Pressure evolution of localized nitrogen cluster states in GaAsN alloys

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Localized-Delocalized Transition in GaAsN

Kent and Zunger PRL 86 2613 (2001)

- Impurity Regime
- Dilute Regime
- Conventional Regime

Nitrogen Localized Cluster States (CS) Fixed in Energy

Increasing nitrogen concentration
Pressure coefficient of CS reduced compared to bulk
Disappearance of highest energy CS!
How do the nitrogen CS evolve with pressure and composition?
Computational Modeling of Dilute Alloys

Kent and Zunger PRB 64 115208 (2001)

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 VFF for structural relaxation
Use Empirical pseudopotential method for wavefunctions
Computational Modeling

1. Create nitrogen cluster in dilute alloy
2. Follow localized state with pressure & nitrogen concentration

64000 atom supercells
Isolated nitrogen in bulk GaAs

**Diagram:**
- **Energy (eV) vs. Pressure (GPa)**
- Lines: $a_1(N)$, $a_1(\Gamma_1c)$, $e(X_1c)$
- Diagram highlights localized state emerging into gap
- $\mathbf{L} = $ Localized, $\mathbf{D} = $ Delocalized
Nitrogen triplet in Bulk GaAs

Localized state remains in gap
Low pressure coefficient
Developed alloy

Delocalized states at band edges
Developed alloy with triplet

Delocalized states at band edges
Triplet not within gap or at band edge, as expected
Isosurfaces

(a) Isolated Impurity  
(b) Isolated N-N-N Triplet  
(c) Developed alloy with Triplet

Zero Pressure

High Pressure
Summary

Highest energy CS
Increased pressure coeff.

Lowest energy CS
Small pressure coeff.

Increasing Pressure
Fixed nitrogen concentration
Model Comparison

**Band anticrossing**: Good fit of band edge bowing

*No cluster states (CS)*

**Impurity band**: Predicts broadening of localized states

*Pressure* exposes either broad impurity band, or nothing

*No discrete CS to expose*

**Atomistic model** (This work): Conduction states overtake discrete CS

Some hybridization at higher pressures

*Consistent with experiment*
Summary

In dilute GaAsN

- Deep (low energy) CS emerge into gap with pressure
- Shallowest CS can hybridize
  - Pressure coefficient increased
  - Do not emerge into gap

Anticrossing/repulsion between band edge and localized states drives band gap down.
Pressure Dependence of GaPN Alloys

![Graph showing the pressure dependence of GaPN alloys. The graph plots the pressure coefficient (meV/GPa) against nitrogen concentration (%). The data points are marked with red squares for calculation and blue circles for photoluminescence. The inset shows the bulk GaP with a linear relationship between energy and pressure, with a slope of -14 meV/GPa.]
Red Shift of PL vs PLE

- Emission from localized minority states
- Absorption to majority states

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