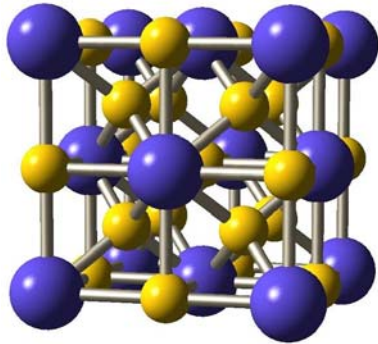# Cubic Lithium Nitride to 200 GPa

Amy Lazicki[1,2]
Choong-Shik Yoo[1], Warren Pickett[2], Richard Scalettar[2]

[1]Lawrence Livermore National Laboratory
[2]University of California at Davis

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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**

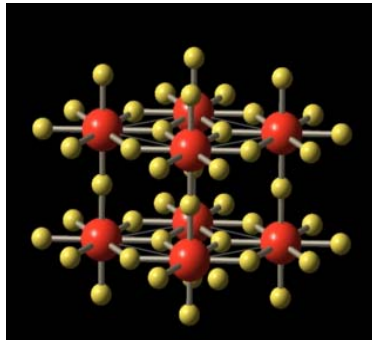- **X-Ray Raman Scattering**
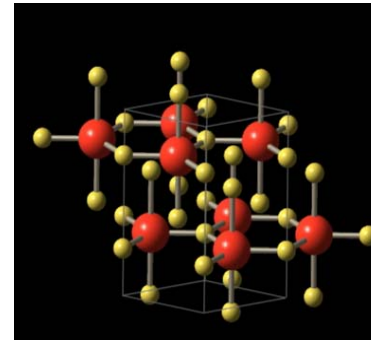
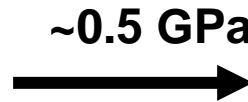- **Total energy DFT calculations**

Conclusions

Li$_3$N (previously known info)

- Two low pressure phases had been observed:

~0.5 GPa

(α) P6/mmm   **(β) P6$_3$/mmc**

- α phase is a superionic conductor via hopping of Li^{1+} ions within Li$_2$N 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.
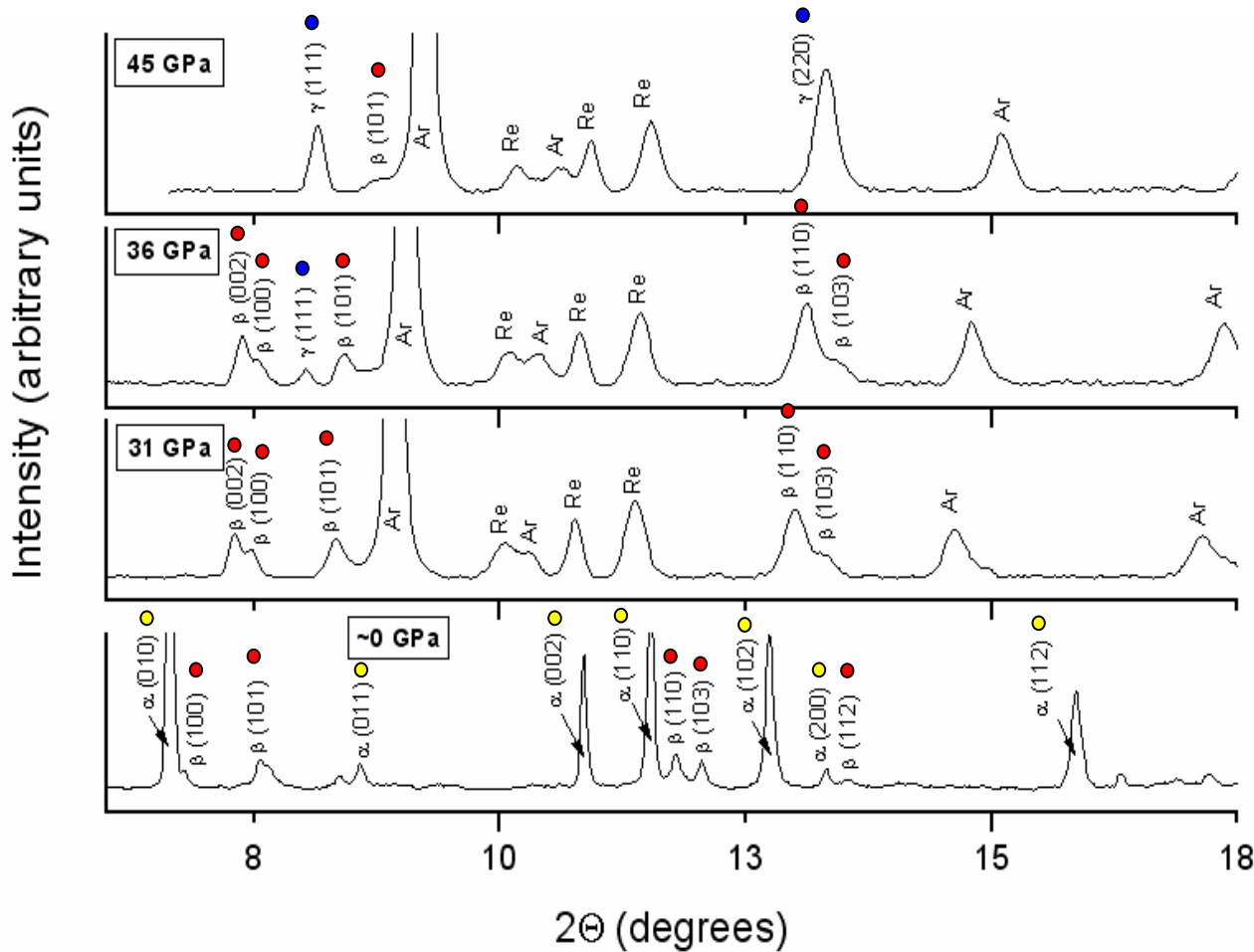
Technological applications:
- possible electrolyte material for lithium-based batteries
- possible hydrogen storage material

Thrust of this research:

   Determine structure, equation of state, stability of any
   novel high pressure phase.
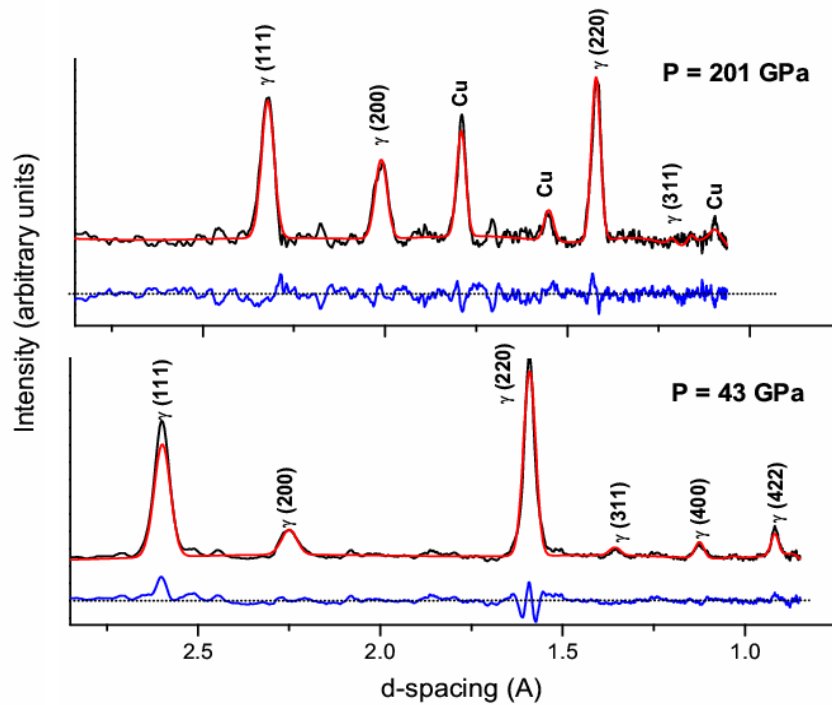
X-Ray Diffraction Results

- 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 Li_3N in cubic Fm3m phase

- peak broadening at 200 GPa very minimal even under non-hydrostatic conditions – very little internal stresses/strains
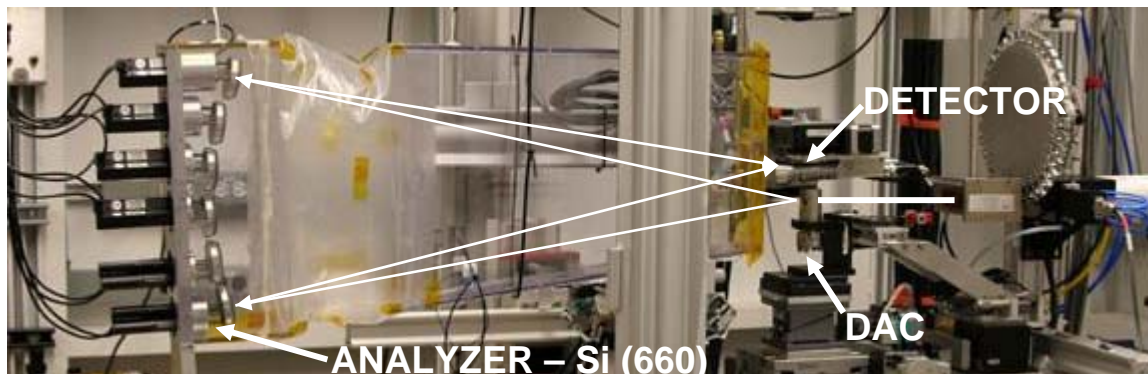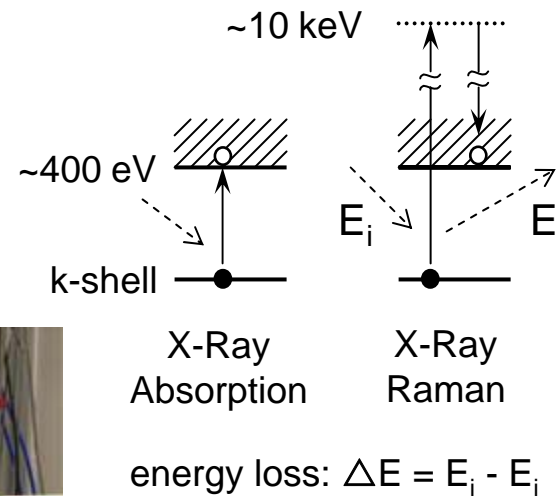

- cubic Li_3N takes on simple rocksalt structure, with Li^{1+} ions tetrahedrally coordinated with 4 nitrogen ions in all tetrahedral holes in lattice.
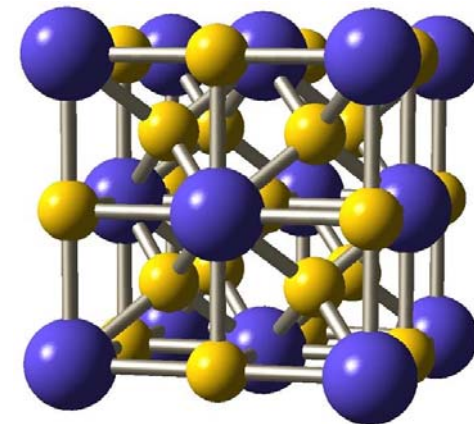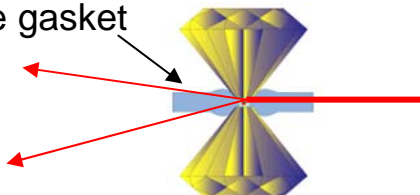
Inelastic X-Ray (Raman) Scattering

- 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)
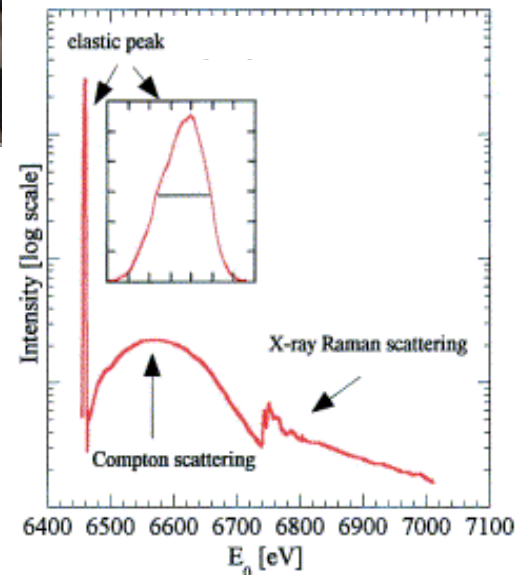
~10 keV

~400 eV

k-shell

E_i E_j

X-Ray Absorption   X-Ray Raman

energy loss: $\triangle E = E_i - E_j$

DETECTOR

DAC

ANALYZER – Si (660)

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
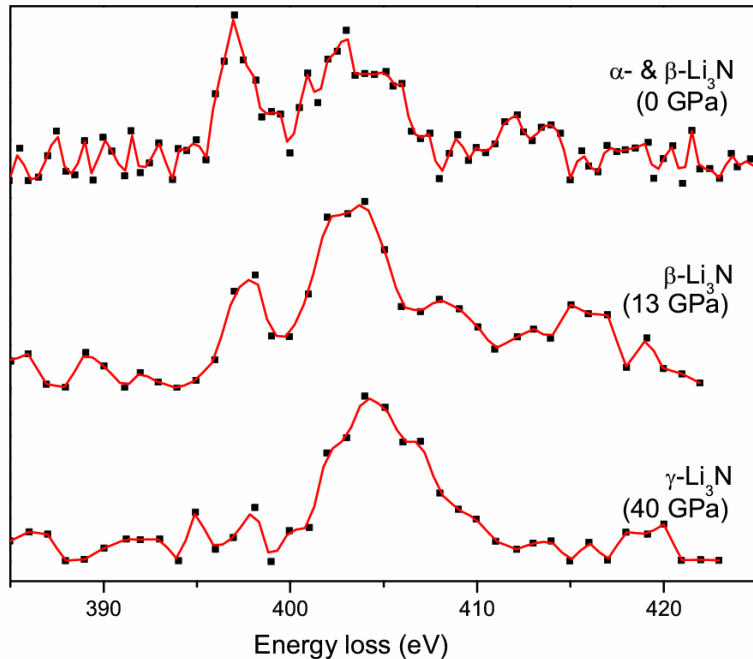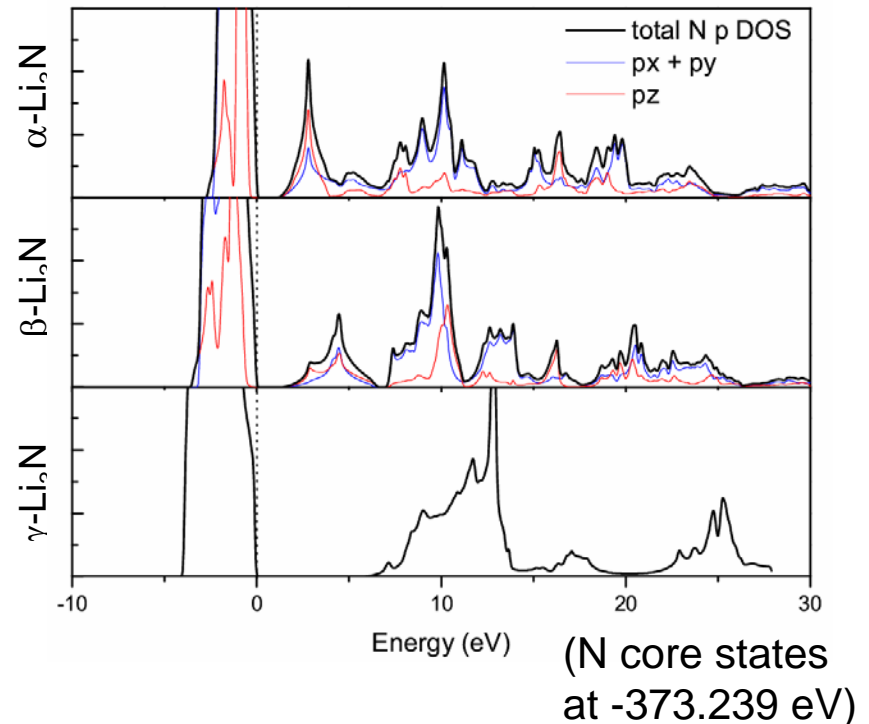
elastic peak

X-ray Raman scattering

Compton scattering

Intensity [log scale]

6400 6500 6600 6700 6800 6900 7000 7100

E_0 [eV]

X-Ray Raman Results

Nitrogen k-edge spectra of Li$_3$N
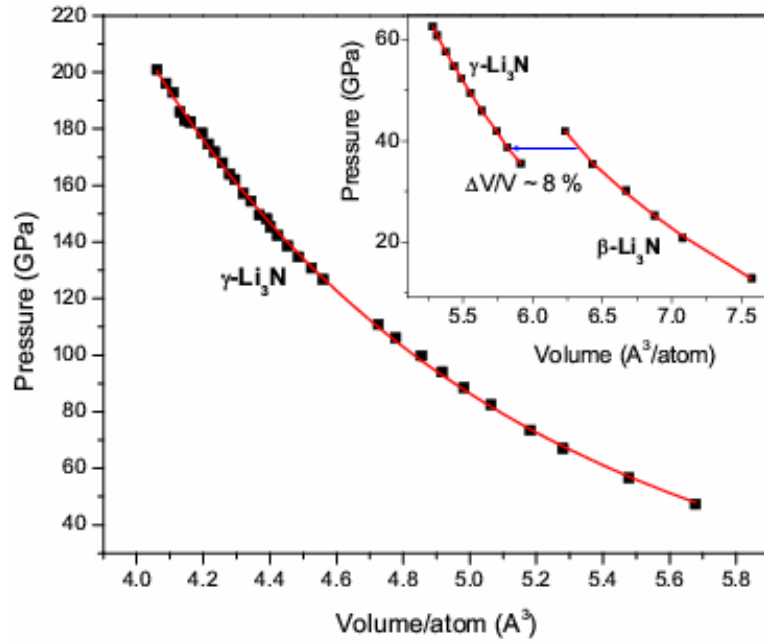
Projected Nitrogen p Density of States

(N core states at -373.239 eV)

- 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 (A^3/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 ± 0.5 %	40 ± 5
	Fm3m	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
	Fm3m	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
	P43m	7.02	82.75	3.84		
Theory (Schon et al) (J. Mater. Chem. 11, 69 (2001))	$P6_3/mmc$ Fm3m					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*
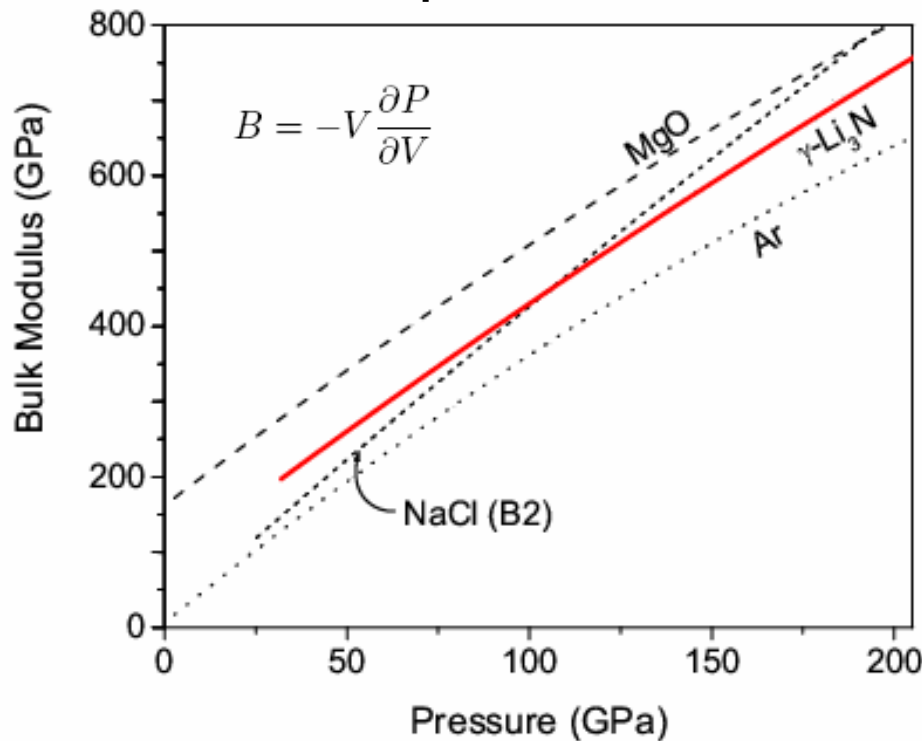
γ-Li_3N is a good candidate for an internal pressure indicator for ultra-high pressure applications

- 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

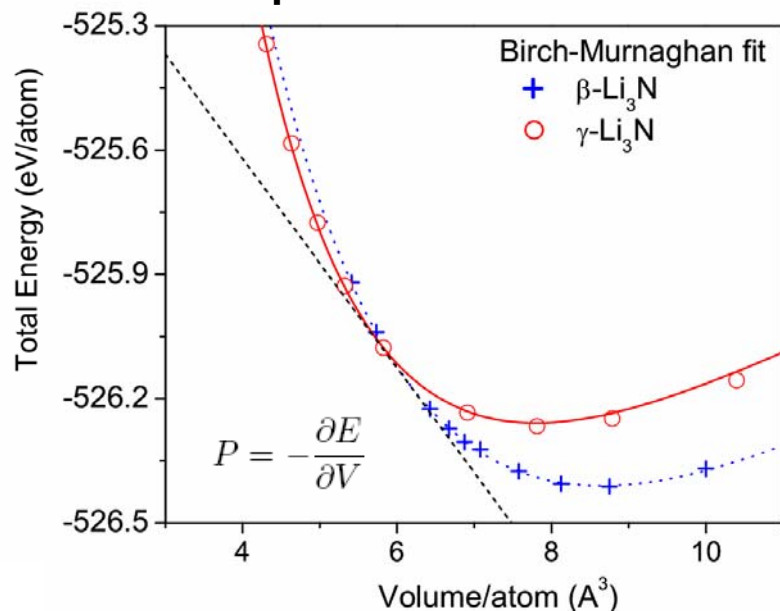Possible problem: reactivity, especially at high pressures, is unknown.
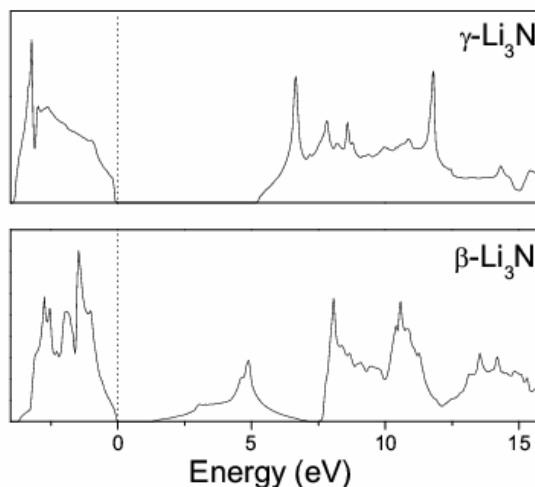
DFT Calculation Results

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.
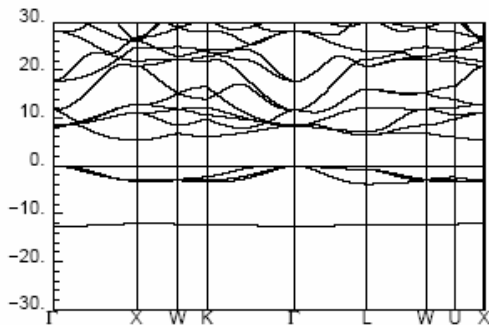
Comparison with experimental results

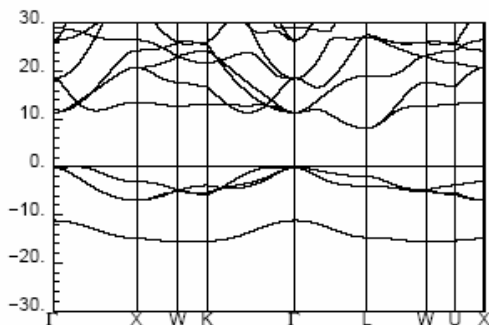|	crystal structure	V_0 (A^3/atom)	B_0 (GPa)	B_0'	volume collapse	transition pressure (GPa)
Experiment (this work)	$P6_3/mmc$	8.6 ± 0.2	71 ± 19	3.9 ± 0.9	$8 \pm 0.5\ \%$	40 ± 5
	$Fm3m$	7.7 ± 0.2	78 ± 13	4.2 ± 0.2		
Theory (this work)	$P6_3/mmc$	8.61 ± 0.02	68 ± 3	3.6 ± 0.1	6.7%	40.4
	$Fm3m$	7.79 ± 0.02	73.1 ± 0.8	3.85 ± 0.01		

Predicted Metallization

Electronic band structure (eV)
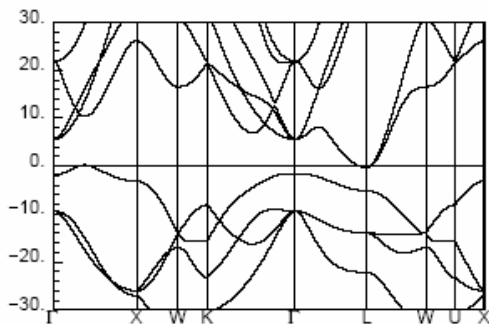
P = **40 GPa**

(transition to cubic phase)

P ~ **760 GPa**
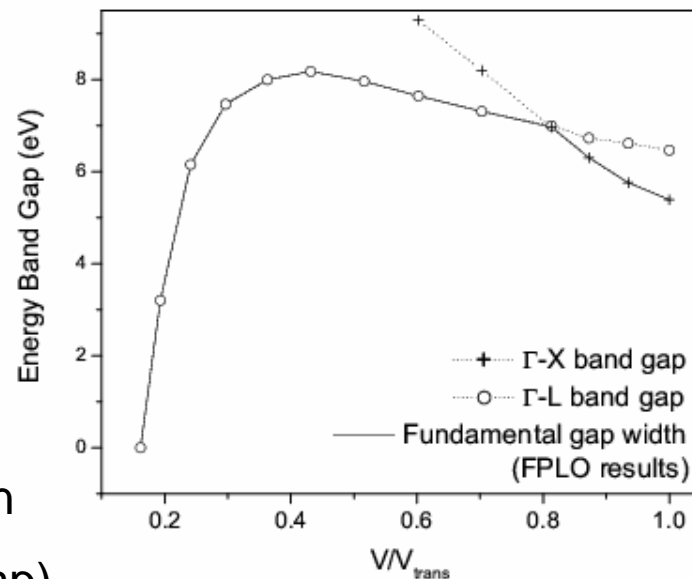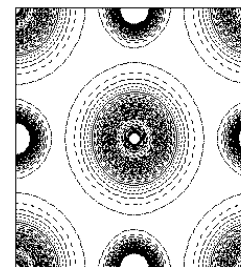43% of unit cell volume at transition

(maximum band gap)

P ~ **7.9 TPa**
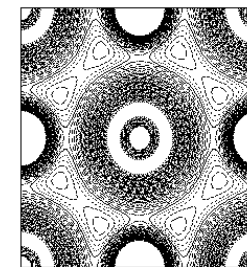16% of unit cell volume at transition.

(metallization)

Band gap pressure dependence

Energy Band Gap (eV)

Γ-X band gap
Γ-L band gap
Fundamental gap width (FPLO results)

V/V_{trans}

(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