# Experimental and Computational Studies of Molecular and Lattice Symmetries of Energetic Materials at High Pressure


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# Report Documentation Page

*Form Approved*
*OMB No. 0704-0188*



| 1. REPORT DATE | 2. REPORT TYPE | 3. DATES COVERED |
|---|---|---|
| **2002** | **N/A** | **-** |

| 4. TITLE AND SUBTITLE | 5a. CONTRACT NUMBER |
|---|---|
| **Experimental and Computational Studies of Molecular and Lattice Symmetries of Energetic Materials at High Pressure** | 5b. GRANT NUMBER |
| | 5c. PROGRAM ELEMENT NUMBER |
| 6. AUTHOR(S) | 5d. PROJECT NUMBER |
| | 5e. TASK NUMBER |
| | 5f. WORK UNIT NUMBER |
| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Naval Surface Warfare Center - Indian Head Division, Research and Technology Department Indian Head, MD 20640** | 8. PERFORMING ORGANIZATION REPORT NUMBER |
| 9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) | 10. SPONSOR/MONITOR'S ACRONYM(S) |
| | 11. SPONSOR/MONITOR'S REPORT NUMBER(S) |

12. DISTRIBUTION/AVAILABILITY STATEMENT
**Approved for public release, distribution unlimited**

13. SUPPLEMENTARY NOTES
**The original document contains color images.**

14. ABSTRACT

15. SUBJECT TERMS

| 16. SECURITY CLASSIFICATION OF: | | | 17. LIMITATION OF ABSTRACT | 18. NUMBER OF PAGES | 19a. NAME OF RESPONSIBLE PERSON |
|---|---|---|---|---|---|
| a. REPORT | b. ABSTRACT | c. THIS PAGE | | | |
| **unclassified** | **unclassified** | **unclassified** | **SAR** | **18** | |

# Overall Research Objectives

To study energetic materials of interest to the Navy/DoD at the high-pressure and high-temperature of detonation.

- **To study the initiation mechanism of detonation**
- **To learn the phase, lattice, and molecular symmetry, and measure theoretical maximum density (TMD) of a material at high pressure and temperature just before initiation**
- **To understand exactly what chemical bonds are most energetic and why, at the pressure and temperature of detonation**
- **To model the global kinetics and reaction mechanisms of energetic materials during detonative reactions**

# Impact of this Basic Research

• This research generates phase and density data essential for **deciding if a new material could be used in a weapon**

• The relevant data and thermodynamic parameters for each material is presented and published **to enhance predictive modeling** and simulation software.

• The results **transition into all areas of energetic materials systems** in keeping with the NAVSEA Grand Challenges of:

- Sixth Generation Energetics
- Assured Lethality/effects
- Scalable Combat Power Materials

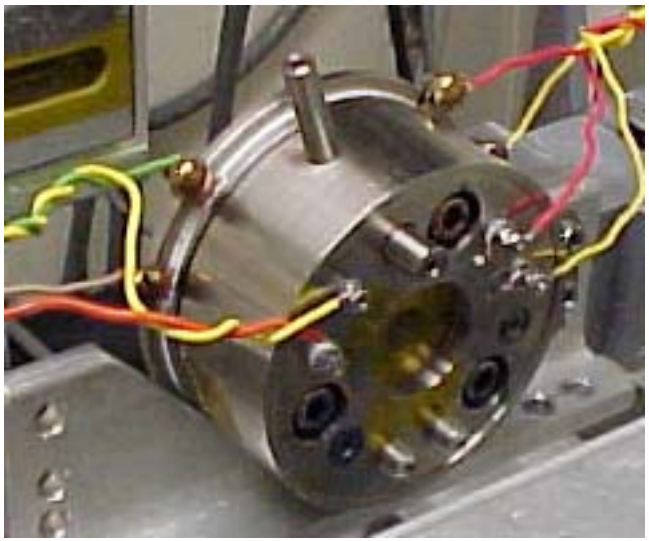
• Successful completion of the goals of this program will help develop Navy After Next enabling technologies such as:

- High Strength Materials
- Long-life, High-Energy, Insensitive, Solid Propellants
- Energetic Structural Composites

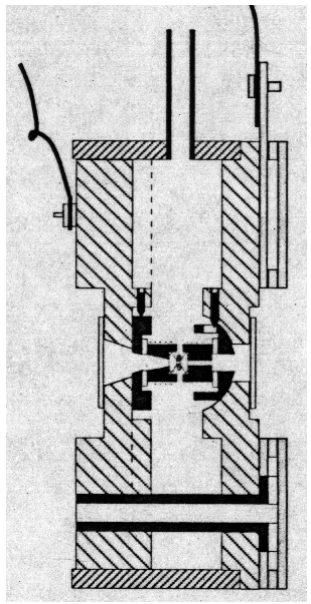
# Experimental Methodology

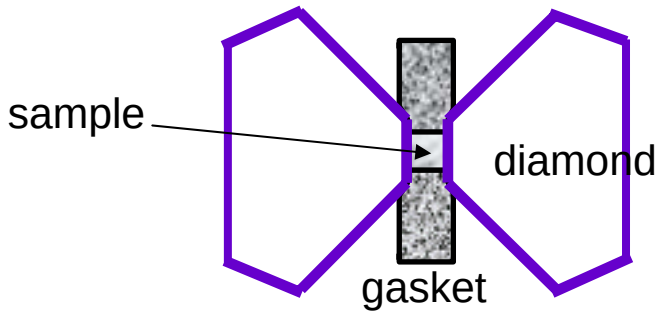
Use **Diamond Anvil Cells** (DAC) with coil Heaters (HDAC) to achieve

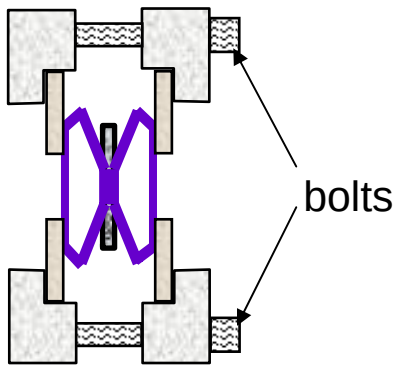
- High pressures (P) to 10 GPa (100 kbars)
- High temperatures (T) to 300°C (up to 1000 °C possible under Argon)
- Any P, T in that range



HDAC

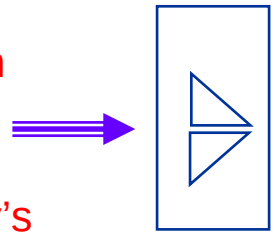




# Angle-Dispersive X-ray Diffraction

White radiation from Cornell University's Synchrotron Source



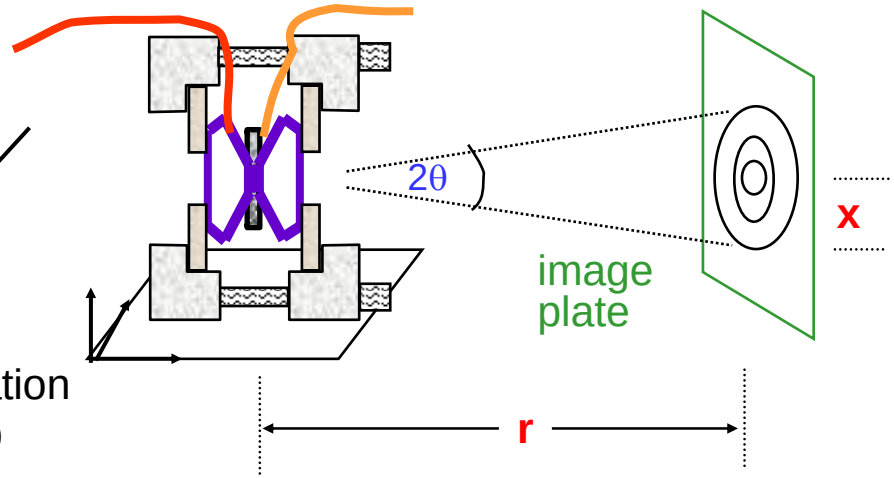
Ge crystals monochromator

collimator

$\lambda$ = 0.48 Å

slits

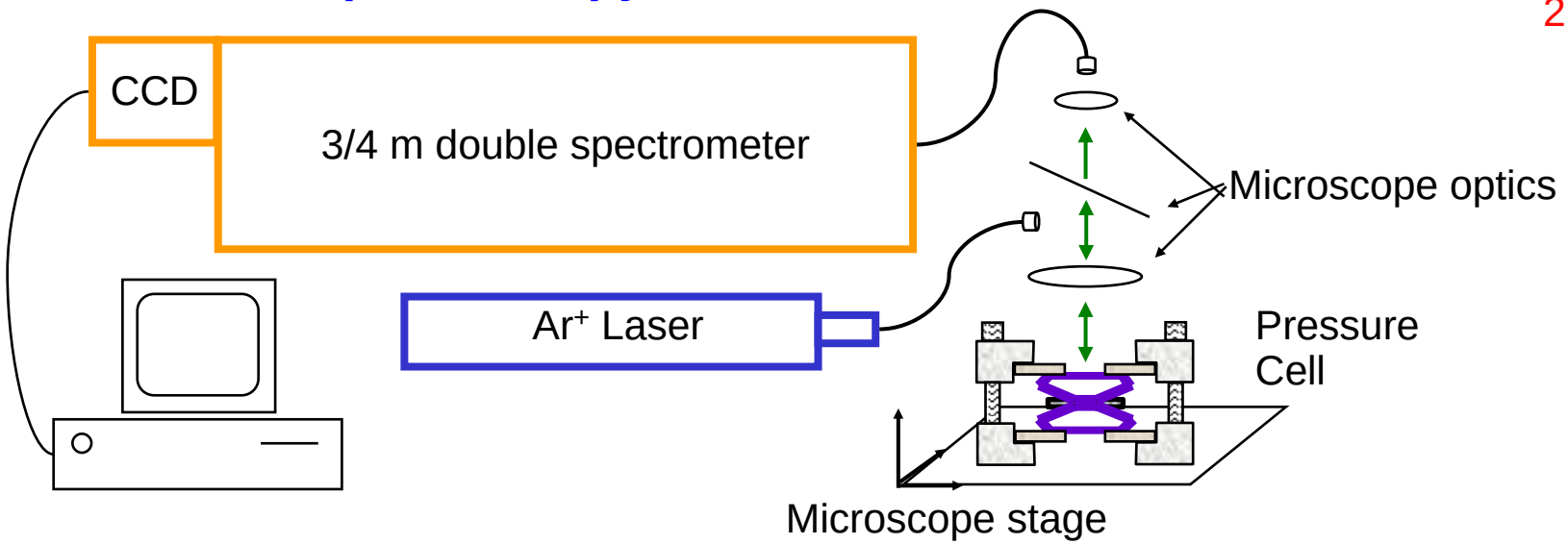
x-y-z translation and 2$\theta$ rotation




$\tan \theta = x/r$

$d = \frac{\lambda}{2 \sin \theta}$.

# Micro-Raman Spectroscopy



# Theoretical Method

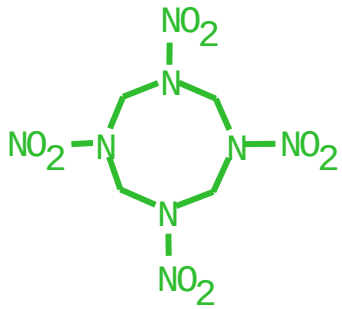
- The zero degree isotherm may be calculated directly from ab-initio techniques
- Both Hartree-Fock method and Density Functional Theory have been used
- Commercially available computer programs such as GAUSSIAN 98[i] and CRYSTAL 98[ii] provide a starting point
- Rigid molecule approximation with additional refinements such as:
  - Self-consistent geometry optimization (the crystalline lattice and the molecule structure)
  - Electronic correlation corrections to correct the total energy
- Calculations require state of the art computational capability and sometimes take 2-4 days to complete


[i]. A. Frisch, M. J. Frisch, *GAUSSIAN98 User's Reference* (Gaussian, Inc., Pittsburgh, 1998).

[ii]. R. Dovesi, V. R. Saunders, C. Roetti, et al., *CRYSTAL98 User's Manual*, University of Torino.

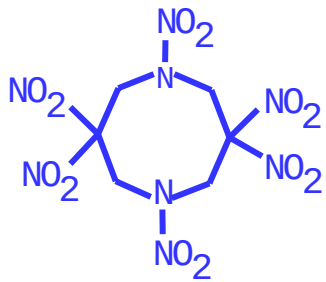
# **Results -** Comparison of HMX, -$NO_2$ and -$NF_2$ analogs

**HMX**



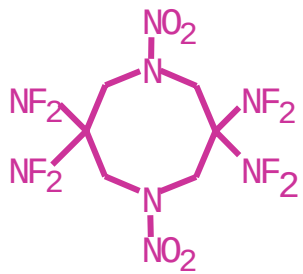

β-HMX = Monoclinic structure
2 molecules/unit cell
ambient P,T density=1.91 g/cc

**HNNX**
**ESW-21**



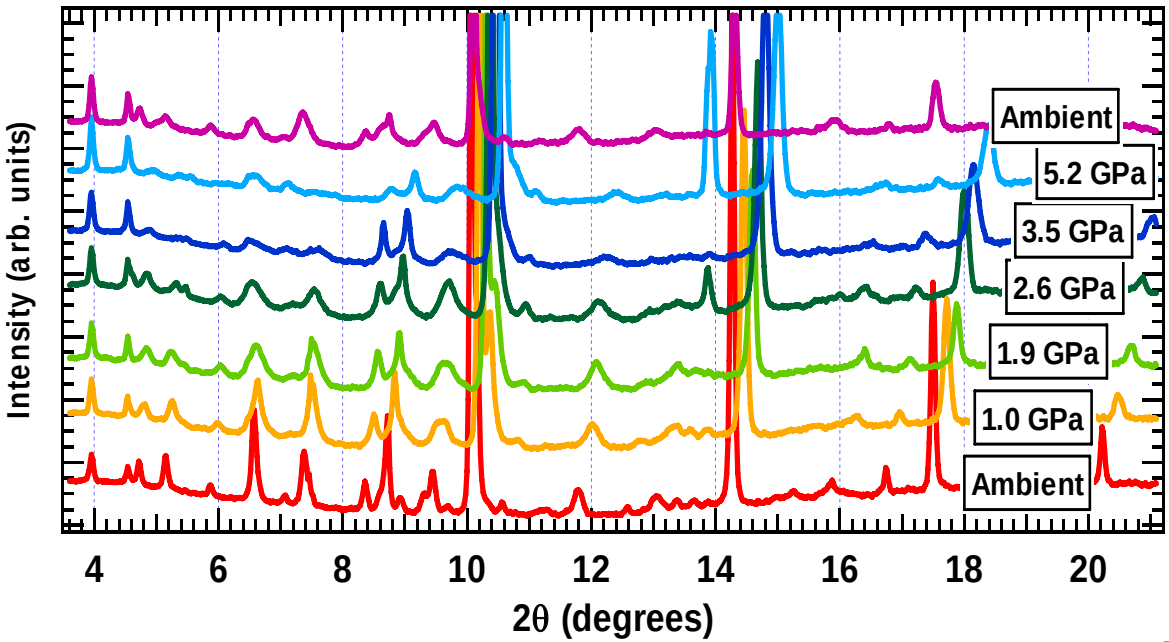

HNNX or ESW-21 = Orthorhombic structure
4 molecules/unit cell
ambient P,T density=1.86 g/cc

**HNFX**



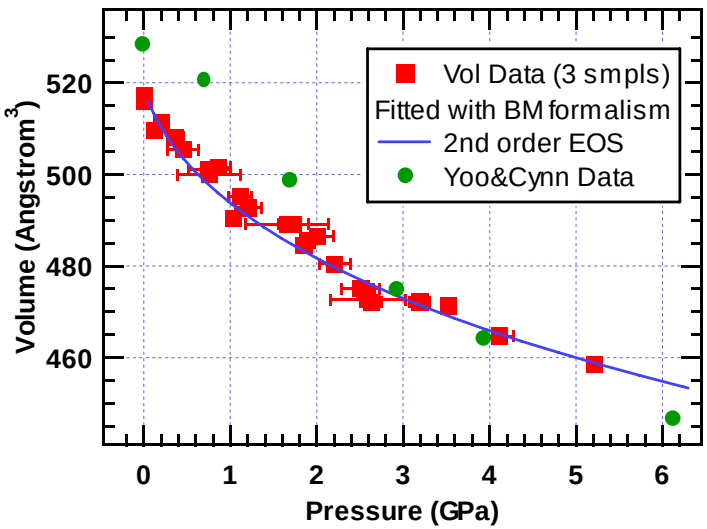

HNFX = Rhombohedral structure
9 molecules/unit cell
ambient P,T density=1.81 g/cc

# HMX Compression at Ambient Temperature




β-HMX is monoclinic with space group: $P2_1/c$

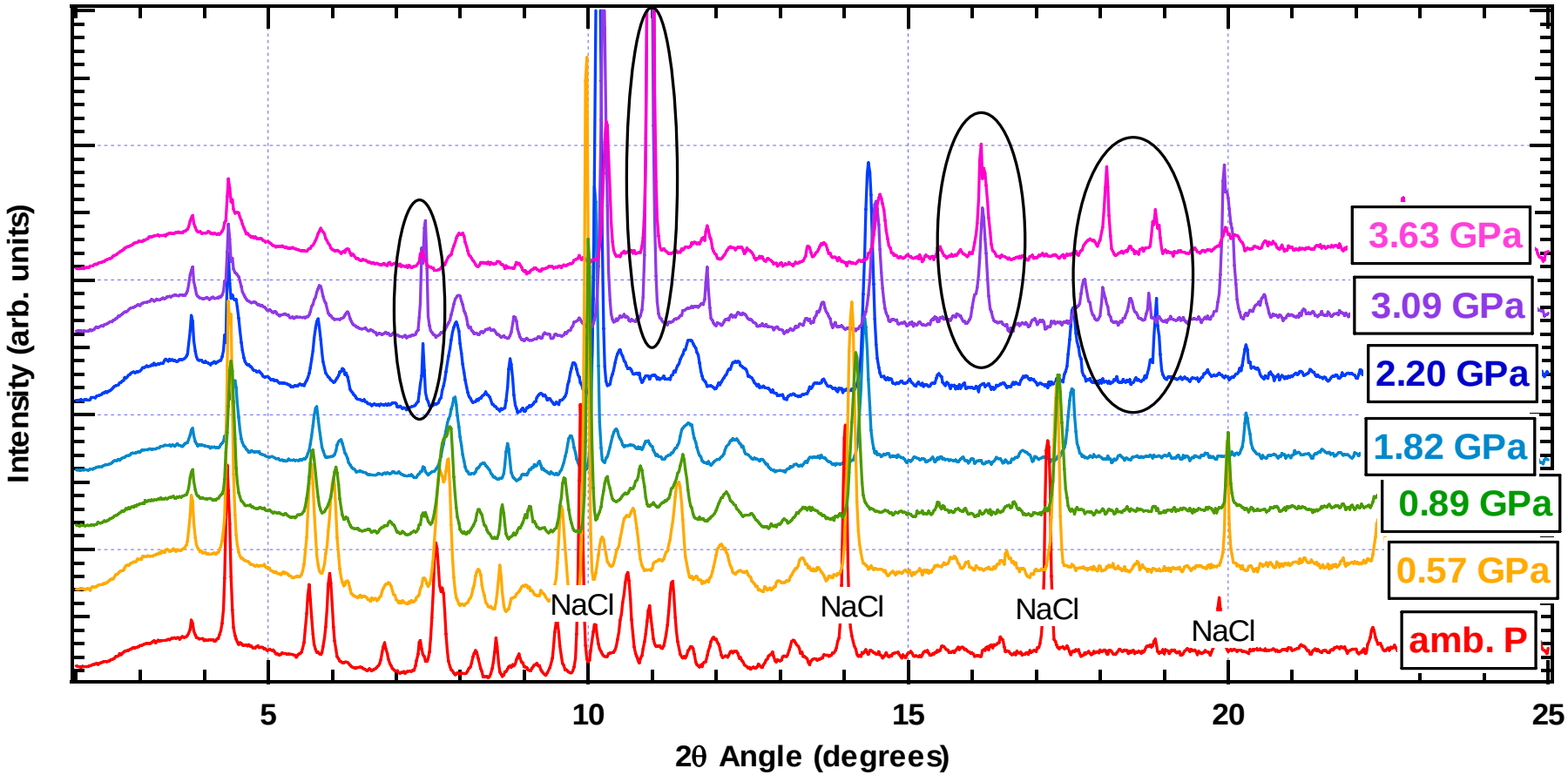
3rd order Birch-Murnaghan Equation of State yields :
Bulk Modulus: 8.9 GPa
Derivative: 46.5




Previous study by Yoo and Cynn (LLNL)
Bulk Modulus: 14.4 GPa  Derivative: 13.3
*non-hydrostatic using 7 data points to 10GPa*

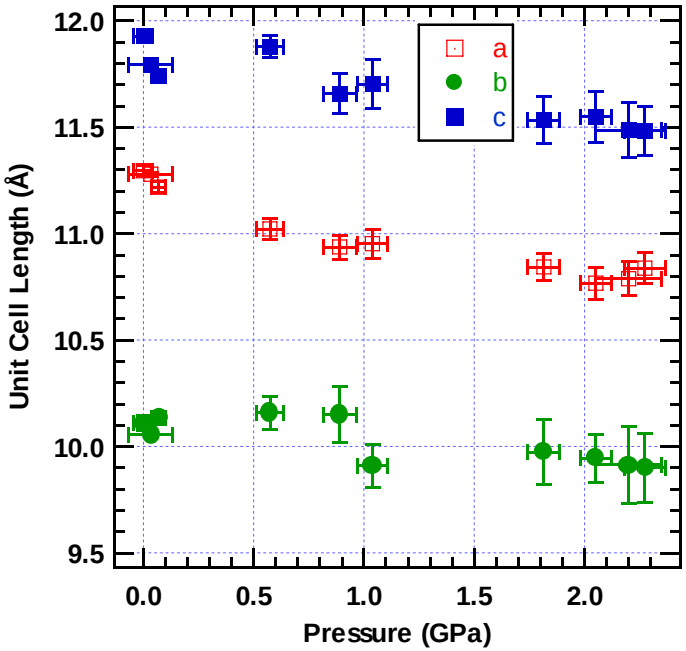
- We have a lot more (26) lower-pressure data.
- Also our data is on RDX-free HMX.
- Our $V_0$ = 518 Å$^3$ as published in ICDD.

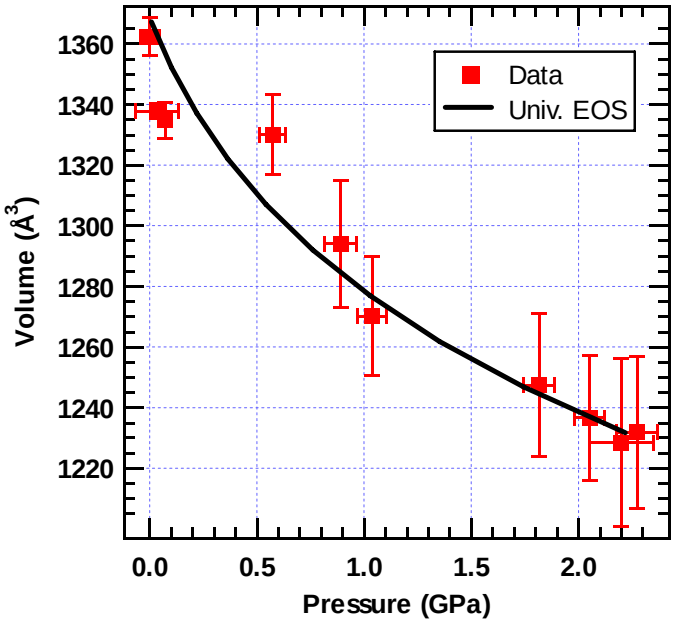
# HNNX Compression at Ambient Temperature




- Ambient pressure orthorhombic lattice is stable to about 2.2 GPa.
- Above that pressure new peaks appear indicating a phase transition.

# Isothermal EOS of HNNX



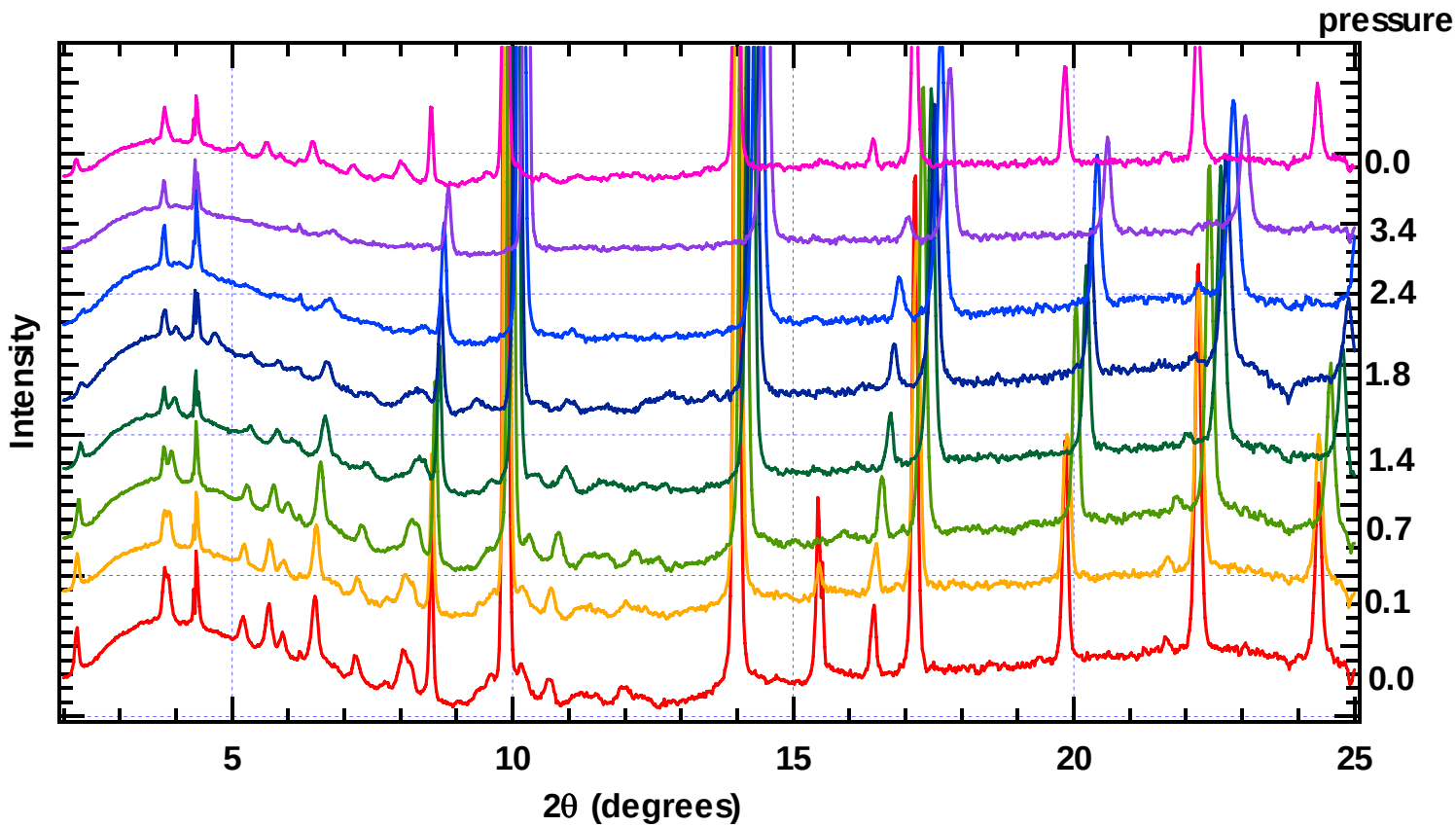

- The compression of the unit cell a, b and c axes flatten towards 2.0 GPa also indicating a phase transition
- Above 2.3 GPa, the ambient pressure orthorhombic lattice can no longer be assumed.

Univ. EOS formalism (using data to 2.3 GPa):

$K_0$ = 7.46 ± 2.45 GPa

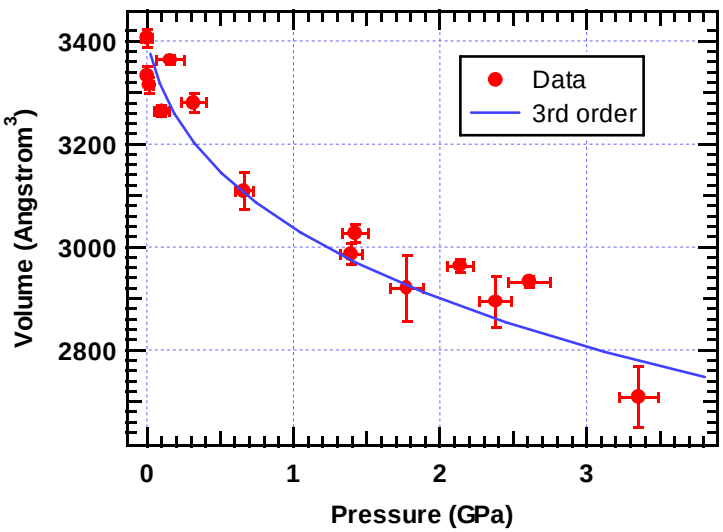
$K_0$' = 20.0 ± 7.3

# HNFX Compression at Ambient Temperature




- The ambient pressure Rhombohedral (R-3) lattice is stable to 3.4 GPa, the highest pressure achieved in study.
- Decompression returns the ambient pressure structure with lower density!

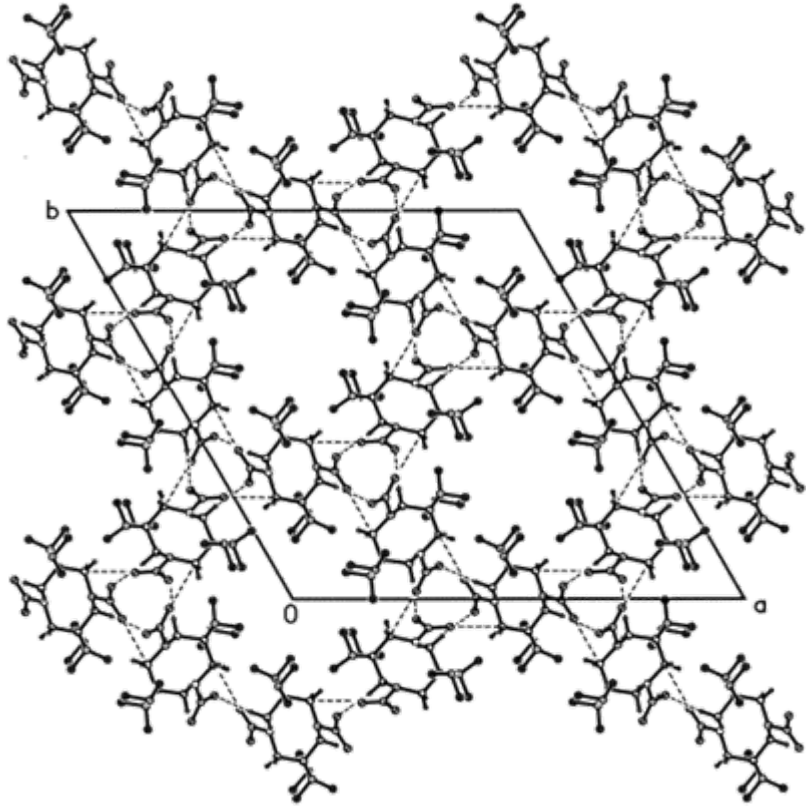
# High Compressibility of HNFX




Bulk Modulus: 2.0 GPa
Derivative : 44

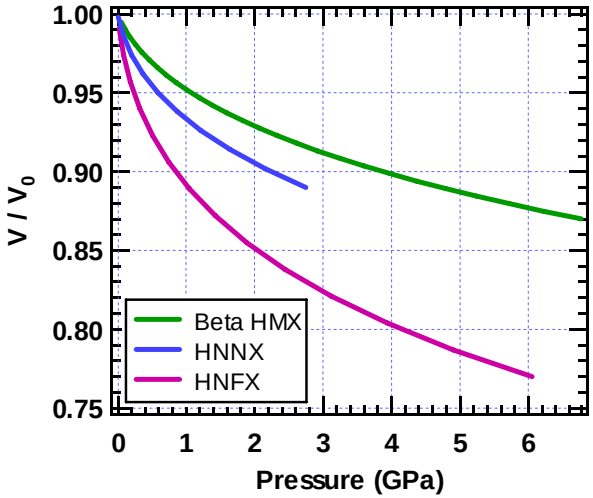
Extremely compressible at near-ambient pressure.

**Decompresses with a larger volume than pre-compression $V_0$**

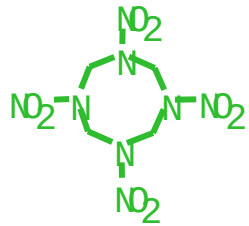



A view down the *c* axis showing the packing of HNFX. Empty channels occur along the 3-fold axes at (0,0,z), a corner of the cell, and at ( 1/3, 2/3, z) and ( 2/3, 1/3, z) within the cell.
From: Chapman, Gillardi et al. *J. Org. Chem.,* **64***,* 963 (1999).

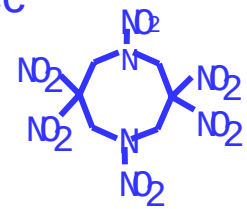
# Comparison



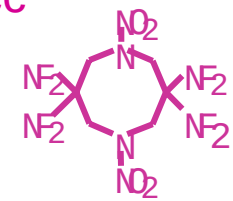

β-HMX = Monoclinic structure ρ=1.91 g/cc
Bulk Modulus: 8.9 GPa
**Compressibility = 0.11**
Derivative: 46.5



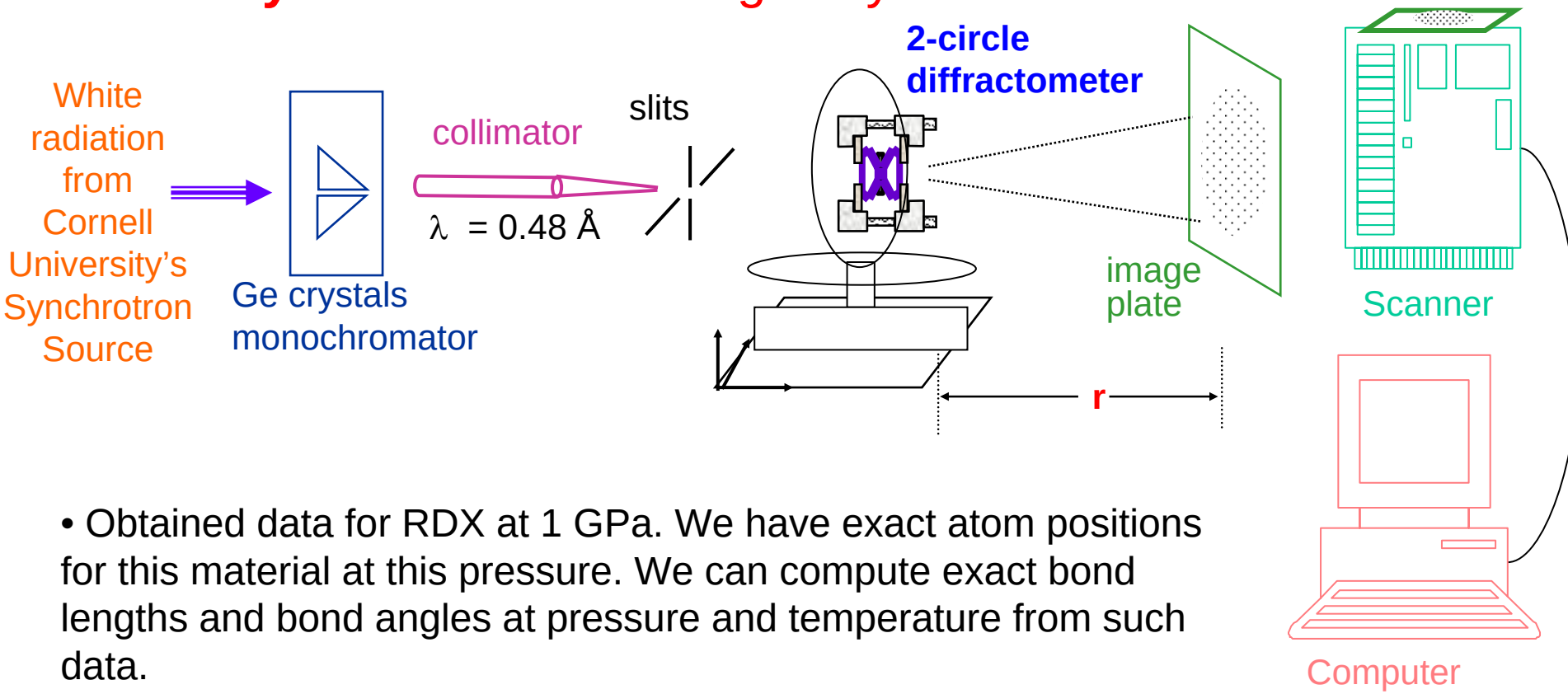
HNNX = Orthorhombic structure ρ=1.86 g/cc
Phase transition at 2.2 GPa
Bulk Modulus: 7.46
**Compressibility = 0.14**
Derivative = 20.0 ± 7.3



HNFX = Rhombohedral structure ρ=1.81 g/cc
Bulk Modulus: 2.0 GPa
**Compressibility = 0.50**
Derivative : 44.3



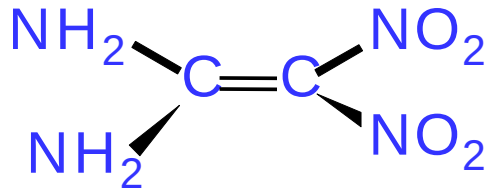
# **Preliminary Results -** RDX single crystal diffraction

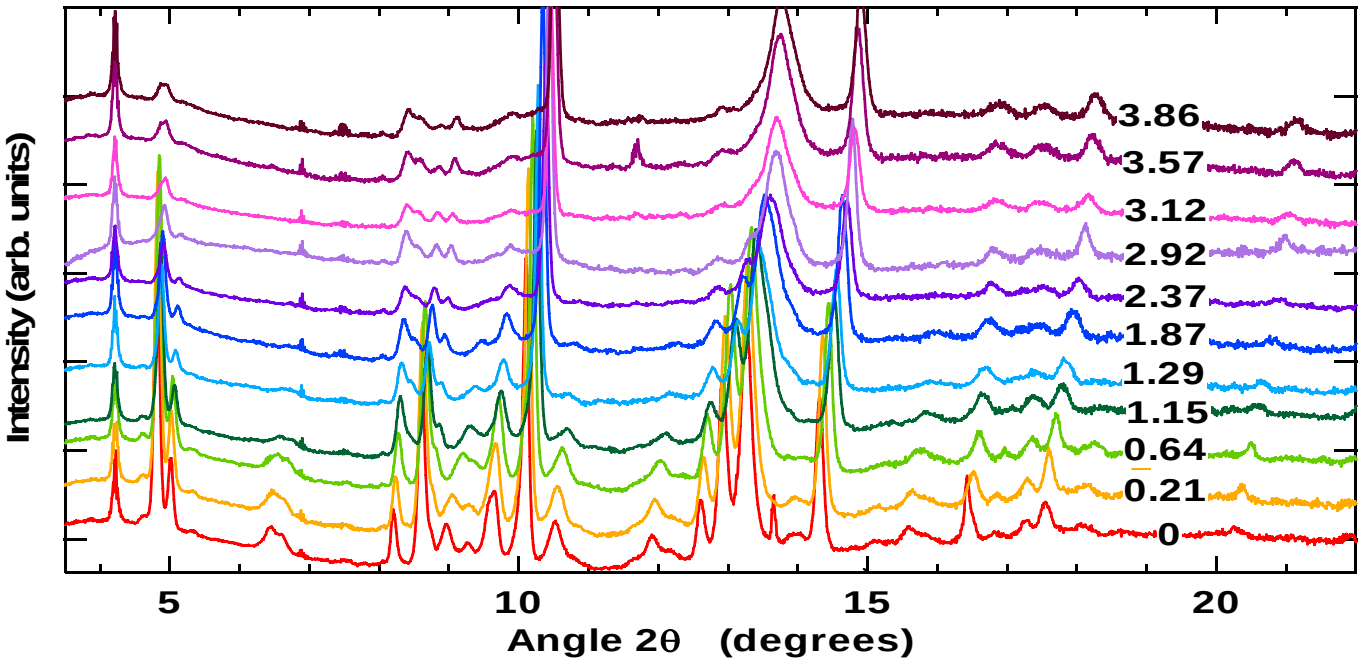



- Obtained data for RDX at 1 GPa. We have exact atom positions for this material at this pressure. We can compute exact bond lengths and bond angles at pressure and temperature from such data.
- Previously published phase transition of RDX at 3.5 GPa to a high-pressure phase.
- We intend to find the lattice symmetry of this high pressure and identify that phase.

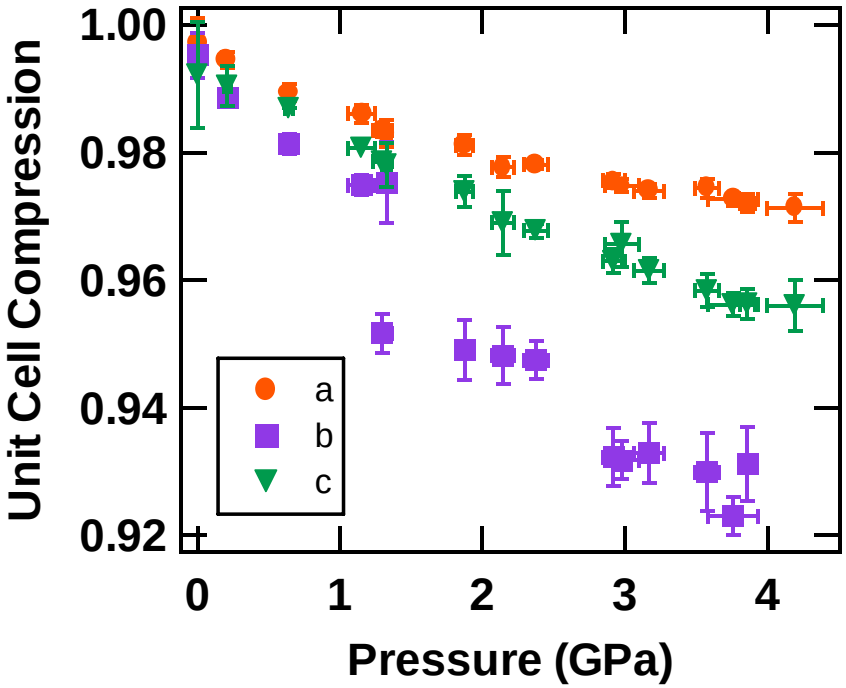
# Compression of FOX-7 at ambient temperature: Lattice and molecular symmetry changes

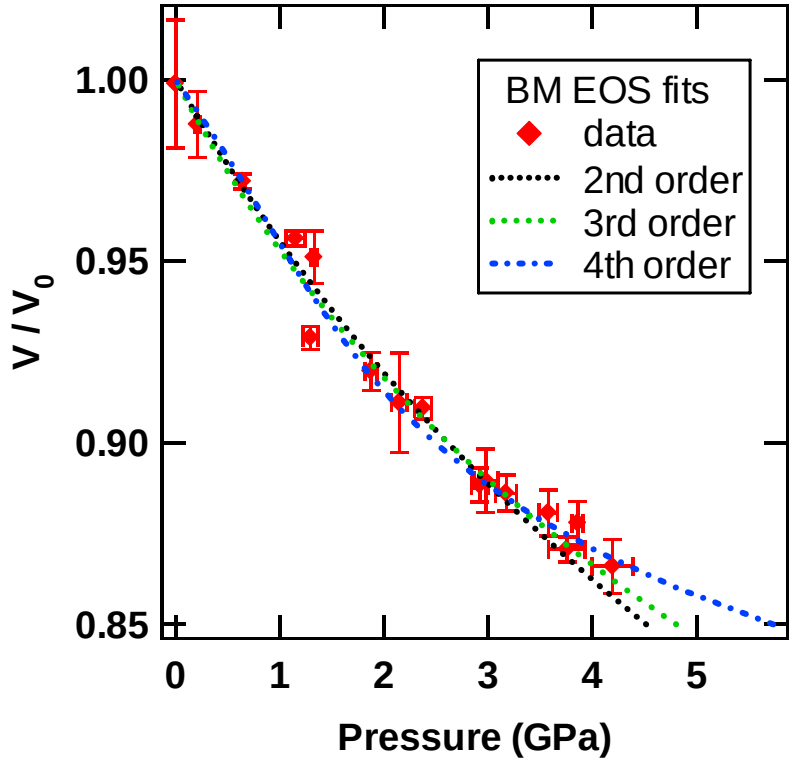
**FOX-7 = DiAmino DiNitro Ethylene (DADNE)**




- Monoclinic lattice is stable to 4.2 GPa (possibly a transition above 5 GPa)
- Some peaks indicate faster compression than others = **anisotropic compression**




- Above 1.1 GPa, the “b” axis (inter layer) compresses faster than the “a” or “c”.

- Anisotropic compression but no change in lattice symmetry

Birch-Murnaghan : 3rd order

**$K_0$ = 17.9 ± 1.4 GPa**

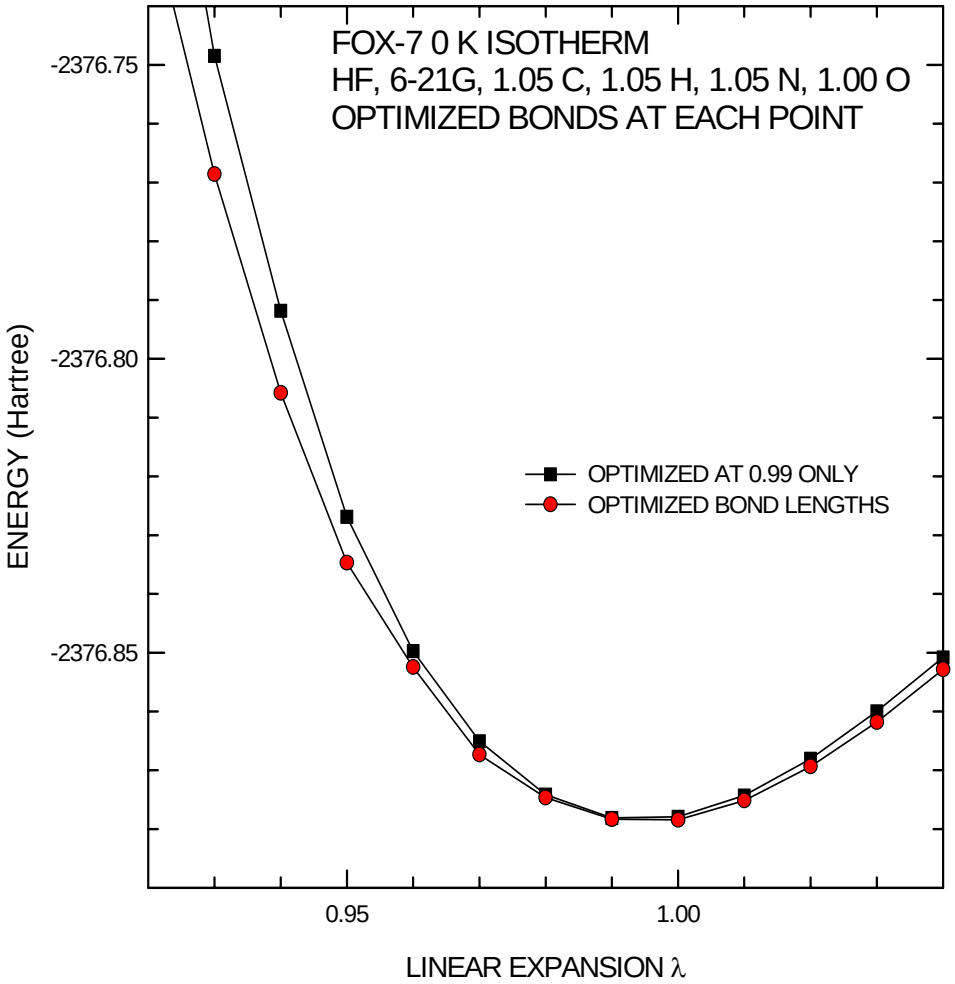
**$K_0'$ = 6.6 ± 4.2**

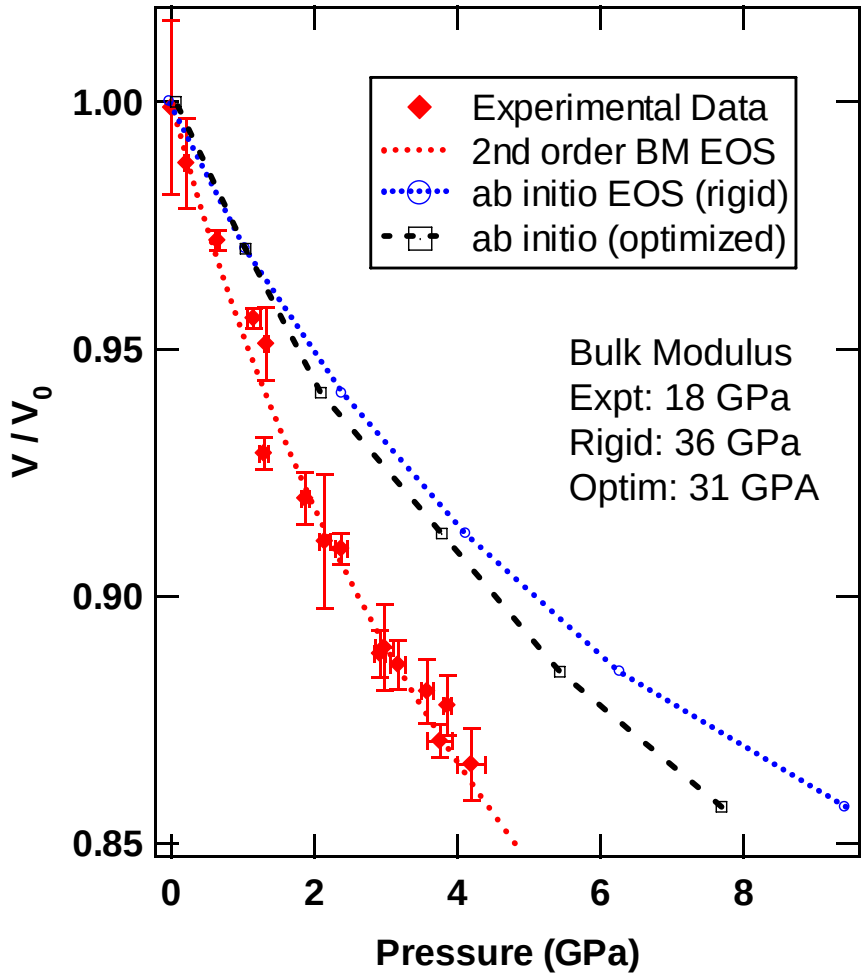
Latest results indicate a phase transition in FOX-7 at above 5 GPa, at room temperature - the data is not yet analyzed completely.

# Ab-initio Hartree-Fock Isothermal (0K) EOS Calculations using Gaussian 98

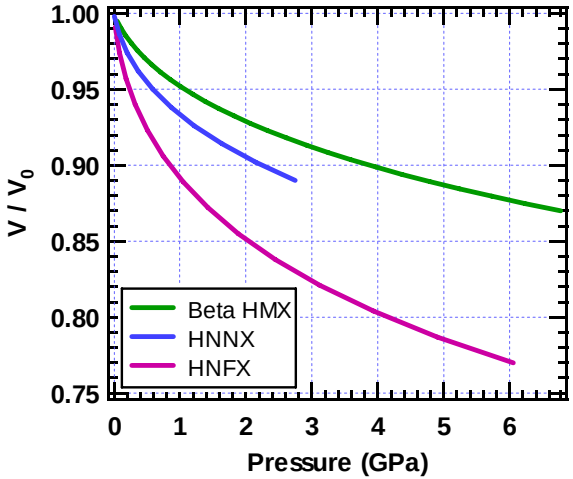
- simple rigid-molecule approximation
- molecule (bonds and angles) optimized using Crystal 98

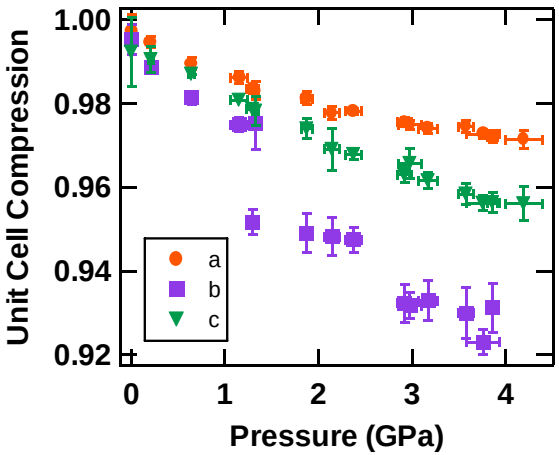
Calculations by Dr. F. J. Zerilli and M. M. Kukla



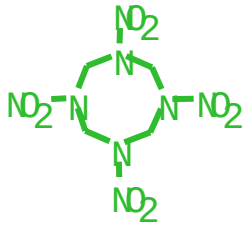



# Conclusions

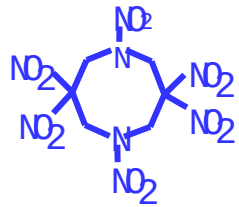


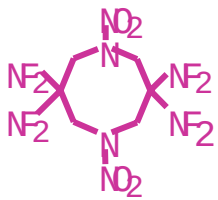




- We are just beginning to understand the effect of high P and T. These effects will be greater as P and T approach that of detonation.



- Experimental and ab-initio EOS and lattice symmetry studies for **HMX**, **HNNX** and **HNFX** show a phase transition in HNNX, with HNFX being extremely compressible.
- Ab-initio calculations show that accuracy for molecules more complex than HMX require less assumptions





- **FOX-7** experiments show anisotropic compression with a discontinuous change at about 1.1 GPa. Other vibrational mode shifts show increased H-bonding. Symmetry changes above 5 GPa are being investigated.
- Ab-initio calculations with optimized bonds do result in better fits to real data