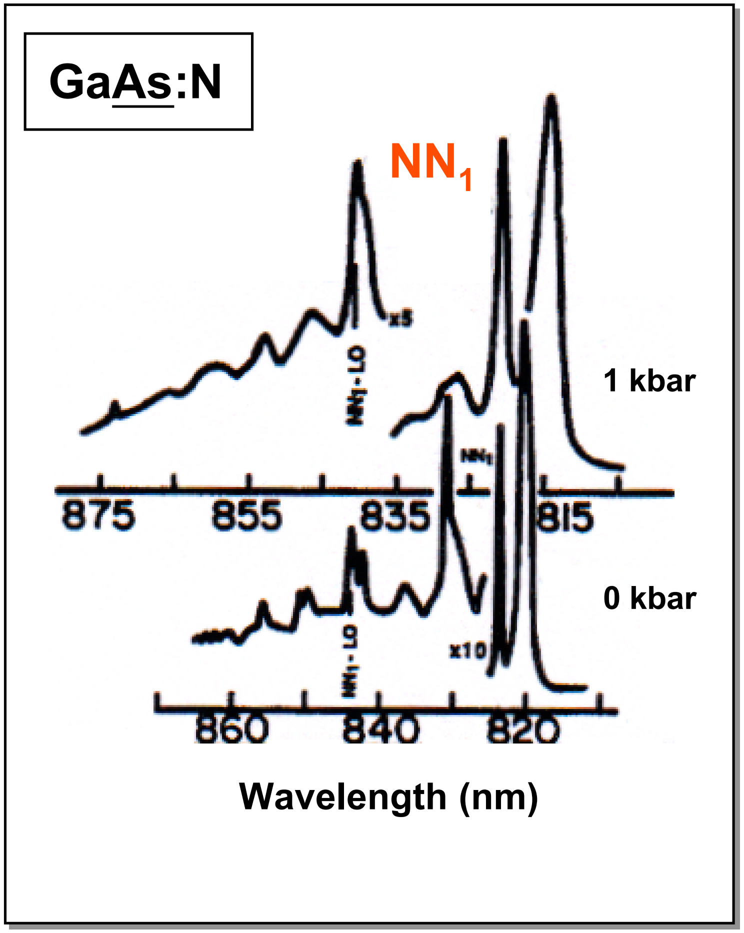


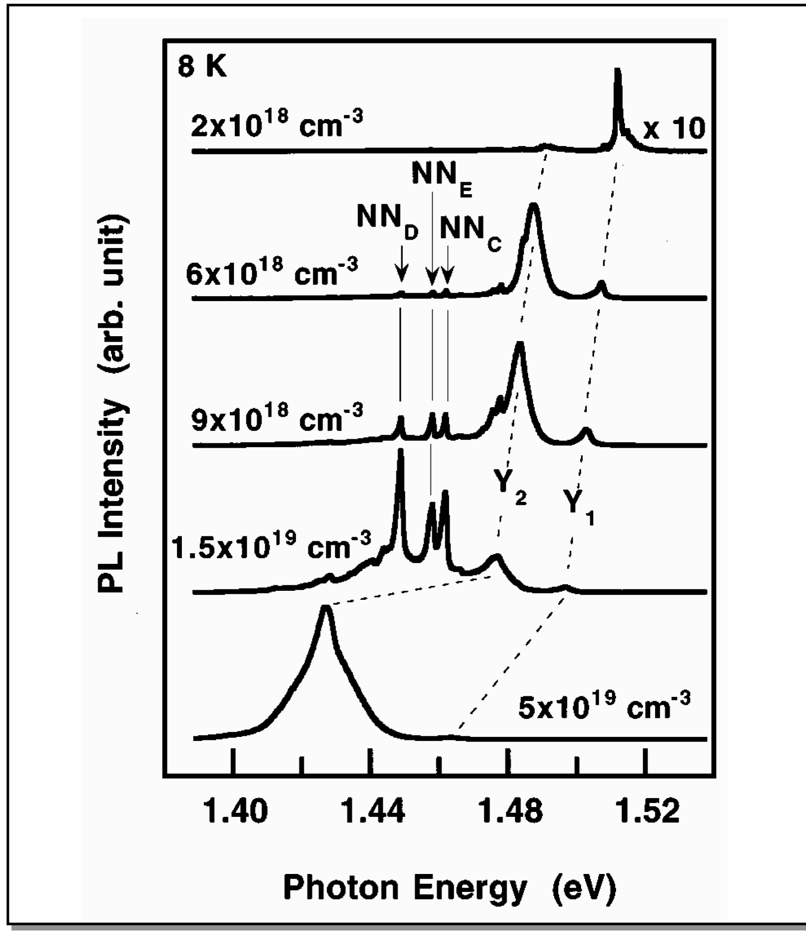


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**Many sharp lines seen in emission!**

# N in GaAs, GaP

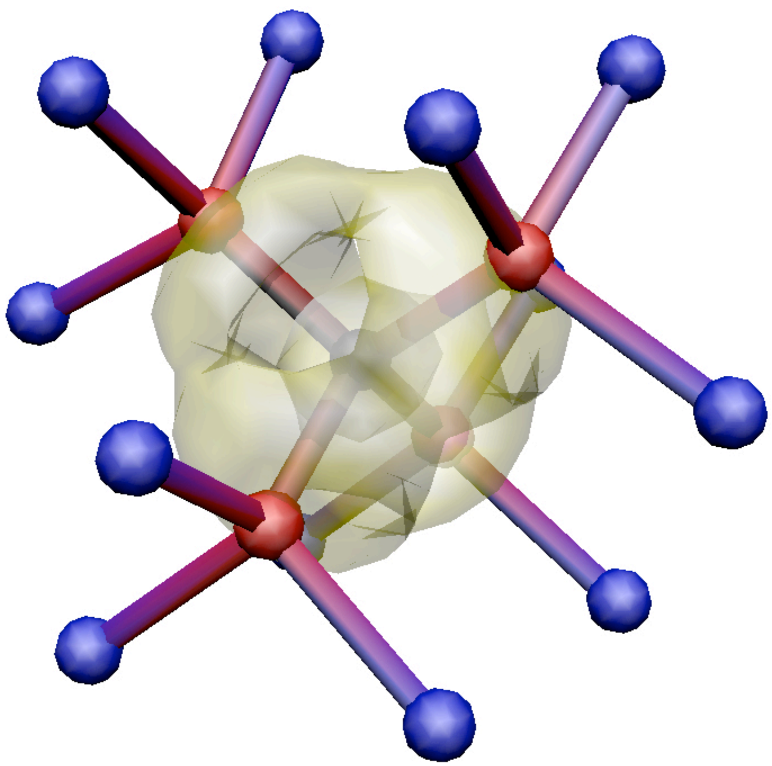
I will discuss three cases:

**1. Isolated Nitrogen**

2. Pairs and clusters

3. Well-developed alloys

# GaP:N



Nitrogen localized $a_1$(N)

In GaP:N (0.01%):

Level ~30 meV below CBM
Introduces  character

*Any concentration* of nitrogen in GaP creates "direct gap" character

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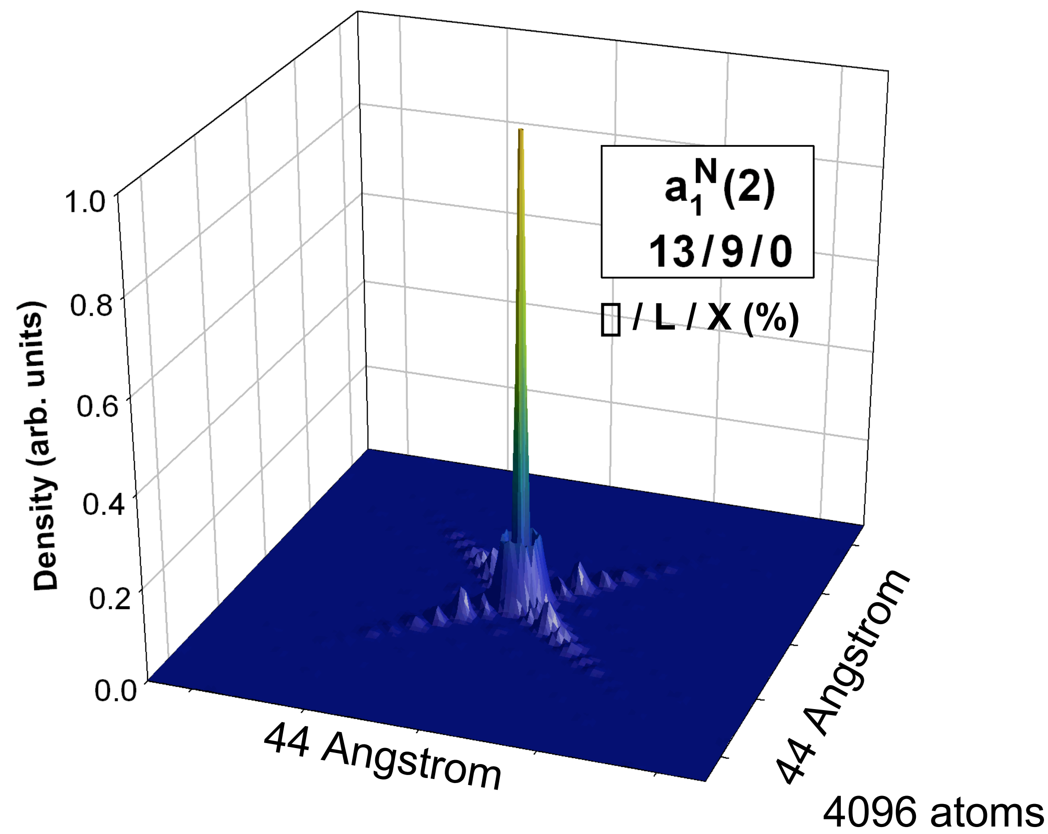
# Localized Level in GaAs:N




Nitrogen localized level ~ 150 meV inside conduction band

# N in GaAs, GaP

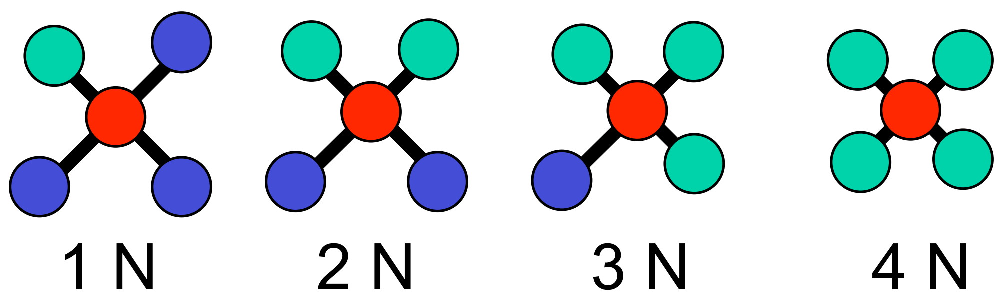
1. Isolated Nitrogen

**2. Pairs and clusters**

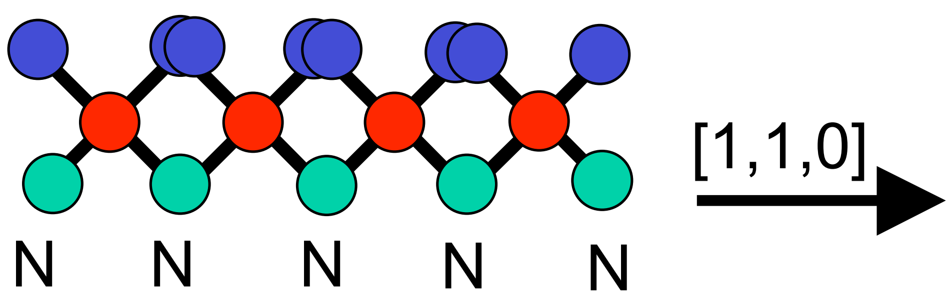
3. Well-developed alloys

# N Clusters in GaAs, GaP

1. $Ga(P_mN_{4-m})$ Clusters




2. [1,1,0]-Oriented Nitrogen Chains

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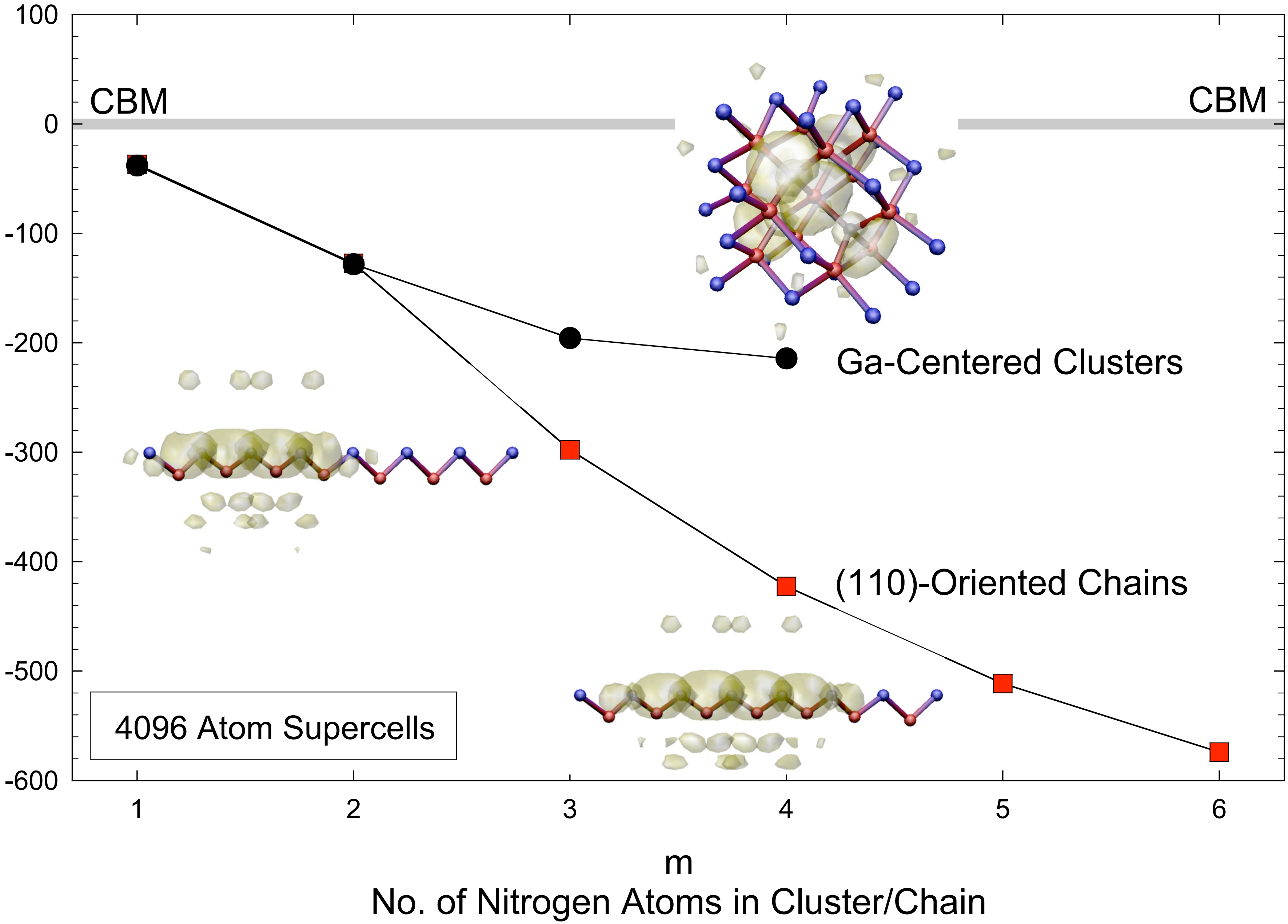
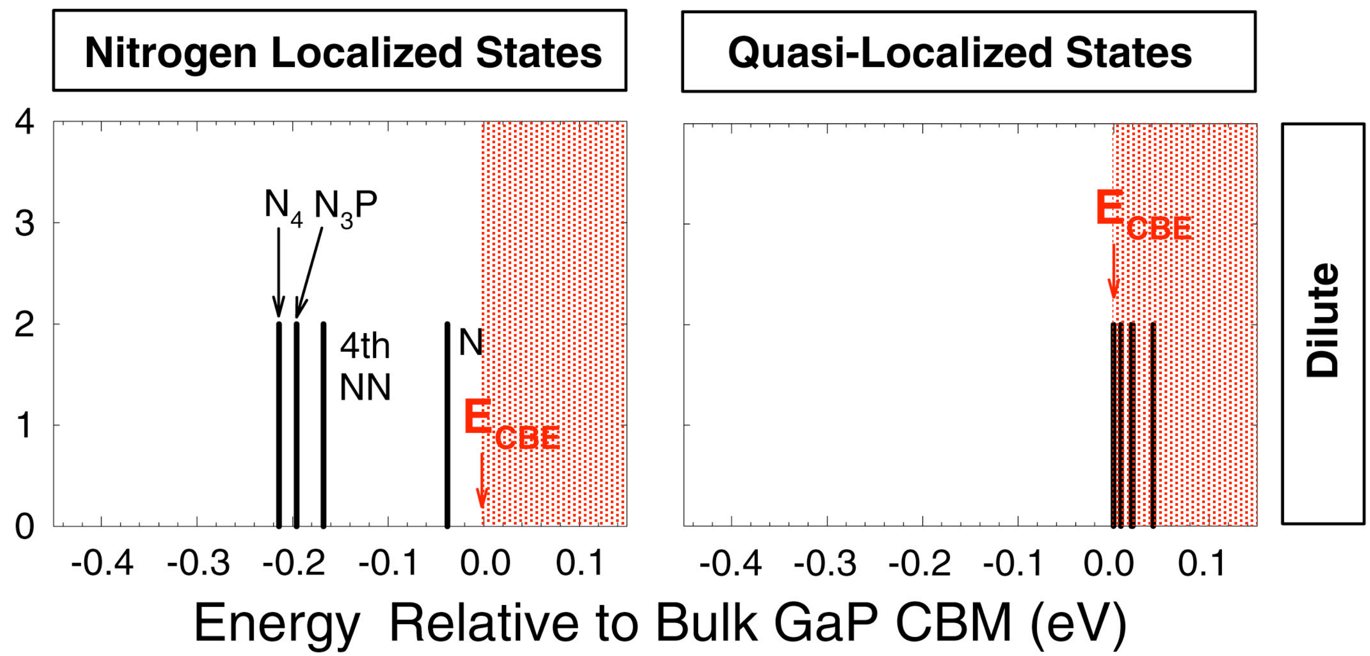
# Energy levels of Clusters and Chains in GaP

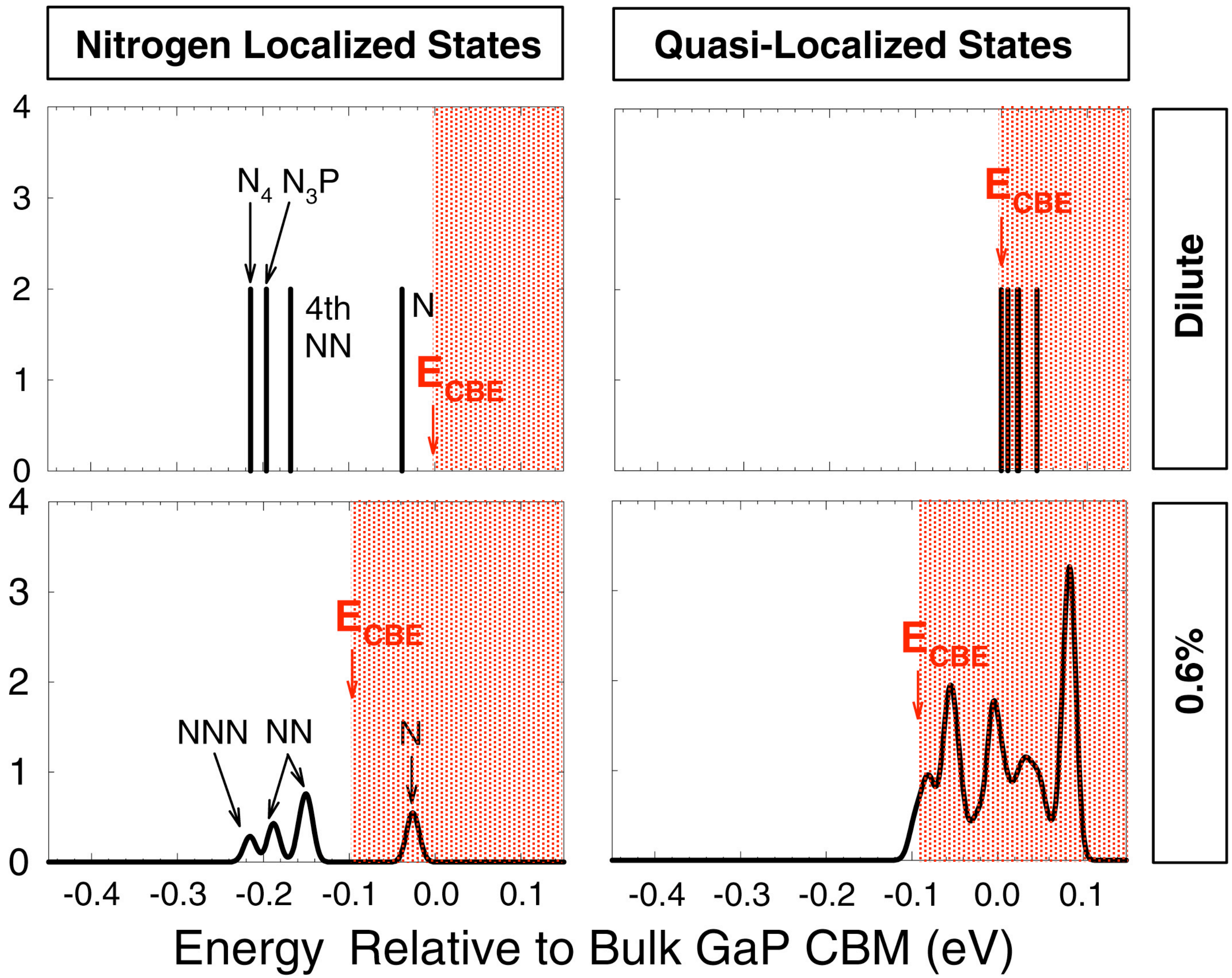


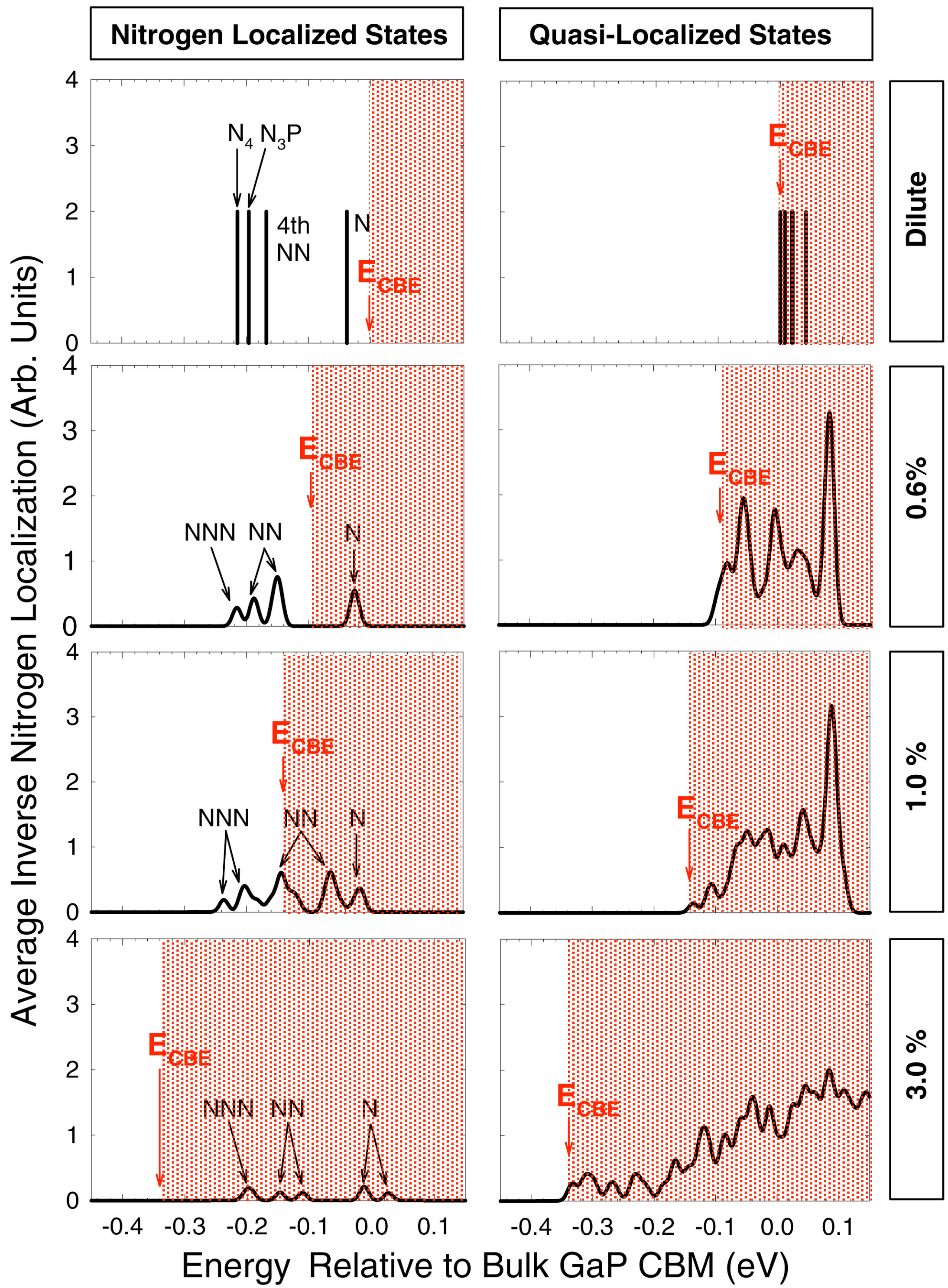
# N in GaAs, GaP

1. Isolated Nitrogen
2. Pairs and clusters
3. **Well-developed alloys**

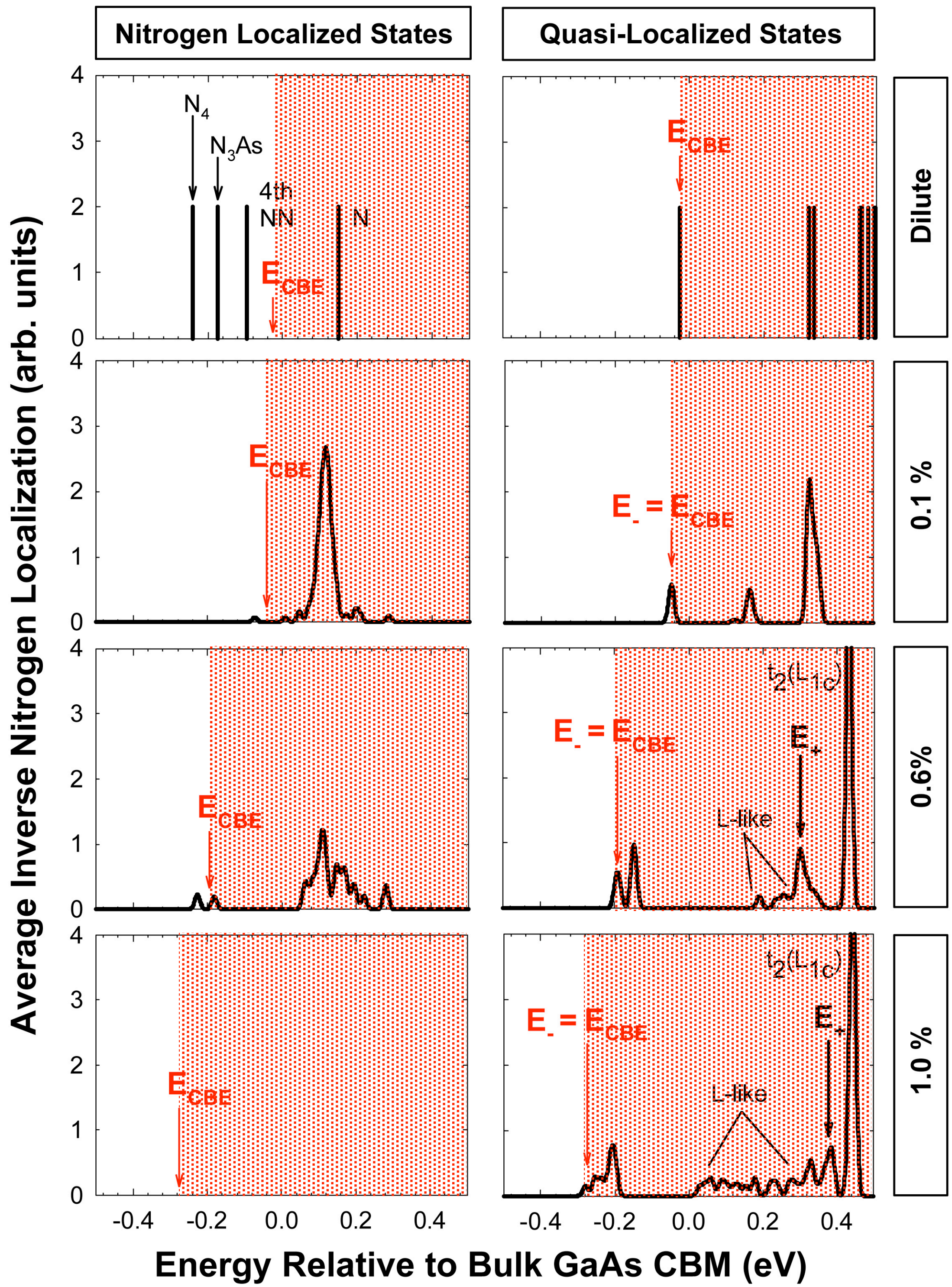



**$E_{CBE}$ = Delocalized Conduction Band Edge**

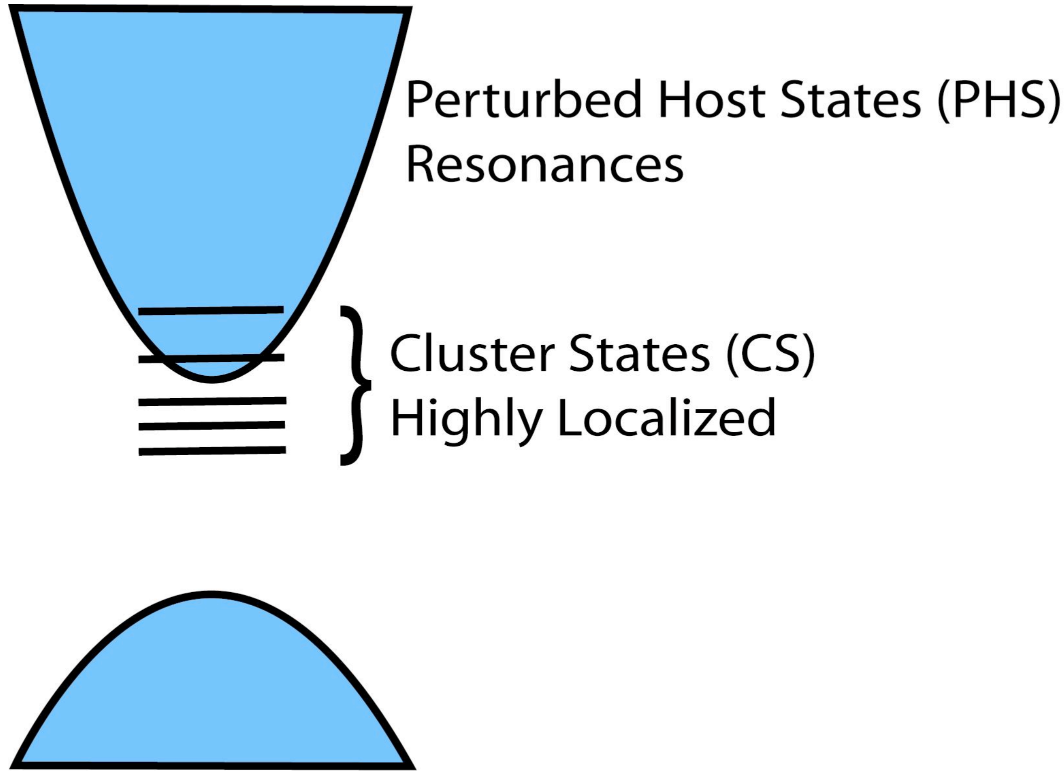

Nitrogen Localized States
Quasi-Localized States
N4 N3P
4th NN
N
ECBE
Dilute
0.6%
NNN NN
N
Energy Relative to Bulk GaP CBM (eV)



Nitrogen Localized States
Quasi-Localized States
Dilute
0.6%
1.0 %
3.0 %
N4 N3P
4th NN
N
NNN
NN
E CBE
Average Inverse Nitrogen Localization (Arb. Units)
Energy Relative to Bulk GaP CBM (eV)
-0.4 -0.3 -0.2 -0.1 0.0 0.1
0 1 2 3 4


Nitrogen Localized States
Quasi-Localized States
Dilute
0.1 %
0.6%
1.0 %
N4
N3As
4th NN
N
ECBE
E- = ECBE
t2(L1c)
E+
L-like
Average Inverse Nitrogen Localization (arb. units)
Energy Relative to Bulk GaAs CBM (eV)
-0.4
-0.2
0.0
0.2
0.4

# Two types of state observed



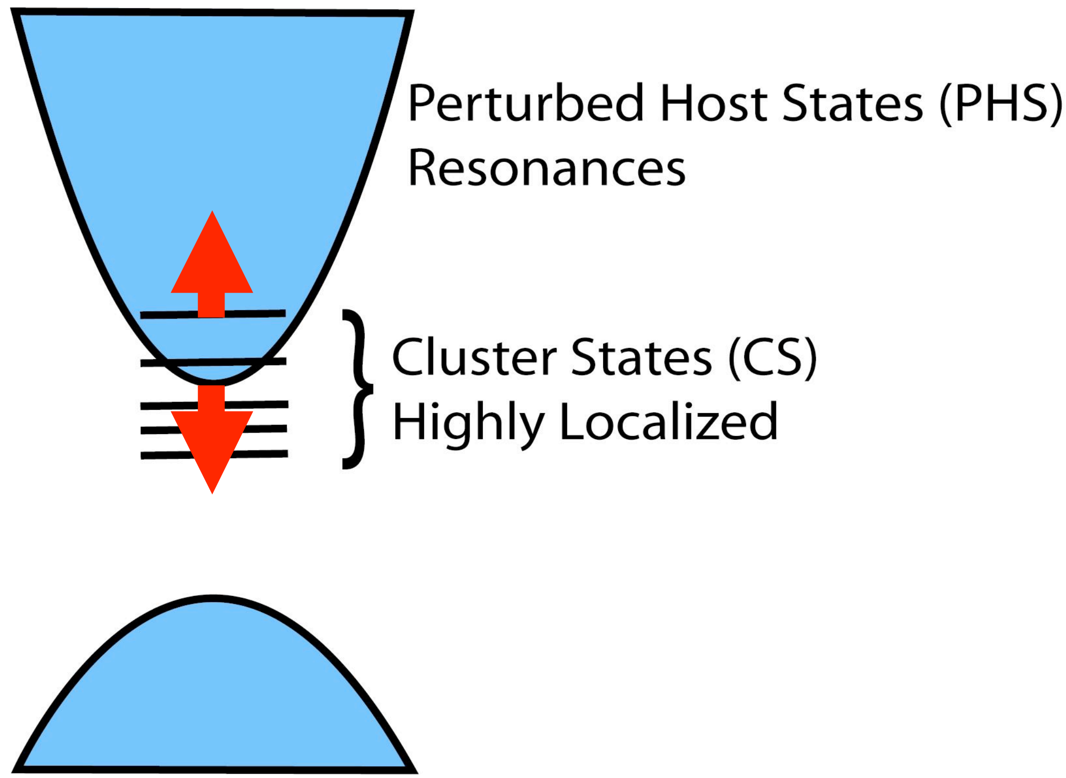

**Dilute Limit:** PHS in conduction band and pair/cluster CS in gap

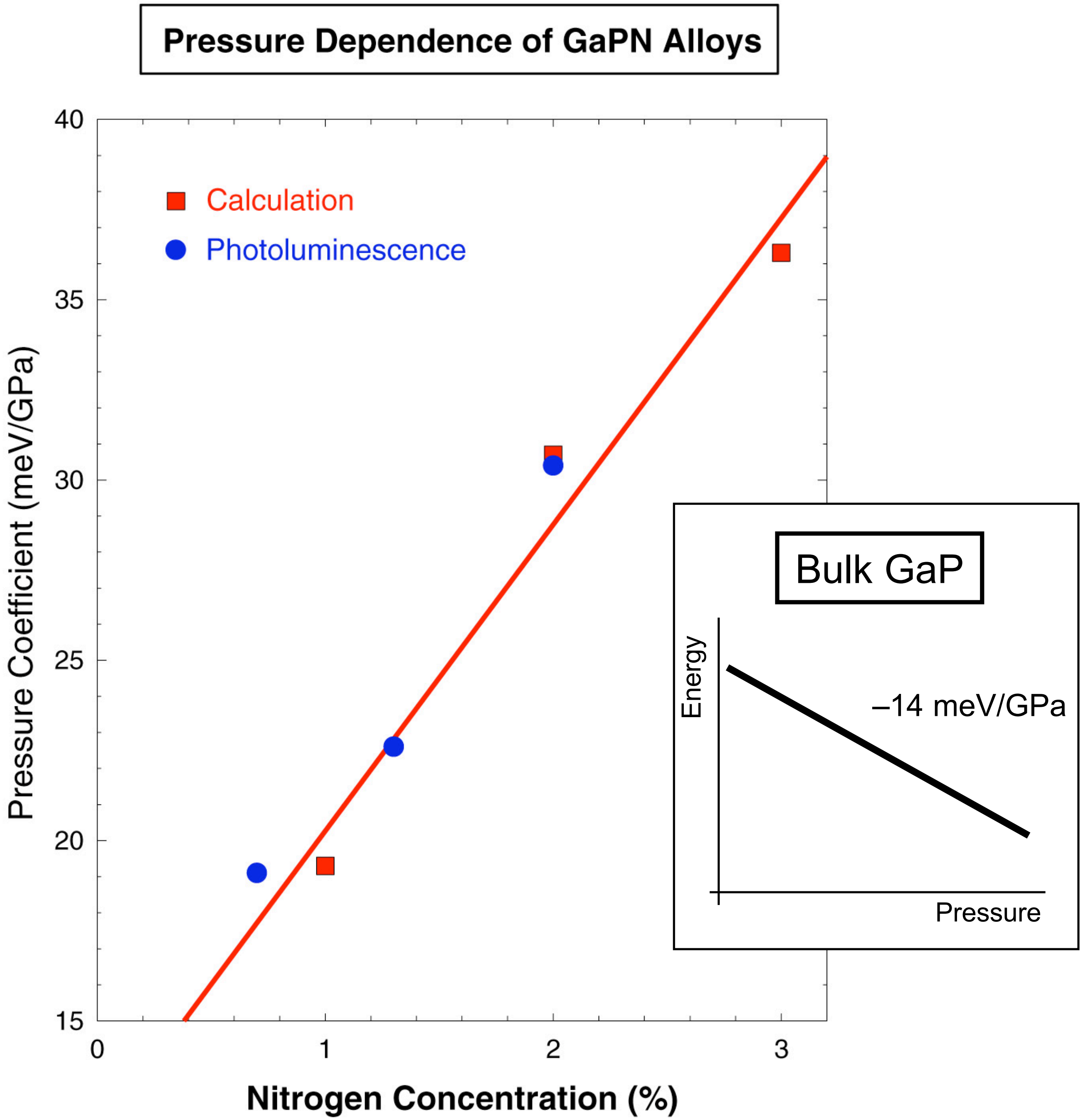
**Intermediate Range:** CS do not move
PHS plunge down in energy

**Amalgamation Point:** Lowest energy PHS just below CS

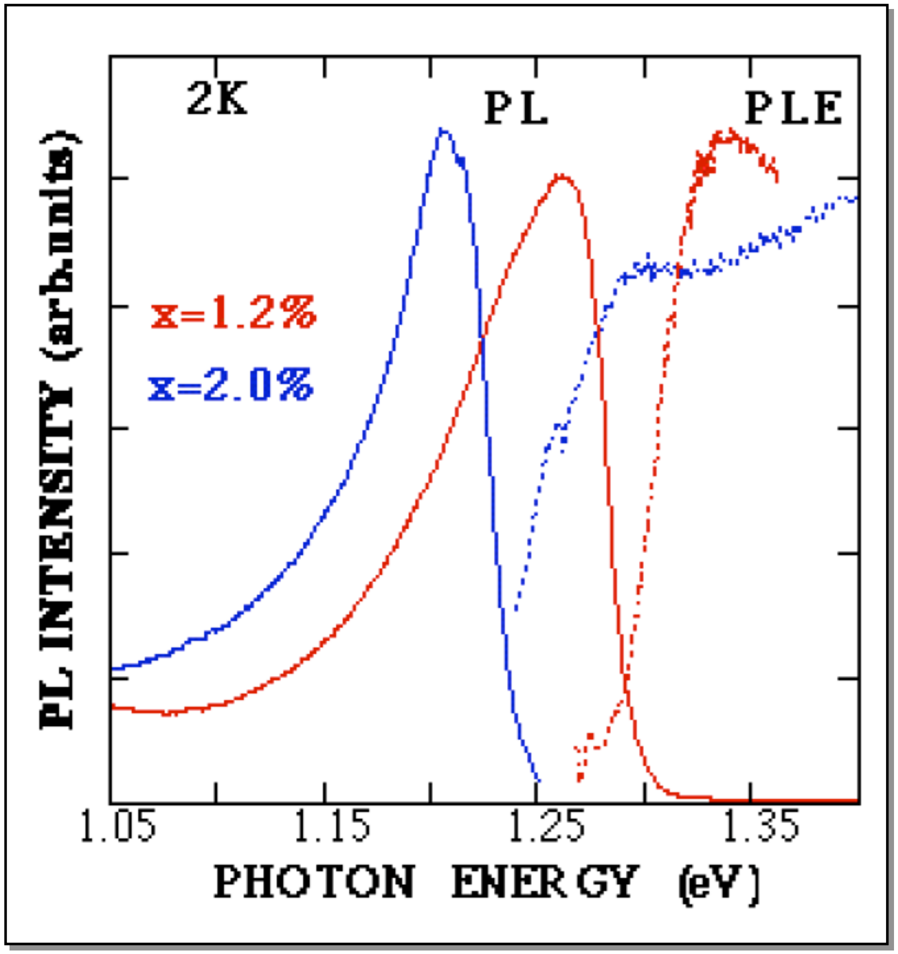
# Band gap reduction

**Anticrossing/repulsion between band edge and localized states drives band gap down**

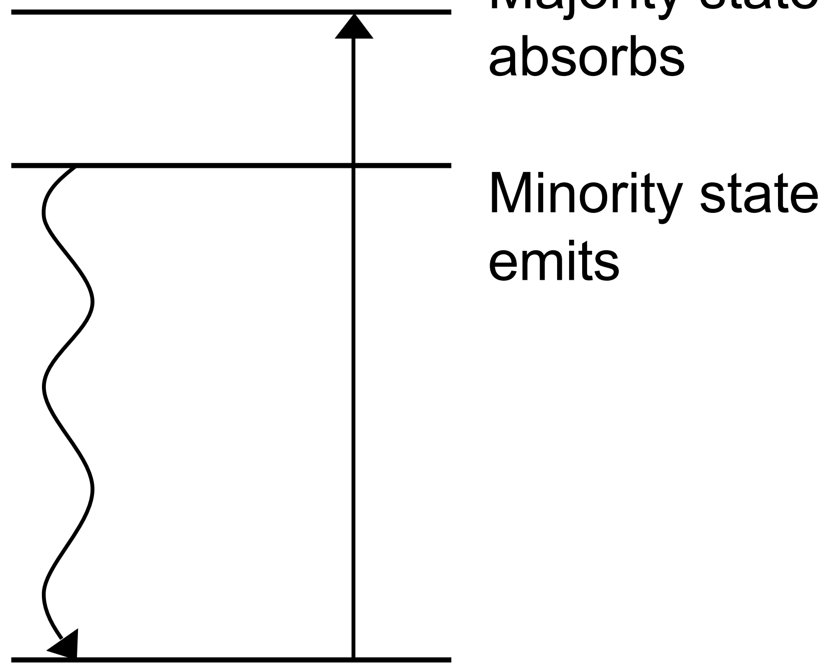



Pressure Dependence of GaPN Alloys
40
35
30
25
20
15
Pressure Coefficient (meV/GPa)
Calculation
Photoluminescence
0
1
2
3
Nitrogen Concentration (%)
Bulk GaP
Energy
–14 meV/GPa
Pressure

# Red Shift of PL *vs* PLE




I. A. Buyanova *et al.* MRS IJNSR **6** 2 (2001)




- *Emission from localized minority states*
- *Absorption to majority states*

# Summary: GaAsN & GaPN

**1. Small nitrogen aggregates create near-gap levels**

*Some "cluster state" levels are deep, even for small aggregates*

**2. Cluster states are □ fixed in energy**

**3. Host states move down, overtaking the cluster levels, one-by-one**

*Host states repelled from nitrogen resonant levels*

**4. Both localized and delocalized states exist at the band edge**


Kent & Zunger Phys. Rev. Lett. **86** 2613 (2001)

Kent & Zunger Phys. Rev. B **64** 5208 (2001)

Kent & Zunger Appl. Phys. Lett. **79** 2339( 2001)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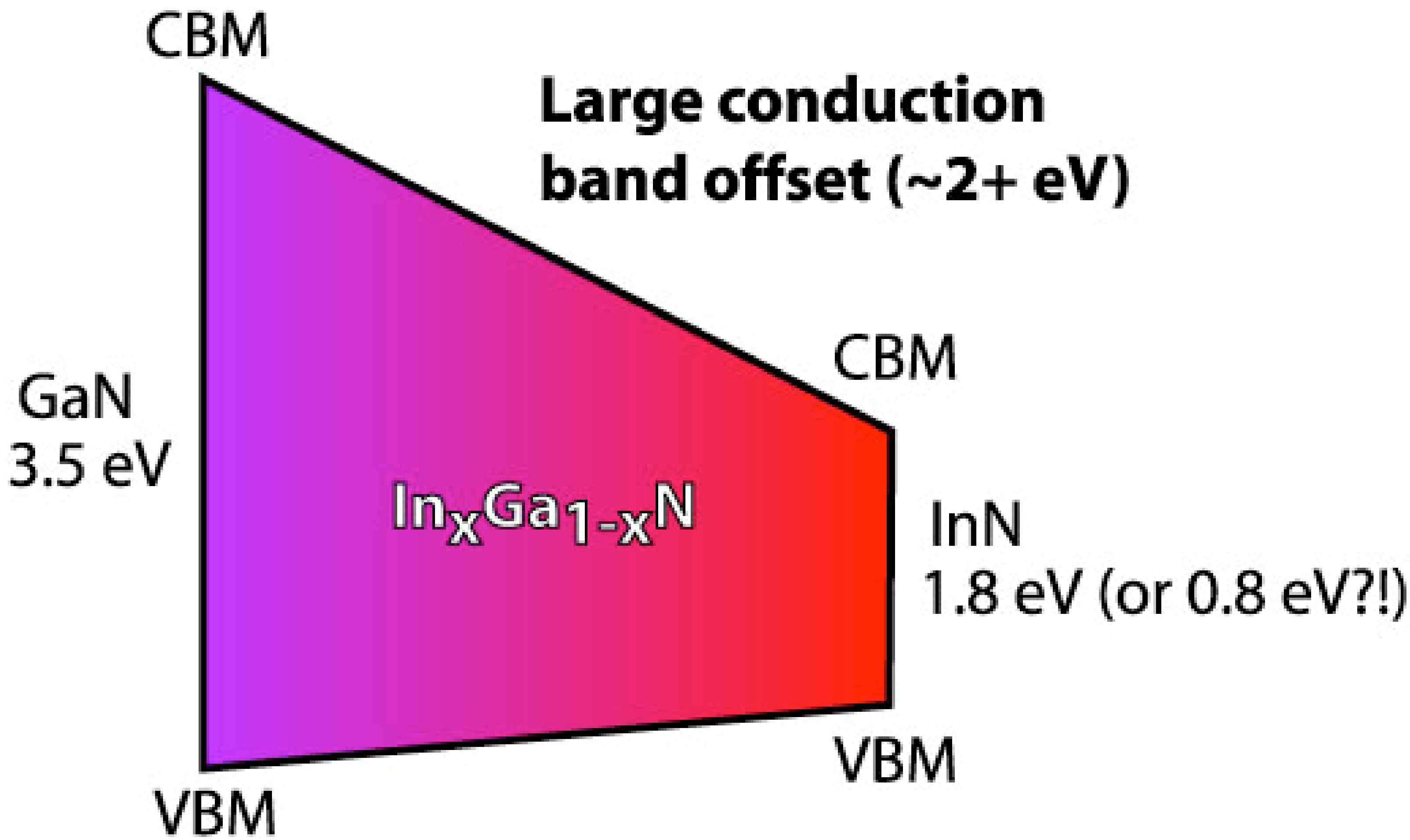
# Why is emission so efficient?

Despite large defect density InGaN alloys emit

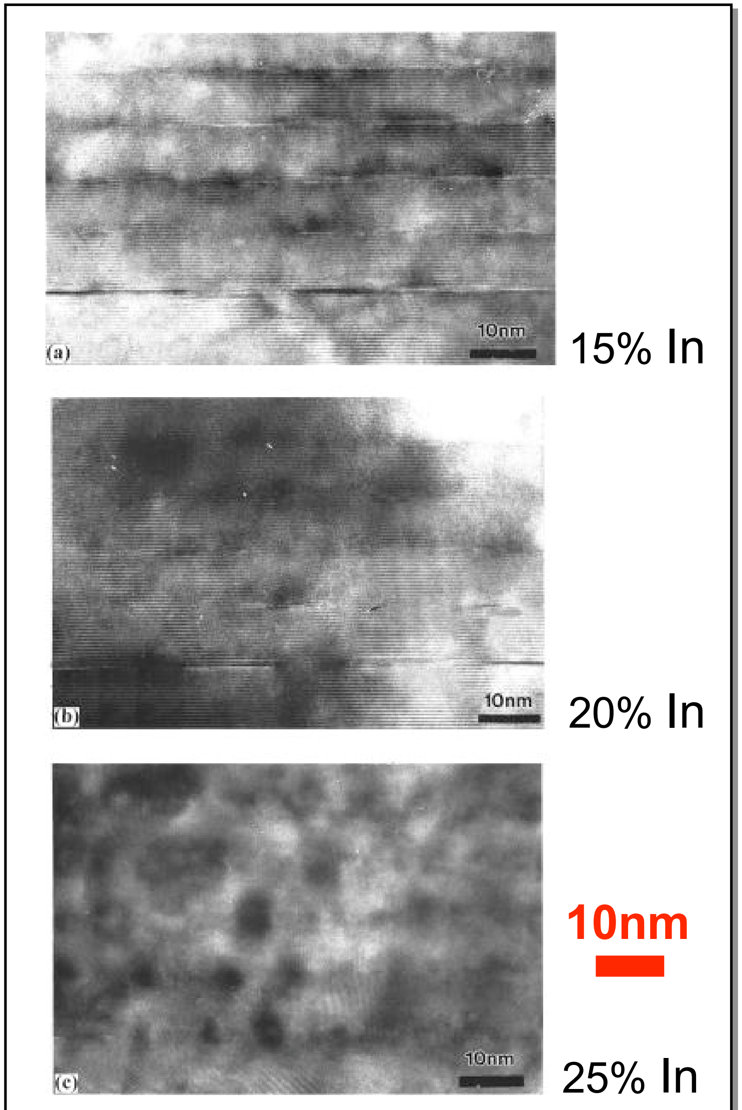
- Time resolved PL – many length (time) scales
- Theory: Bulk InGaN alloys emit weakly

**Q. What is the role of In inhomogeneity?**

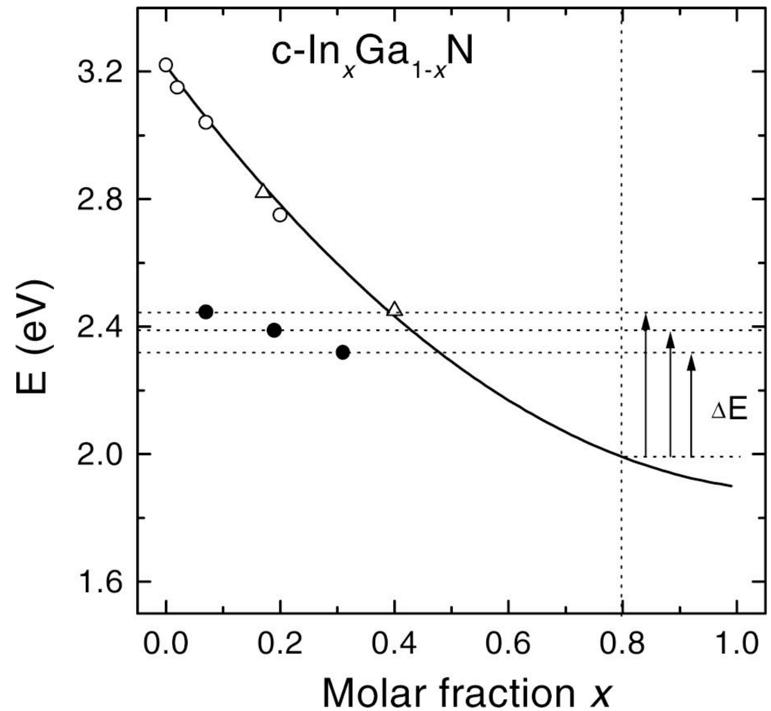
# InGaN band offsets



# Experimental Observations



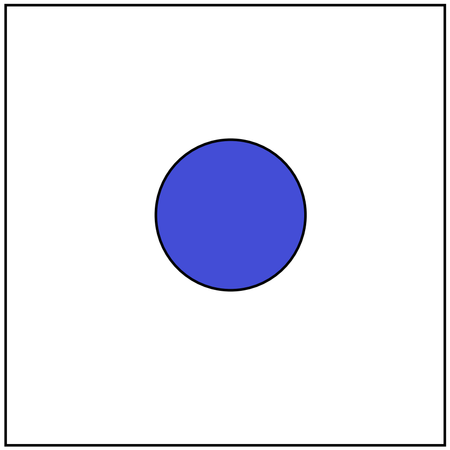

HRTEM InGaN MQW
Lin et al. APL **77** 2988 (2000)




Lemos et al. PRL **84** 3666 (2000)

~300 meV+ lowering in emission energy in 33% c-InGaN samples

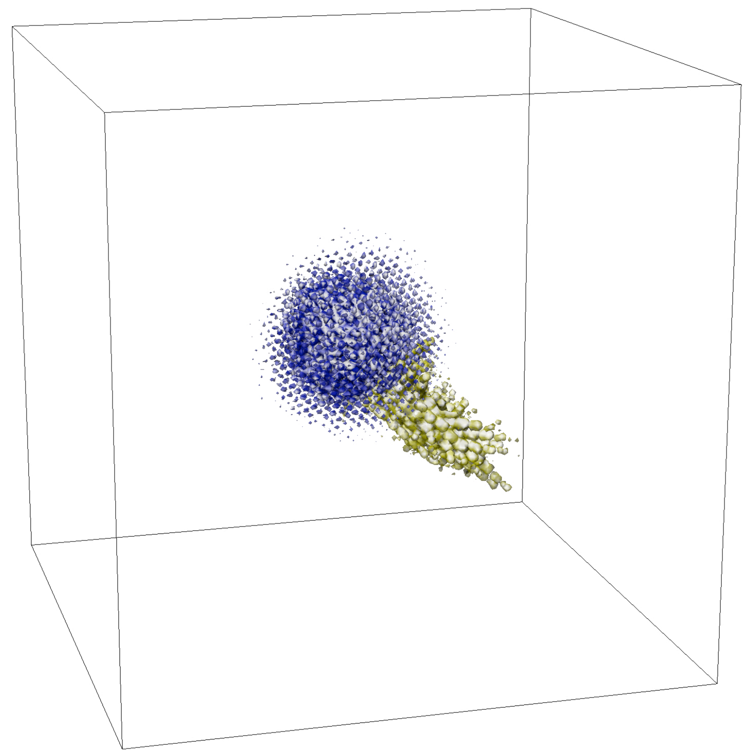
# InGaN Intrinsic Dot Calculations



Spherical dot in 141000 atom supercell

Dot: High In composition 80%+

Alloy supercell: Lower In composition 33%



**Electrons**
**Quantum confined on dot**

Holes
Localized in/near dot
(strain, alloy fluctuations)

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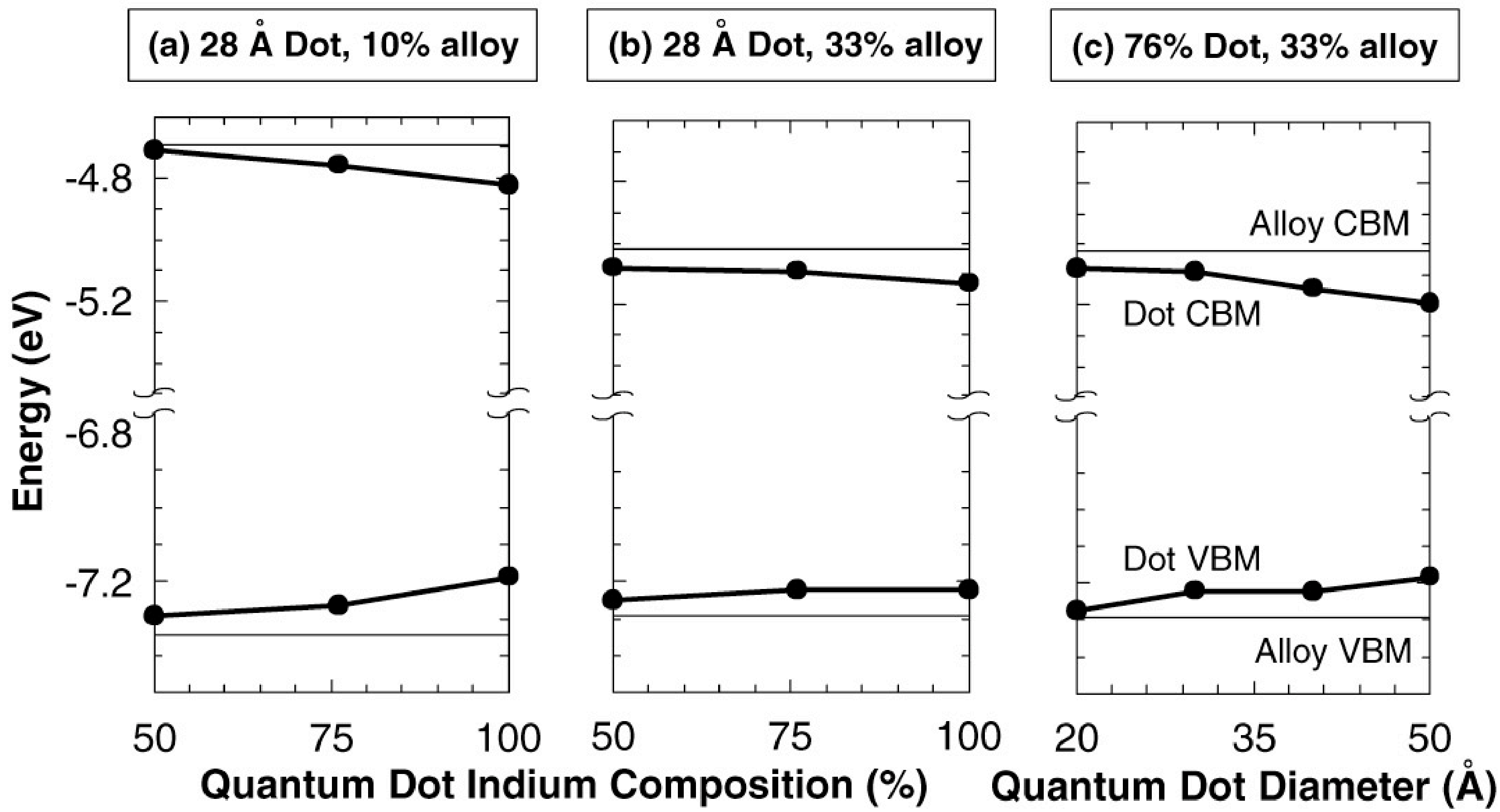
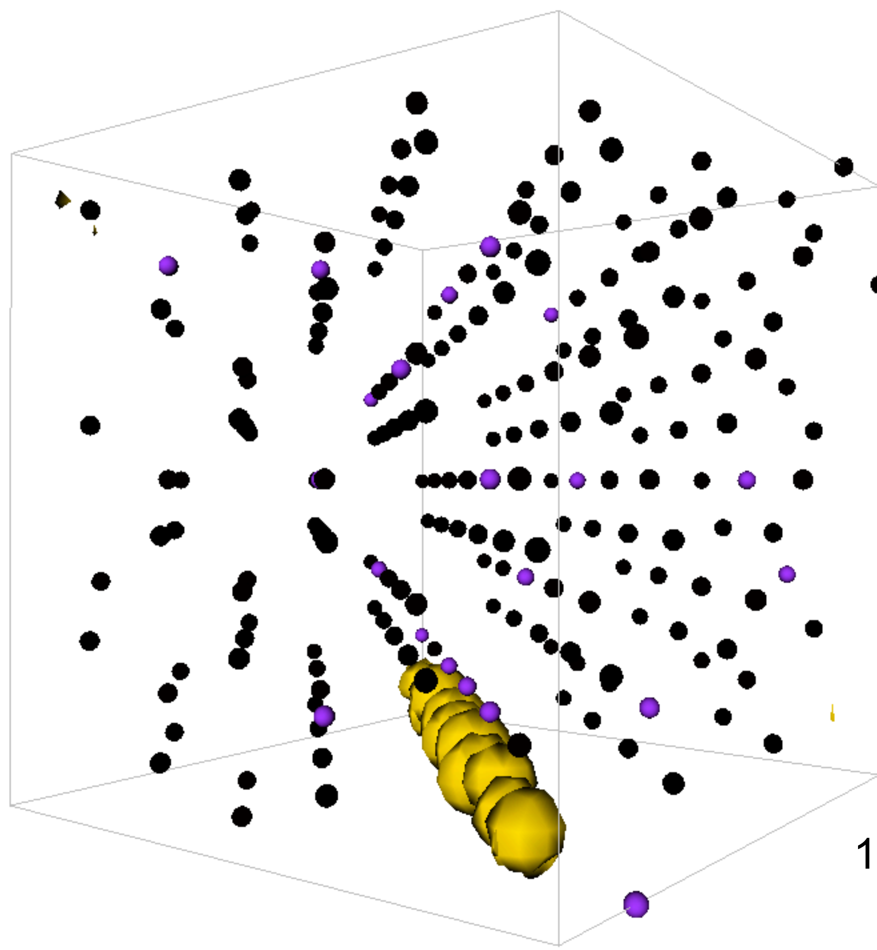
# Quantum Dot Electron and Hole Energies




**Small In-rich regions give large "band gap" reduction**

# Hole Localization in Random Alloys



1000 atom supercell
20% In

***Holes localize near (statistically occurring) (1,1,0)-oriented Indium chains!***

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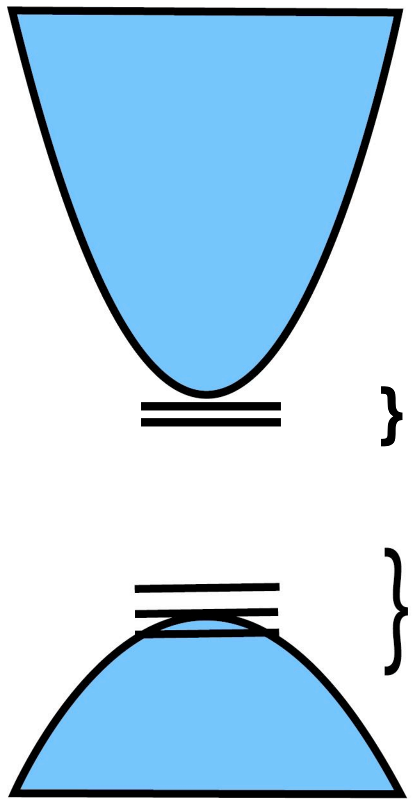
# Indium fluctuations are key




**Localized states occur near VBM, CBM**

# Summary: InGaN

***Indium fluctuations are key - localization easily results***
***=> Can specify quality of growth required for opto devices***

- Small (~30 A) In-rich (80%+) regions cause low energy PL
- Localized hole states exist even in random alloy

Kent & Zunger Appl. Phys. Lett. **79** 1977 (2001)

# Conclusion

**1.** Nitride alloys display “new physics” due to formation of localized states

**2.** Large-scale computational modeling can help explain nitride properties

prc.kent@physics.org http://www.physics.uc.edu/~pkent

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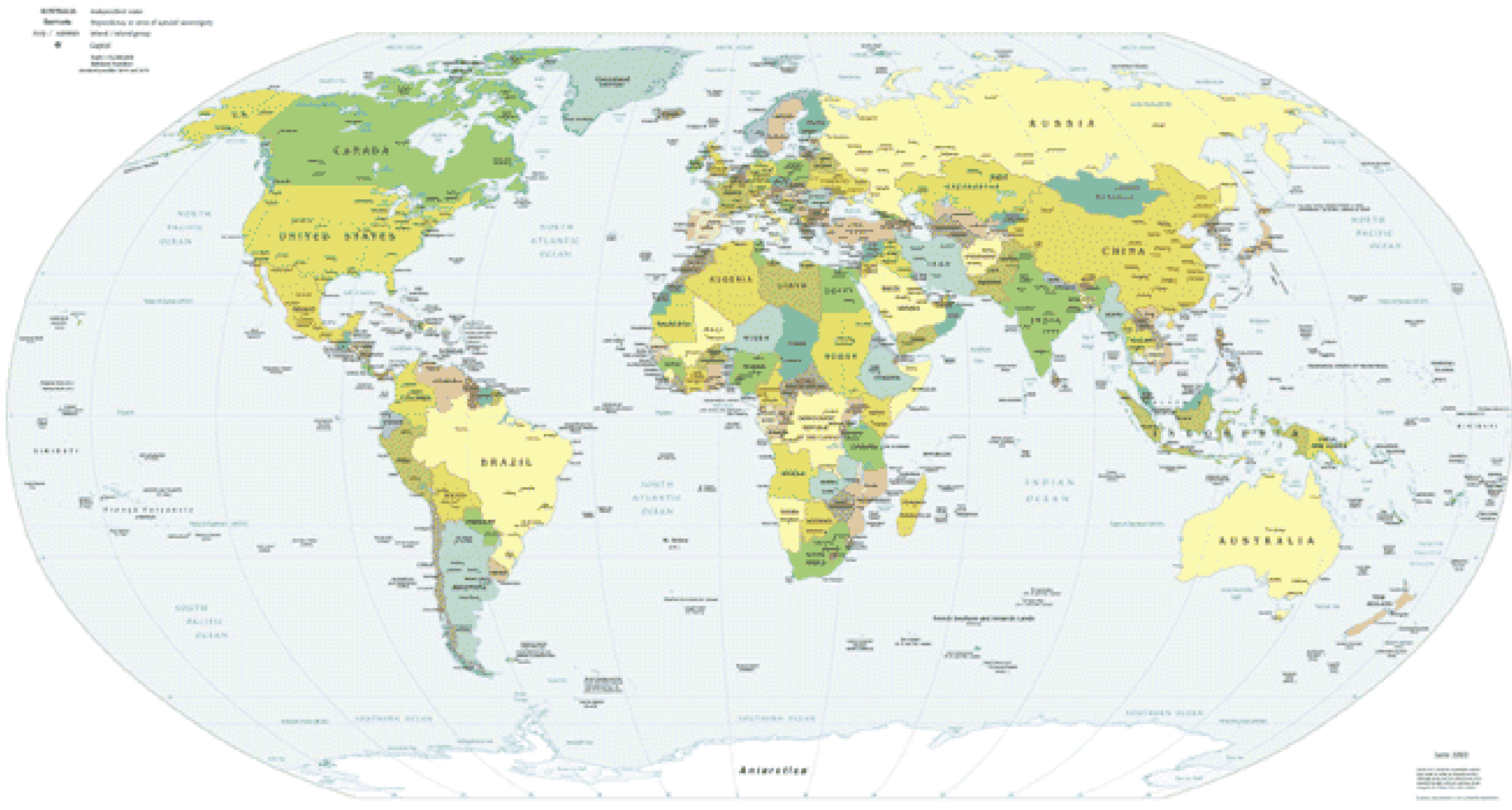
## Political Map of the World, June 2002

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