

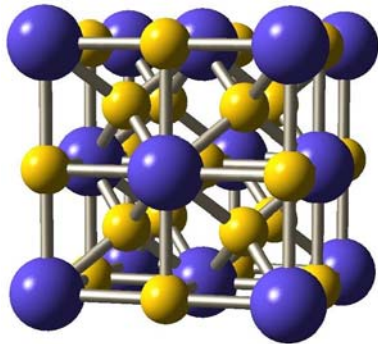
Cubic Lithium Nitride to 200 GPa

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High Pressure Collaborative Access Team

- HPCAT (sector 16 of the APS) at which all experiments were performed; we thank Maddury Somayazulu and Micheal Hu for technical assistance and scientific input.
- Andy McMahan (LLNL), Deepa Kasinathan (UCD) and Jan Kunes (UCD) for help with theoretical aspects





OUTLINE



Background

Results from

- **X-Ray Diffraction**
- **X-Ray Raman Scattering**
- **Total energy DFT calculations**

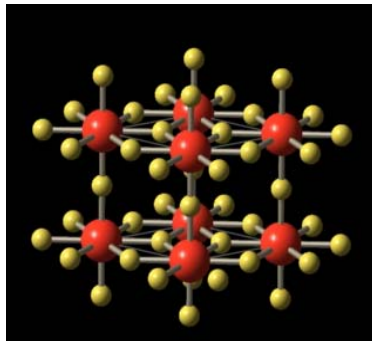
Conclusions



Li₃N (previously known info)

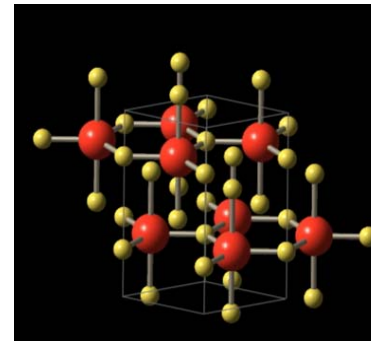


- Two low pressure phases had been observed:



(α) P6/mmm

~0.5 GPa
→



(β) P6₃/mmc

- α phase is a superionic conductor via hopping of Li¹⁺ ions within Li₂N layers, in which N ions exist in 3- ionic state.
- β phase is metastable at 0 GPa, stable up to < 35 GPa.
- high pressure cubic phase was predicted by theory.

Technological applications:

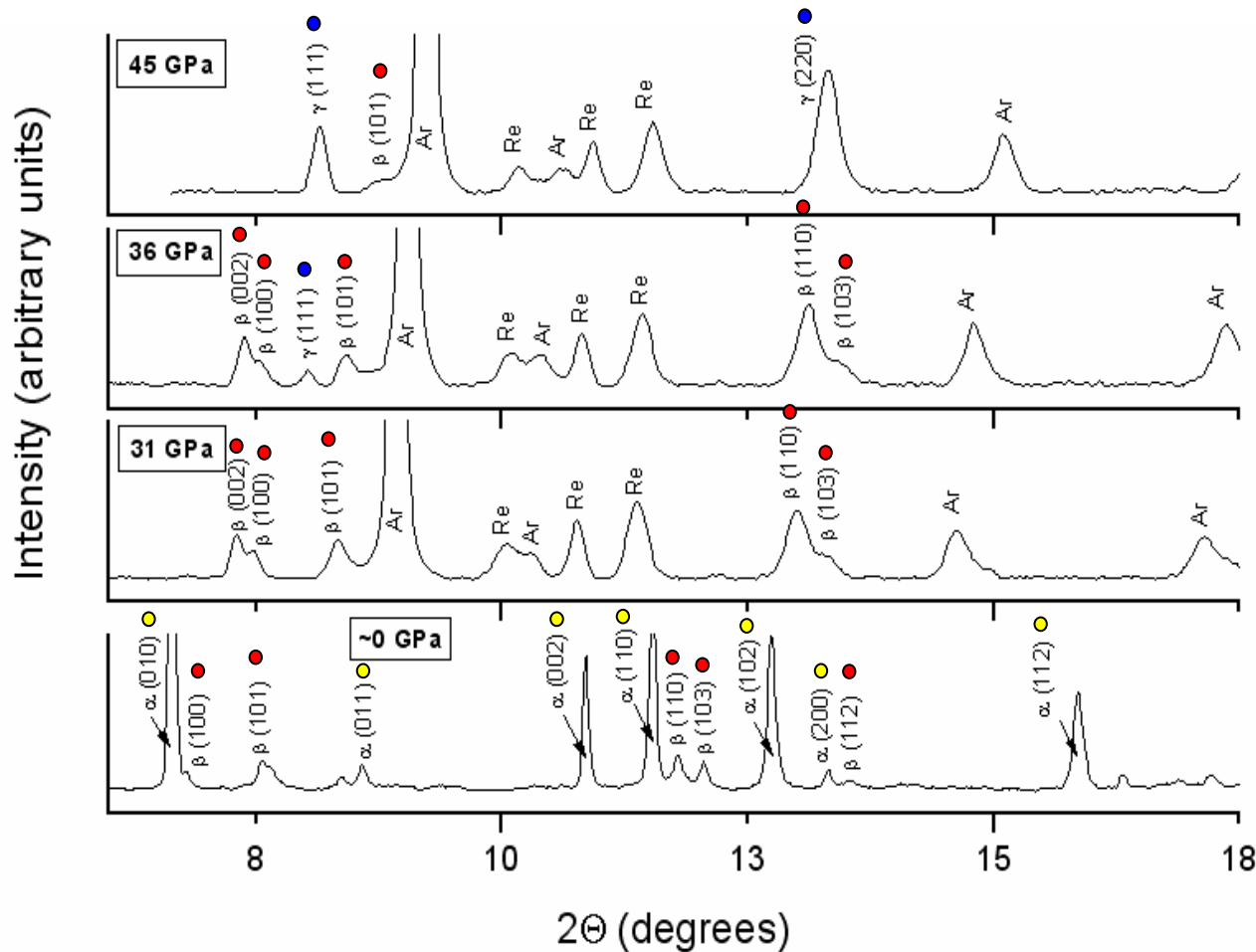
- possible electrolyte material for lithium-based batteries
- possible hydrogen storage material

Thrust of this research:

Determine structure, equation of state, stability of any novel high pressure phase.



X-Ray Diffraction Results



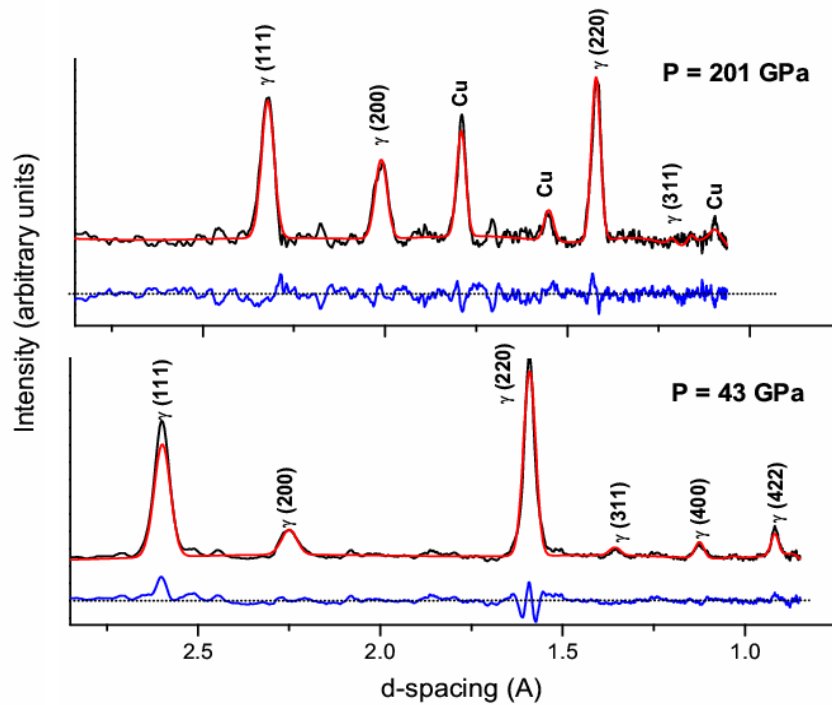
- mixed phase at 0 GPa
- transition to transparent cubic phase between 35 and 45 GPa
- signal from argon pressure medium and rhenium gasket obscure the details



γ -Li₃N – a new cubic phase

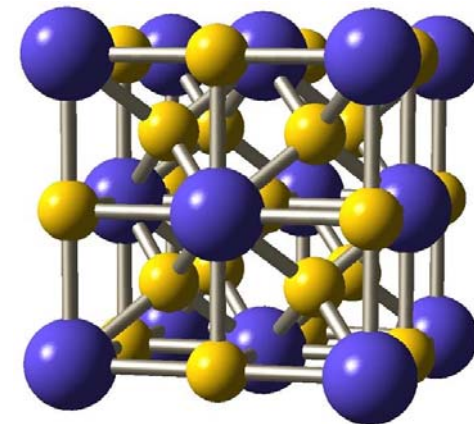


Rietveld-refined XRD structure data



- pattern well understood as a combination of Cu and Li₃N in cubic Fm3m phase
- peak broadening at 200 GPa very minimal even under non-hydrostatic conditions – very little internal stresses/strains

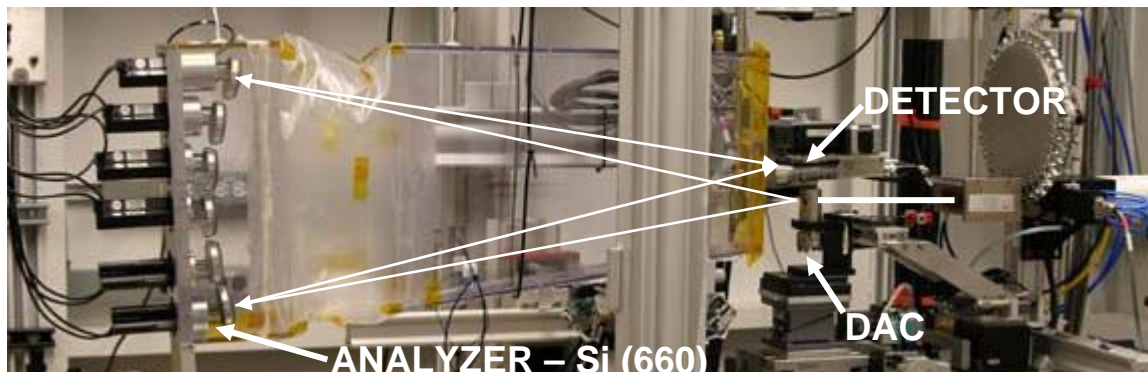
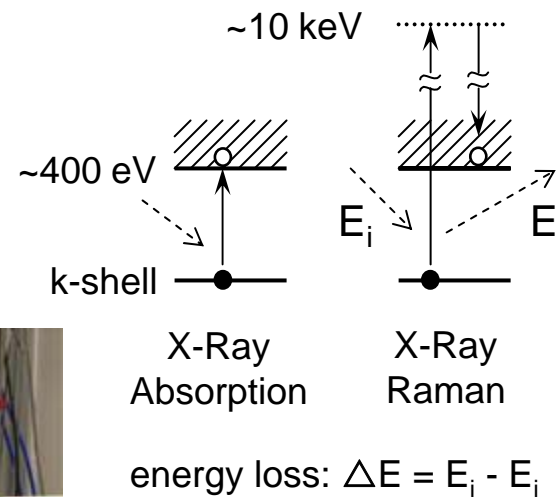
- cubic Li₃N takes on simple rocksalt structure, with Li¹⁺ ions tetrahedrally coordinated with 4 nitrogen ions in all tetrahedral holes in lattice.





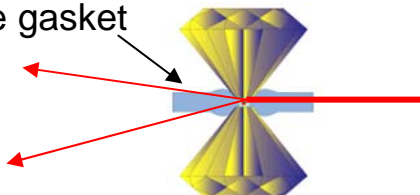
Inelastic X-Ray (Raman) Scattering

- Yields the same information as XAS, but experiment can be done with hard x-rays— (becomes possible to examine k-edges of low-Z materials in bulk)

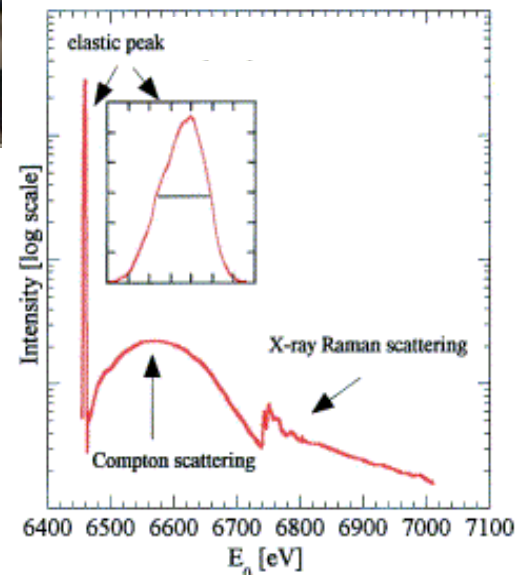


Experimental set-up (16IDD, HPCAT, APS)

x-ray transparent
Be gasket



incident beam energy scanned from 380 – 430 eV above elastic scattering energy (9.6870 eV) to probe nitrogen k-edge

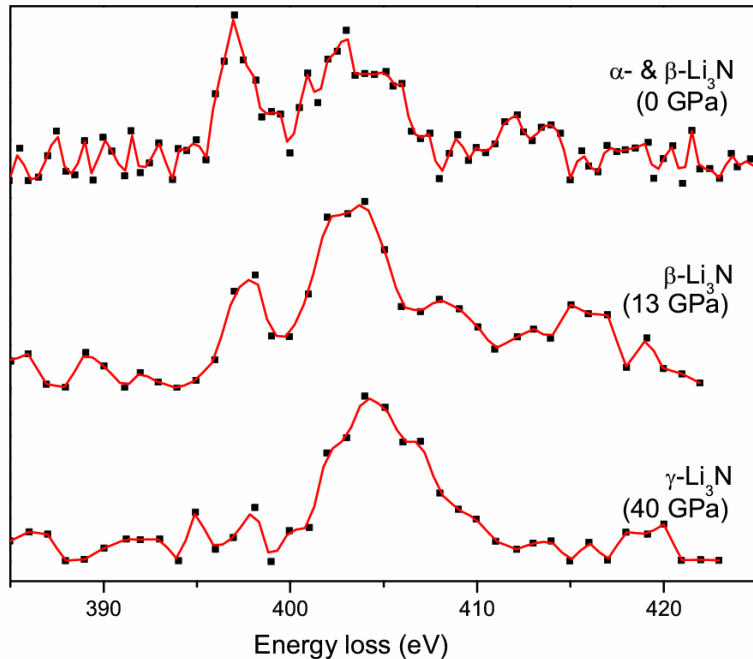




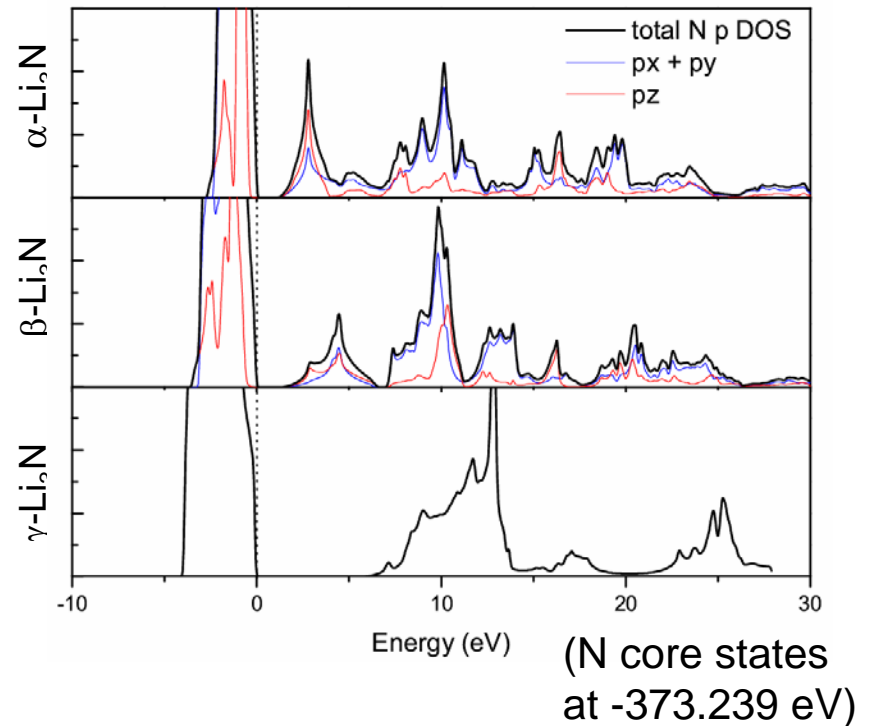
X-Ray Raman Results



Nitrogen k-edge spectra of Li_3N



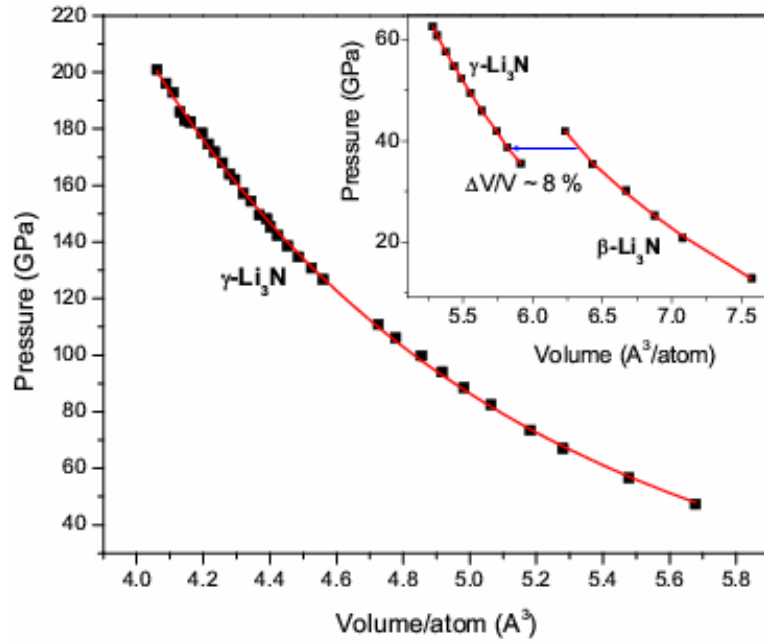
Projected Nitrogen p Density of States



- The x-ray raman spectra can be understood as transitions to low-lying conduction states with nitrogen p character – differences between the XRS and PDOS are indications of the presence of core-hole interactions (excitons) and non-dipole allowed transitions.



Equation of State



- cubic phase of Li_3N remains very compressible up to 200 GPa (maximum pressure achieved in this experiment)
- B_0 , V_0 from fit to non-hydrostatic higher-pressure data agree well with results from fit to lower-pressure hydrostatic data.

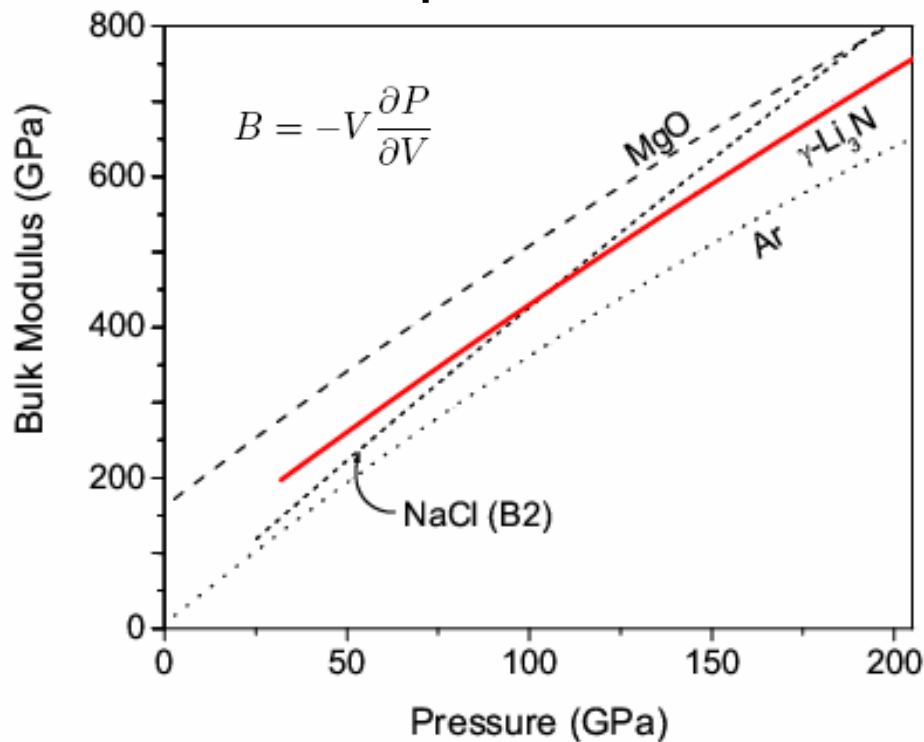
	crystal structure	V_0 ($\text{\AA}^3/\text{atom}$)	B_0 (GPa)	B_0'	volume collapse	transition pressure (GPa)
Experiment (this work)	$P6_3/mmc$	8.6 ± 0.2	71 ± 19	3.9 ± 0.9	$8 \pm 0.5\%$	40 ± 5
	$Fm\bar{3}m$	7.7 ± 0.2	78 ± 13	4.2 ± 0.2		
Theory (this work)	$P6_3/mmc$	8.61 ± 0.02	68 ± 3	3.6 ± 0.1	6.7%	40.4
	$Fm\bar{3}m$	7.79 ± 0.02	73.1 ± 0.8	3.85 ± 0.01		
Experiment (Ho, et al) (PRB 59, 6083 (1999))	$P6_3/mmc$	8.76	74 ± 6	3.7 ± 0.7		
Theory (Ho, et al) (PRB 59, 6083 (1999))	$P6_3/mmc$	7.72	78.17	3.77	8%	37.9
	$P4_3m$	7.02	82.75	3.84		
Theory (Schon et al) (J. Mater. Chem. 11, 69 (2001))	$P6_3/mmc$ $Fm\bar{3}m$					27.6 ± 5.4



Equation of state data was then fit to modified 3rd order Birch-Murnaghan equation*

$$P = \left\{ P_r - \frac{1}{2} (3B_r - 5P_r) \left[1 - \left(\frac{V}{V_r} \right)^{-\frac{2}{3}} \right] + \frac{9}{8} B_r \left(B'_r - 4 + \frac{35P_r}{9B_r} \right) \left[1 - \left(\frac{V}{V_r} \right)^{-\frac{2}{3}} \right]^2 \right\} \left(\frac{V}{V_r} \right)^{-\frac{5}{3}}$$

Bulk Modulus of γ -phase and comparison to common pressure indicators*



γ -Li₃N is a good candidate for an internal pressure indicator for ultra-high pressure applications

- simple cubic crystal structure
- stable up to at least 200 GPa with minimal peak broadening even under non-hydrostatic conditions
- compressibility compares well with other common pressure standards
- low-Z composition makes it particularly suitable for low-Z applications

Possible problem: reactivity, especially at high pressures, is unknown.

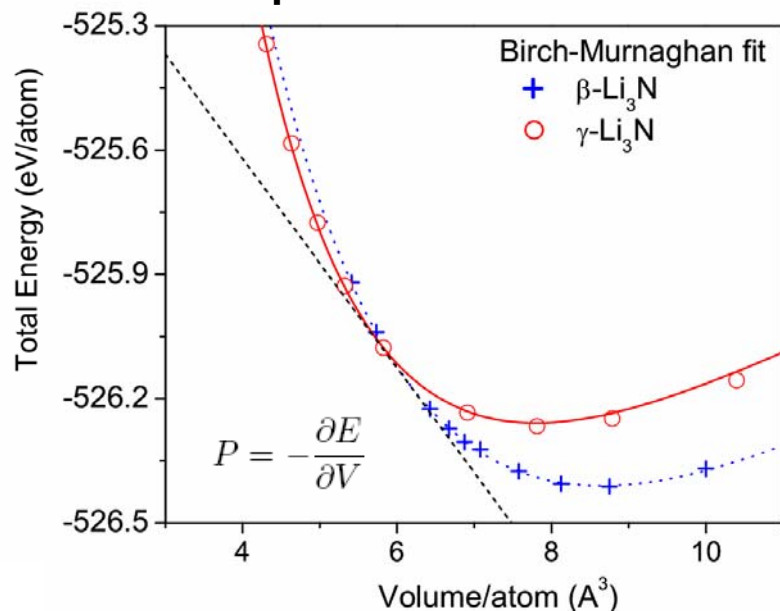
*N. Sata, G. Shen, M. L. Rivers, S. R. Sutton, PRB 65, 104114 (2002)



DFT Calculation Results

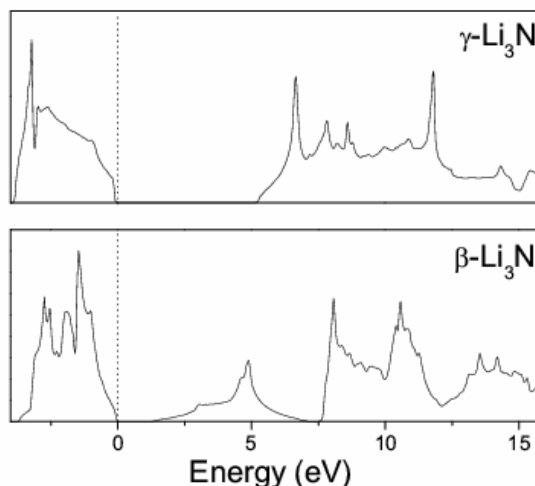


Equation of State



- Total energy calculations yield V_0 , B_0 , B_0' consistent with experiment – Li_3N is well described by theoretical model.

Density of states



- widening of the band gap indicates insulating cubic phase, explains color change from opaque to transparent across hexagonal-cubic phase transition.

Comparison with experimental results

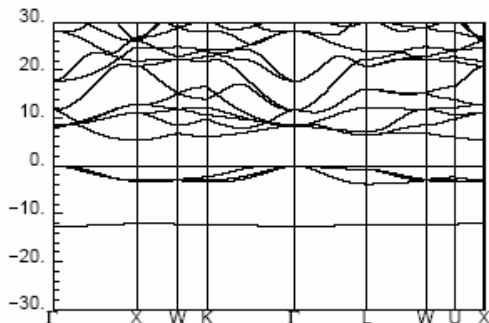
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Predicted Metallization

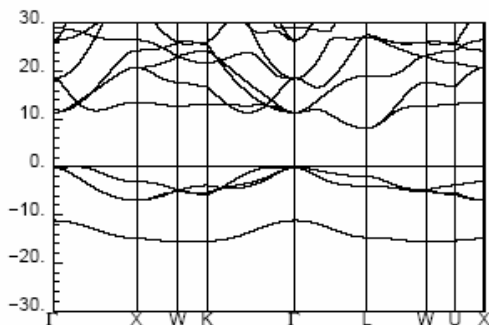


Electronic band structure (eV)



P = 40 GPa

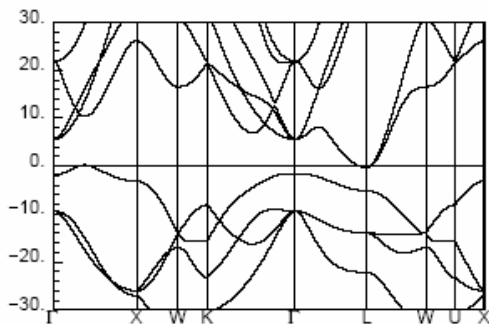
(transition to cubic phase)



P ~ 760 GPa

43% of unit cell volume at transition

(maximum band gap)

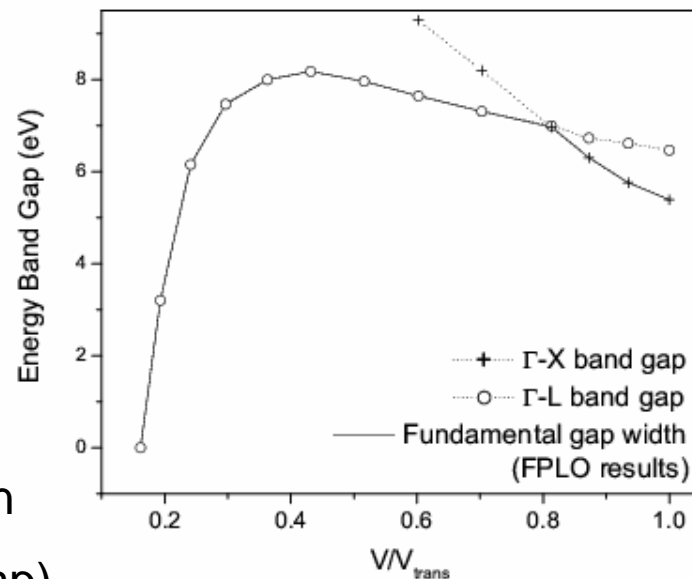


P ~ 7.9 TPa

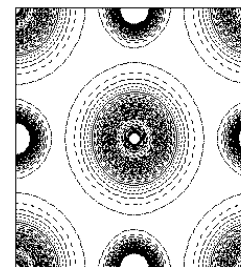
16% of unit cell volume at transition.

(metallization)

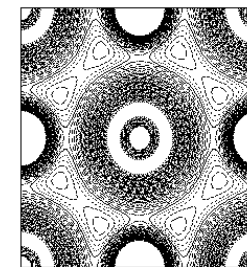
Band gap pressure dependence



(001)



charge density at transition



near metallization



Conclusions



The high pressure cubic phase of Li_3N identified in this study has several interesting properties including:

- Structural transition similar to graphite-diamond and hexagonal-cubic boron nitride**
- Unusually high phase stability at megabar pressures**
- High compressibility on the order of standard pressure indicators used in diamond anvil cell research**
- Metallization at ultra-high gigabar pressures, on the order of closed-shell wide-gap insulators Ne, MgO and NaCl which metallize at 134 TPa, 20.7 TPa, & 0.455 TPa, respectively**