

TNT Polymorphs under Hydrostatic Compression: A Combined Neutron Diffraction and Density Functional Theory Investigation.

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Keywords: Neutron diffraction, Rietveld refinement, Equation of state, High pressure, Energetic materials, TNT.

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Energetic materials (propellants, explosives and pyrotechnics), are widely used in applications that include mining, munitions, and automotive safety. Key properties of these materials include: reliable performance under a range of environmental conditions (pressure, temperature, humidity etc); long-term stability; environmental impact; processability; sensitivity to accidental initiation through stimuli such as impact, shock, friction, and electrostatic discharge. Many of these properties are affected by the crystal structure of the energetic material. Explosives experience elevated pressures and temperatures under detonation conditions – such conditions often induce phase transitions in the energetic material. Hence detailed studies of pressure-induced structural changes in these materials are essential in order to understand and model fully their behaviour.

2,4,6-Trinitrotoluene (TNT) is one of the most widely used secondary explosives, and was the main explosive used throughout the First World War. A high-pressure

neutron diffraction study was conducted on powders of the two known polymorphs of TNT (monoclinic and orthorhombic) under hydrostatic conditions (Figure 1). Isothermal equations of state were measured for both phases. Neither phase was observed to undergo a phase transition in the pressure region 0-5 GPa, with both phases displaying monotonic compression across the pressure range. This differs somewhat from previous XRD and Raman spectroscopy investigations in which discontinuities were observed in the P-V curve and spectral changes were noticed at ~2 GPa. The high-pressure response of these materials is supported by dispersion-correct DFT calculations which, while overestimating the experimental bulk moduli values, give excellent agreement with the observed smooth compression response of both phases. Computed electronic band gaps are very similar for both polymorphs, suggesting, within the band gap criterion model, that the reactivity of both forms of TNT will be very similar.

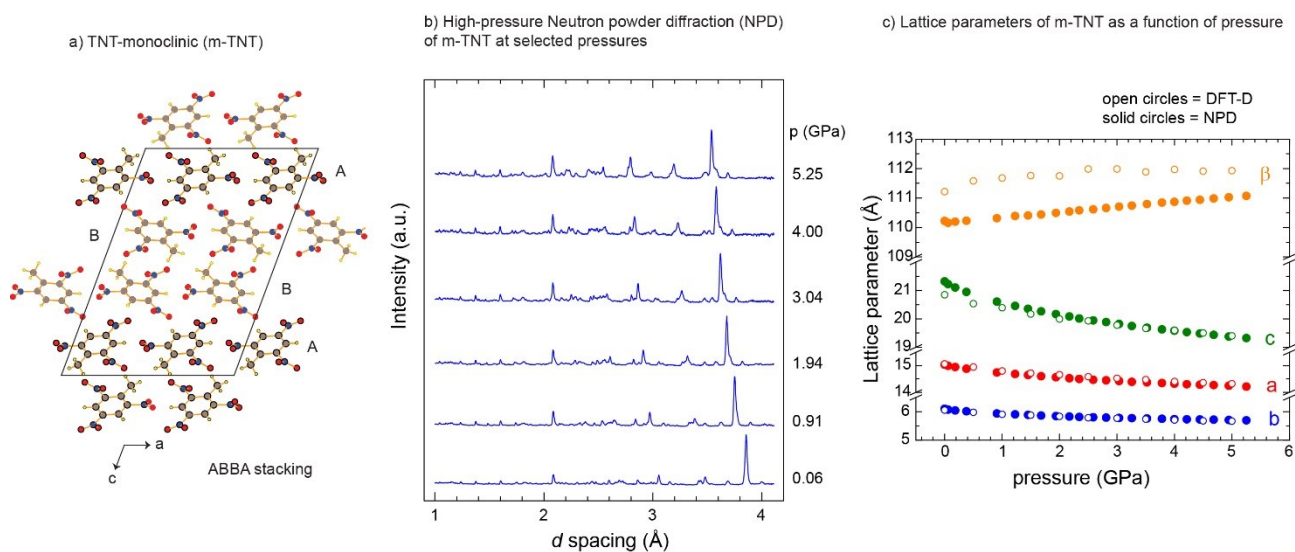


Figure 1: a) Crystal structure of TNT-monoclinic; b) selected high-pressure NPD patterns obtained using paris edinburgh apparatus at PEARL (ISIS); c) changes of lattice parameter with pressure, note there is an excellent between match between DFT-D and experimental results.