First-Principles Studies of Energetic Materials

by

Michael W. Conroy

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Department of Physics
College of Arts and Sciences
University of South Florida

Major Professor: Ivan I. Oleynik, Ph.D.
Dale Johnson, Ph.D.
Lilia Woods, Ph.D.

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First-Principles Studies of Energetic Materials

Michael W. Conroy

ABSTRACT

First-principles density functional theory calculations were performed on a number of important energetic molecular crystals, pentaerythritol tetranitrate (PETN), cyclotetramethylene tetranitramine (HMX), cyclotrimethylene trinitramine (RDX), and nitromethane. Simulations of hydrostatic and uniaxial compressions, as well as predictions of ground-state structures at ambient conditions, were performed using the DFT codes CASTEP and VASP.

The first calculations done with CASTEP using GGA-PW yielded reasonable agreement with experiment for the calculated isothermal EOS for PETN-I from hydrostatic compression data, yet the EOS for $\beta$-HMX shows substantial deviation from experiment. Interesting anisotropic behavior of the shear-stress maxima were exhibited by both crystals upon uniaxial compression. It was predicted that the $\langle 100 \rangle$ direction, the least sensitive direction of PETN, has significantly different values for shear stress maxima $\tau_{yx}$ and $\tau_{zx}$, in contrast to the more sensitive directions, $\langle 110 \rangle$ and $\langle 001 \rangle$. In addition, non-monotonic dependence of one of the shear stresses as a function of strain was observed upon compression of PETN in the $\langle 100 \rangle$ direction.
VASP calculations were later performed, and the results yielded good qualitative agreement with available experimental data for the calculated isothermal EOS and equilibrium structures for PETN-I, β-HMX, α-RDX, and nitromethane. Using VASP, uniaxial compression simulations were performed in the <100>, <010>, <001>, <110>, <101>, <011>, and <111> directions for all crystals up to the compression ratio V/V₀ = 0.70. The VASP calculations of PETN reproduced the CASTEP results of significantly different values of τyx and τzx for the insensitive <100> compression, and relatively high and equal values of τyx and τzx for the sensitive <110> and <001> compressions. A correlation between this behavior of shear stress upon uniaxial compression and sensitivity was suggested, and predictions of anisotropic sensitivity of HMX, RDX, and nitromethane were made.

Further analysis of the VASP results for PETN do not indicate a correlation between sensitivity and shear stress maxima as a function of longitudinal stress, where longitudinal stress is an appropriate experimental independent variable for comparison. The validity of a correlation between shear stress maxima and sensitivity requires further investigation. Further characterization of the anisotropic constitutive relationships in PETN was performed.
First principles calculations treat systems on the atomic level using quantum mechanics, with the intent of using as few approximations as feasibly possible. An exceptional theoretical tool for the implementation of first-principles calculations is density-functional theory (DFT), which the development of DFT earned Walter Kohn a Nobel Prize in Chemistry in 1998. DFT was a revolutionary development in that it made accurate calculations possible for large systems, such as solids and large molecules. Numerous additional efforts to make calculations of this type possible have been undertaken, and the advance in computer hardware technology has made very accurate first-principles calculations on large systems possible in the last two decades. In particular, energetic materials, with large unit cells and complex molecular geometries, have only recently become possible to study via the first-principles methodology.

The use of first-principles calculations has allowed for exceptional insight into the fundamental physics and chemistry involved in energetic materials research. Since experimentation with these materials can be difficult and costly, the use of theoretical simulation has proven to be a time- and cost-effective strategy for the investigation of energetic materials. Importantly, the physical processes involved in the initiation of detonation in these materials at the atomic level are not well understood. Simulation from
first-principles and comparison with experimental data may help elucidate the microscopic mechanisms responsible for the explosive reactions that these materials are known for.

PETN (pentaerythritol tetranitrate) exhibits anisotropic shock-initiation sensitivity upon uniaxial compression, which was discovered by J. Dick\textsuperscript{1}. In fact, detonation has occurred when the crystal is compressed in sensitive directions at longitudinal stresses that may be simulated by first-principles calculations. By investigating the calculated atomic-scale properties upon compression in the sensitive directions in contrast to the properties observed from compression in less sensitive directions, it may be possible to identify fundamental factors due to intrinsic structural and chemical properties of PETN contributing to this strong anisotropy. Importantly, once mechanisms of sensitivity to detonation are identified, it is quite possible that these mechanisms may be extended to predict the initiation behavior in several other important energetic materials with similar properties, such as HMX, RDX, and nitromethane.

This work presents first-principles calculations of the energetic materials PETN, HMX, RDX, and nitromethane. In Section II, a brief overview of the important ideas and methods involved in first-principles calculations is provided. Section III provides a summary of the motivation and goals of this work, as well as the important accomplishments and conclusions. Sections IV-VIII each contain articles that either have been published or will be submitted for publishing, and these articles summarize the work that we have done in the application of first-principles simulation to energetic materials.
II. FIRST-PRINCIPLES CALCULATIONS

The goal of employing first-principles methods is to calculate the physical and chemical properties of materials by using the fundamental equations of quantum mechanics with minimal approximations. Calculations of this type are also called *ab-initio* calculations, meaning “from the beginning” in Latin. The purpose of this section is to briefly describe some of the important equations and approximations used in the first-principles calculations described in Sections IV-VIII.

A. A system of interacting electrons and nuclei

The fundamental particles considered in a treatment of solids are the nuclei (neutrons and protons) and the electrons. A system of this type may be described by the many-body Hamiltonian\(^2\)

\[
\hat{H} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_i \frac{\hbar^2}{2M_i} \nabla_i^2 - \sum_{i,j} \frac{Z_i e^2}{|r_i - R_j|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} + \frac{1}{2} \sum_{i \neq j} \frac{Z_i Z_j e^2}{|R_i - R_j|} \tag{2.1}
\]

where the lower-case subscripts represent electrons and the upper-case subscripts are used for the nuclei. The first two terms represent the kinetic energy of the electrons and the nuclei, respectively. The third term represents the interaction of the electrons with the
nuclei, the fourth is due to the electron-electron interaction, and the fifth term describes the interactions between nuclei. A very brief description of the approximations used to handle this Hamiltonian is given below.

1. **Kinetic energy of the nuclei**

   The only term in (2.1) that can be considered small is the term that provides the kinetic energy of the nuclei\(^2\). Since the mass of the nucleus is very large compared to the electrons, the quantity \((1/M)\) is very small. Using the Born-Oppenheimer approximation, one may essentially “freeze” the positions of the nuclei and abate the many-body problem by considering only the dynamics of the electrons\(^3\). Hence, the kinetic energy of the nuclei would be neglected under this approximation. Equation 2.1 can then be reduced to

   \[
   \hat{H} = \hat{T} + \hat{V}_{\text{int}} + \hat{V}_{\text{ext}} + E_H \tag{2.2}
   \]

   where \(\hat{T}\) denotes the kinetic energy of the electrons, \(\hat{V}_{\text{int}}\) describes the electron-electron interaction, \(\hat{V}_{\text{ext}}\) is the interaction between the nuclei and the electrons (or the external potential), and \(E_H\) is composed of the additional energy terms that are not inherent to the electrons, such as the classical nuclei-nuclei interaction\(^2\).

2. **Electron-electron interactions**
The most difficult interaction to model is the electron-electron interaction. In the
calculations that follow in Sections IV-VIII, density-functional theory (DFT) was used to
treat this interaction. The two major works that formulated DFT were by Hohenberg and
Kohn\(^4\) in 1964 and by Kohn and Sham\(^5\) in 1965.

In the first work, Hohenberg and Kohn\(^4\) showed that there exists a unique external
potential \(\hat{V}(r)\) that determines a given ground-state charge density \(n(r)\) of a system of
interacting electrons in the presence of nuclei, which was named the Hohenberg-Kohn
theorem. An important consequence of this theorem is that the ground-state charge
density uniquely determines the ground-state energy of such a system, and hence the
ground-state energy \(E[n(r)]\) is a functional of the 3-dimensional charge-density function
\(n(r)\),

\[
E[n(r)] = \langle \Psi | \hat{T} + \hat{V}_{\text{int}} + \hat{V}_{\text{ext}} | \Psi \rangle = \langle \Psi | \hat{T} + \hat{V}_{\text{int}} | \Psi \rangle + \langle \Psi | \hat{V}_{\text{ext}} | \Psi \rangle,
\]

where \(F[n(r)]\) is a functional of \(n(r)\)\(^6\) describing the electron-electron interaction and the
integral of the product of density and the external potential depicts the electron-nuclei
interaction. Approximations used in first-principles calculations for dealing with the latter
will be covered in the next section. When the functional \(E[n(r)]\) is minimized with
respect to \(n(r)\), this yields the ground-state energy of a system. The advantage of this
result is that the original many-body problem is exactly reduced to finding the 3-
dimensional charge-density that minimizes the functional $E[n(r)]$. However, $F[n(r)]$ is not known, which does not allow the direct application of (2.3).

In the second work, Kohn and Sham\(^5\) showed that a system of interacting electrons with ground-state density $n(r)$ can be mapped exactly to a system of non-interacting electrons with the same density, facilitating the solution of the problem. In this framework, single-electron orbitals, named Kohn-Sham orbitals $\psi_j$, are the solutions of the self-consistent Kohn-Sham equations\(^6\),

$$\left[\hat{T}_s + \hat{V}_{\text{ext}}(r) + \hat{V}_{\text{H}}(r) + \hat{V}_{\text{xc}}(r)\right] \psi_j(r) = E_j \psi_j(r),$$  \hspace{1cm} (2.4)

and the energy functional (2.3) can be rewritten as\(^6\)

$$E[n(r)] = T_s[n(r)] + E_H[n(r)] + E_{\text{xc}}[n(r)] + \int n(r) V_{\text{ext}}(r) \, dr.$$  \hspace{1cm} (2.5)

$T_s$ is the kinetic energy of the non-interacting electrons\(^6\),

$$T_s[n(r)] = -\frac{\hbar^2}{2m_e} \sum_j \int \nabla \psi_j^*(r) \nabla \psi_j(r) \, dr,$$  \hspace{1cm} (2.6)

$E_H$, which includes electrostatic interactions, is known as the Hartree energy,

$$E_H[n(r)] = \frac{e^2}{2} \int \frac{n(r)n(r')}{|r-r'|} \, dr \, dr',$$  \hspace{1cm} (2.7)

and $E_{\text{xc}}$, which is known as the exchange-correlation energy, is made up of all the terms that remain\(^6\). In other words, the terms which provide a large contribution to the total energy and are easy to calculate have been clearly expressed, and the rest of the terms are hidden in $E_{\text{xc}}$, whose exact functional form is not known. Fortunately, there are approximations to the exchange-correlation energy functional, such as the local-density approximation.
approximation\textsuperscript{7} (LDA) and the generalized-gradient approximation (GGA) with the PW91\textsuperscript{8, 9} and PBE\textsuperscript{10, 11} functionals, that have been successful in describing physical properties of systems, such as energy differences between structures and structural parameters, to within a few percent of experiment\textsuperscript{3}.

In a first-principles calculation, the Kohn-Sham equations are solved self-consistently, such that an initial guess for the density is made to calculate the potential used to solve the Kohn-Sham equations, and the resulting density is compared with the original guess for self-consistency\textsuperscript{2}. If the two densities are not equal within a specified tolerance, the density is strategically updated and another cycle begins, and this whole process continues until self-consistency is reached\textsuperscript{2}.

3. Electron-nuclei interactions

The valence electrons participate in almost all of the important chemical and solid-state phenomena for which first-principles calculations are used to predict, but the core electron states stay almost unchanged. The use of pseudopotential theory\textsuperscript{12} in first-principles calculations replaces the real potential experienced by the valence electrons from the nucleus and core states by a weaker potential, called a pseudopotential. The weakening of the potential allows the wavefunctions to be expanded in a much smaller set of plane-waves, making the calculation of this interaction computationally feasible\textsuperscript{3}. Meanwhile, several of the important features of the real potential are maintained by the pseudopotential, and these vary depending on the type of pseudopotential used for a calculation.
B. Periodic systems

For periodic solids, the Bloch theorem states that the wavefunction for each electron can be written as the product of a periodic function and a plane wave,

$$\psi_j(r) = f_{jk}(r) \exp[i\mathbf{k} \cdot \mathbf{r}],$$  \hspace{1cm} (2.8)

where the periodic function $f_{jk}(r)$ has the same periodicity as the underlying crystal lattice. The periodic portion of the wavefunction $f_{jk}(r)$ may be expanded with a discrete set of plane waves as basis functions

$$f_{jk}(r) = \sum_{G} c_{jk} \exp[i\mathbf{G} \cdot \mathbf{r}],$$  \hspace{1cm} (2.9)

where $\mathbf{G}$ are the reciprocal lattice vectors of the crystal. Thus, the wavefunctions can be written as a sum of plane waves

$$\psi_j(r) = \sum_{G} c_{j,k+G} \exp[i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}].$$  \hspace{1cm} (2.10)

This allows the electronic wavefunctions at each $\mathbf{k}$ point to be expanded in a discrete set of plane waves. Though discrete, the basis set would still need to be infinite to completely expand the wavefunction. However, the constants $c_{j,k+G}$ corresponding to lower kinetic energy are more important than those at higher kinetic energy. A cutoff kinetic energy can be specified to truncate the basis set, allowing a finite basis to expand the electronic wave functions at each $\mathbf{k}$ point. In practice, one can determine an
appropriate cutoff by increasing the kinetic energy cutoff of the basis set until the total energy of the system converges.

The occupied states at each \( k \)-point contribute to the electronic potential, and there are an infinite number of \( k \) points to consider in an infinite solid. However, the electronic wave functions do not change much in a region around a given \( k \) point. Thus, a single \( k \) point can be used to represent a small region of \( k \) space. Procedures for finding a special set of \( k \) points that will yield accurate total energies have been devised, and in the calculations that follow, the Monkhorst-Pack method was used. Briefly, this method sets up a grid in the Brillouin zone wherein the intersections of the lines forming the grid are the \( k \) points used for a calculation. For practical purposes, the number of grid lines, and hence the density of \( k \) points, can be increased until convergence of the total energy is achieved.

C. Calculation of forces and stress

The Hellmann-Feynman theorem can be used to find the force conjugate to any parameter in the Hamiltonian that is used to describe a system. For instance, the force conjugate to the position of a nucleus \( R_i \) is given by

\[
F_i = -\frac{\partial E}{\partial R_i}.
\]  

(2.11)
By designating the Hamiltonian $H_e$ to include all the terms involving electrons and $E_{II}$ to describe the classical interaction of the nuclei with one another, the derivative above can be expressed from first-order perturbation theory as:

$$-\frac{\partial E}{\partial \mathbf{R}_I} = -\langle \Psi | \frac{\partial \hat{H}_e}{\partial \mathbf{R}_I} | \Psi \rangle - \left\langle \frac{\partial \Psi}{\partial \mathbf{R}_I} | \hat{H}_e | \Psi \right\rangle - \left\langle \Psi | \frac{\partial \hat{H}_e}{\partial \mathbf{R}_I} | \Psi \right\rangle - \frac{\partial E_{II}}{\partial \mathbf{R}_I}. \quad (2.12)$$

Since, in the ground state, energy is a minimum with respect to all variations in the parameters of the wave function, the terms with derivatives of $\Psi$ vanish. Thus, the force conjugate can be found from taking the derivatives of terms with explicit dependence on the parameter $\mathbf{R}_I^2$, given by:

$$-\frac{\partial E}{\partial \mathbf{R}_I} = -\langle \Psi | \frac{\partial \hat{H}_e}{\partial \mathbf{R}_I} | \Psi \rangle - \frac{\partial E_{II}}{\partial \mathbf{R}_I}. \quad (2.13)$$

In the calculations of Sections IV-VIII, the stress tensor is calculated, and stress is a generalized force that may be calculated using the Hellmann-Feynman theorem as well. The stress tensor element $\sigma_{ij}$ is given by:

$$\sigma_{ij} = -\frac{1}{V} \frac{\partial E}{\partial \varepsilon_{ij}}, \quad (2.14)$$

where $V$ is volume, $\varepsilon_{ij}$ is strain, and $i, j$ are Cartesian indices.

Approximations are made in first-principles calculations to reduce the complexity of the interactions of electrons and nuclei via the application of pseudopotentials. Further, these approximations have made first-principles calculations of systems containing hundreds of atoms computationally feasible, and the results yielded have shown remarkable agreement with experiment.
III. SUMMARY OF RESULTS OBTAINED

The first-principles calculations described in Sections IV-VIII were performed on the energetic materials PETN-I, β-HMX, α-RDX, and solid nitromethane. These materials are solids composed of organic molecules arranged in a lattice, and are thus called molecular crystals. Each of these crystals are high explosives\textsuperscript{14} used in mainly military applications. In fact, PETN and RDX played an important role in the explosive compositions employed in World War II\textsuperscript{15}. These materials detonate at high pressures, which makes them excellent systems for the study of microscopic mechanisms responsible for initiation of detonation. Presently, these mechanisms are not well understood.

Further, PETN exhibits a strong shock-induced detonation anisotropy\textsuperscript{1,16-18} upon uniaxial compression. For example, detonation has taken place in the $\langle 110 \rangle$ direction under shock strengths of about 4 GPa\textsuperscript{17}, whereas the first report of detonation in the least sensitive direction, $\langle 100 \rangle$, has been reported at a pressure of about 31 GPa\textsuperscript{18}. Under the hypothesis that mechano-chemical reactions may arise in regions of great shear stress in these materials, the investigation of a correlation between shear stresses and shock-initiation sensitivity was performed. The articles in Sections IV-VIII report the results of this analysis.
The major accomplishments of the work that follows are

- The equilibrium structures, hydrostatic compression, and uniaxial compressions of PETN-I and β-HMX along selected crystallographic directions were calculated using the DFT code CASTEP\textsuperscript{19}.
- The CASTEP results indicate non-monotonic dependence of shear stress maxima on strain in PETN for the insensitive direction <100>, but not for the sensitive direction, <110>. A correlation is suggested and further work was started to investigate this possibility.
- The equilibrium structures, hydrostatic compressions and expansions, and uniaxial compressions and expansions in the <100>, <010>, <001>, <110>, <101>, <011>, and <111> directions of PETN-I, β-HMX, α-RDX, and solid nitromethane were calculated using the DFT code VASP\textsuperscript{20, 21} with the PBE functional\textsuperscript{10, 11} and PAW potentials\textsuperscript{22, 23}.
- The VASP results indicate that the shear-stress maxima at compression ratio \( V/V_0 = 0.7 \) are greater for uniaxial compression of PETN in the sensitive directions than for the insensitive directions. Based on this observation, a suggestion of possible anisotropic shock-initiation sensitivity was made for β-HMX, α-RDX, and solid nitromethane.
- Upon further investigation of the shear-stress maxima as a function of longitudinal stress and comparison with experimental data, no clear correlation between shear-stress maxima and shock-initiation sensitivity is indicated by the uniaxial-compression data of PETN.
IV. ENERGETIC MATERIALS AT HIGH COMPRESSION: FIRST-PRINCIPLES DENSITY FUNCTIONAL THEORY AND REACTIVE FORCE FIELD STUDIES

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ENERGETIC MATERIALS AT HIGH COMPRESSION: FIRST-PRINCIPLES DENSITY FUNCTIONAL THEORY AND REACTIVE FORCE FIELD STUDIES

I.I. Oleynik\textsuperscript{1}, M. Conroy\textsuperscript{1}, S.V. Zybin\textsuperscript{2}, L. Zhang\textsuperscript{2}, A.C. van Duin\textsuperscript{2}, W.A. Goddard III\textsuperscript{2} and C. T. White\textsuperscript{3}

\textsuperscript{1}Department of Physics, University of South Florida, Tampa, FL 33620
\textsuperscript{2}Materials and Process Simulation Center, California Institute of Technology, Pasadena, CA 91125
\textsuperscript{3}Naval Research Laboratory, Washington, DC 20375

Abstract. We report the results of a comparative study of pentaerythritol tetranitrate (PETN) at high compression using classical reactive interatomic potential ReaxFF and first-principles density functional theory (DFT). Lattice parameters of PETN I, the ground state structure at ambient conditions, is obtained by ReaxFF and two different density functional methods (plane wave and LCAO pseudopotential methods) and compared with experiment. Calculated energetics and isothermal equation of state (EOS) upon hydrostatic compression obtained by DFT and ReaxFF are both in good agreement with available experimental data. Our calculations of the hydrostatic EOS at zero temperature are extended to high pressures up to 50 GPa. The anisotropic characteristics of PETN upon uniaxial compression were also calculated by both ReaxFF and DFT.

Keywords: Energetic materials, PETN, interatomic potentials, molecular dynamics, EOS
PACS: 62.50.+p, 82.40.Fp, 81.30.Hd, 46.40.Cd

INTRODUCTION

Prediction of properties of energetic materials using atomic-scale simulations techniques is one of the challenging areas of energetic materials (EM) research. Molecular dynamics (MD) simulation of EM using classical reactive interatomic potentials is a powerful modeling technique that is capable of addressing sub-nanometer and sub-picosecond length and time scales of shock compression and detonation phenomena. However, the results of computer simulations can only be as reliable as the ability of the interatomic potentials to properly describe a variety of chemical effects including bond-breaking and bond-making. Recently, the reactive force field ReaxFF has been developed based on fitting of an ab-initio database of H-C-N-O chemistry and is currently being actively used for MD simulations of EM [1-3]. One of the important issues is the transferability of ReaxFF, i.e. its ability to describe a rich chemistry and physics of energetic materials compressed at high pressures and temperatures. The reliable experimental data mostly exist only for static volumetric compressions that produce the isothermal equation of states (EOS) in a limited range of pressures and temperatures. Although this information is useful to validate reactive interatomic potentials, it is very limited in nature. Additional atomic-scale information is urgently needed to understand the fundamental mechanisms
of shock compression and detonation of EM materials. The modeling/simulation is able to provide such information that is very difficult or sometimes impossible to obtain from experiment.

Density functional theory (DFT) has been very successful in recent years in simulating and predicting properties of a wide spectrum of materials from first-principles, i.e. without ad-hoc parameters that are usually present in empirical and semi-empirical methods. In many cases the accuracy of DFT in simulating properties of condensed phases is within a few percent compared to experiment. However, systems with weak van der Waals interactions, such as energetic molecular crystals, comprise a real challenge for DFT, because various density functionals, including the local density approximation (LDA) and the generalized gradient approximation (GGA) face difficulties in describing systems having very small overlap of electronic densities from atoms constituting the system. Nevertheless, the DFT should work reasonably well for energetic materials at high pressures (because of substantial overlap of electronic densities from atoms) and can be a very efficient tool for generating a database of first-principles data that can be used for validation and fitting of interatomic potentials.

The purpose of this work is to perform a comparative study of static high pressure properties of pentaerythritol tetranitrate PETN using both density functional theory (DFT) and ReaxFF. PETN is one of the classical energetic materials that has been extensively studied in recent years [4]. In addition to being an important secondary explosive, PETN exhibits an interesting property of strong anisotropy in the response to shock initiation of detonation [4]. Therefore, we decided to use PETN as a test bed for comparative studies using ReaxFF and DFT. We are particularly interested in equilibrium properties of the PETN stable crystalline phase at ambient conditions (PETN-I), see FIGURE 1, and its equation of state (EOS) in a wide range of applied pressures, see FIGURE 2.

**COMPUTATIONAL DETAILS**

The reactive force field (ReaxFF) is a bond-order dependent interatomic potential that includes covalent interactions via bond-orders. The bond-order is calculated from the instantaneous interatomic distances that are continuously updated in the course of simulation, thus allowing creation and breaking of chemical bonds. In addition to covalent interactions, ReaxFF includes Coulomb and van der Waals interactions traditionally present in classical force fields. However, these terms that are calculated for each atomic pair are effectively screened at short interatomic distances, thus reducing their contribution in the region where covalent interactions dominate. The ReaxFF was fitted to an extensive database of molecular and crystal structures of C-H-N-O containing species including reaction pathways, crystal structures and binding energy curves for all possible bonds including bond angle and torsional angle dependences [1-3]. Recently, ReaxFF has been successfully applied to study thermal decomposition of nitromethane [2] and RDX [3].

Density functional calculations were performed by using different basis sets: plane waves (PW) and linear combination of atomic orbitals (LCAO). In both cases, high quality pseudopotentials were employed to remove the core electrons from calculations, thus making first-principles calculations feasible. We carefully studied the completeness of the plane wave basis set by optimizing energy cutoff to get the convergence in energies, forces and stresses better than 0.01 eV/atom, 0.05 eV/Å and 0.1 GPa respectively. We used Vanderbilt ultrasoft pseudopotentials (USPP) with 500 eV energy cutoff, additional calculations were performed with 700 eV to check the

![FIGURE 1. Crystal structure of PETN-I (space group symmetry P4212).](image)
Table 1. Equilibrium lattice constants of PETN at zero temperature calculated by ReaxFF and DFT codes Castep and SeqQuest using several density functionals (LDA, GGA-PW, and GGA-PBE) and compared with experiment.

<table>
<thead>
<tr>
<th>PETN-I</th>
<th>a=b, Å (error, %)</th>
<th>c, Å (error, %)</th>
<th>c/a (error, %)</th>
<th>Cell Volume, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment</td>
<td>9.38</td>
<td>6.71</td>
<td>0.71</td>
<td>589.5</td>
</tr>
<tr>
<td>LDA (Castep)</td>
<td>8.891 (-5.2%)</td>
<td>6.453 (-3.8%)</td>
<td>0.726 (+2.3%)</td>
<td>510.1 (-13.5%)</td>
</tr>
<tr>
<td>GGA-PW (Castep)</td>
<td>9.600 (+2.3%)</td>
<td>6.796 (+1.3%)</td>
<td>0.708 (-0.3%)</td>
<td>626.3 (+6.2%)</td>
</tr>
<tr>
<td>GGA-PBE (Castep)</td>
<td>9.820 (+4.7%)</td>
<td>6.950 (+3.6%)</td>
<td>0.708 (-0.3%)</td>
<td>670.2 (+13.7%)</td>
</tr>
<tr>
<td>GGA-PBE (SeqQuest)</td>
<td>9.702 (+3.4%)</td>
<td>6.889 (+2.7%)</td>
<td>0.710 ( 0.0%)</td>
<td>648.5 (+10.0%)</td>
</tr>
<tr>
<td>ReaxFF</td>
<td>9.427 (+0.5%)</td>
<td>6.989 (+4.2%)</td>
<td>0.741 (+4.4%)</td>
<td>621.1 (+5.4%)</td>
</tr>
</tbody>
</table>

The Brillouin k-point sampling with k-point density of 0.08 Å⁻¹ was chosen to get the energies, forces and stresses converged to values cited above. We used the plane wave code Castep [5].

LCAO DFT calculations have been performed using LCAO code SeqQuest that uses norm-conserving pseudopotentials (NCPP) and high-quality contracted Gaussian basis sets [6]. It is a computationally efficient code that enables very large-scale calculations using rather modest computational resources. For present the calculations, the basis sets of double-zeta plus polarization (DZP) quality have been used with k-point sampling of the Brillouin zone with similar density as used in plane-wave calculations.

RESULTS AND DISCUSSION

The critical issue in employing DFT methods to study molecular crystals is the choice of the appropriate density functional. We investigated the accuracy of several density functionals including standard local density approximation (LDA) and several generalized gradient approximation (GGA) functionals including Perdew-Wang (PW) and Perdew-Burke-Ernzerhof (PBE) by calculating the equilibrium lattice parameters of PETN-I. Table 1 compares the results of DFT calculations using ReaxFF, CASTEP and PW-USPP and LCAO codes with experiment. As expected, the LDA gives strong overbinding of weak van der Waals forces which results in lattice parameters 5% smaller than experimental values. The best results were obtained using GGA-PW in case of PW-USPP (errors less than 2.3%) and GGA-PBE (errors less than 3.4%) for LCAO-NCPP. ReaxFF also predicts lattice constants in good comparison with experiment.

The hydrostatic equation of states (EOS) for PETN-I was obtained by performing constant pressure calculations at zero temperature. Castep data were generated using variable cell optimization under the constraint of a diagonal stress tensor with fixed values of diagonal matrix elements equal to a desirable pressure. The ReaxFF calculations were performed using damped constant pressure molecular dynamics which is equivalent to conjugate gradient minimization of the total energy. This method also allowed the optimization of the unit cell of the crystal under the constant pressure constraint. The space symmetry of the crystal structure has been removed in order to relax symmetry imposed constraints. The atomic coordinates were also simultaneously optimized to get zero forces on atoms.

Isothermal EOS, i.e. the dependence of pressure on volume, for PETN-I obtained from the constant pressure simulations by Castep and ReaxFF are shown in FIGURE 2 and compared with experimental data by Olinger et al [7]. Both Castep and ReaxFF data compare well with each other as well as with experiment. The pressure range covered by our simulations, extends beyond the experimental pressures up to 50 GPa. The energy changes in eV/atom relative to the equilibrium zero pressure structure of PETN-I are also predicted by ReaxFF in good agreement with DFT results.

We also performed an investigation of uniaxial compression of PETN. It is well-known that PETN shows interesting sensitivity properties, i.e. strong
anisotropy in the response in shock initiation of
detonation. The shock loading conditions are
characterized by fast uniaxial compression of the
crystals along specific crystallographic directions.
Therefore, we decided to investigate the
predictions of both DFT and ReaxFF for uniaxial
loading of the PETN-I.

The calculations were performed by creating a
supercell where the PETN crystal is rotated to be
oriented along a particular direction coinciding
with x-axis of the unit cell, resulting in a non-
tetragonal unit cell. Then, the x-dimension of the
unit cell was strained by an appropriate scaling of
the lattice parameter a. We calculated the
characteristics of uniaxially-loaded PETN-I crystal
in [100], [110], [010], and [001] directions. Due to
space limitations we show only [100] results in
Figure 3. We found that the DFT-SeqQuest and
ReaxFF are in very good agreement and it is not
surprising, because ReaxFF was fitted using a
database generated by SeqQuest. However, Castep
calculations substantially deviate from both
ReaxFF and SeqQuest. One of the sources of this
disagreement is different GGA functionals: Castep
calculations were done with PW but SeqQuest –

with PBE functionals. This results in slightly
different lattice constants for the equilibrium
crystal structures of PETN, see TABLE 1, which
may affect the curvature of the $\Delta E(a/a_0)$ curve.
We are currently investigating the sources of this
disagreement and will report the full results in a
subsequent publication.

ACKNOWLEDGEMENTS

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V. ENERGETIC MATERIALS AT HIGH COMPRESSION: FIRST-PRINCIPLES DENSITY FUNCTIONAL THEORY STUDIES

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ENERGETIC MATERIALS AT HIGH COMPRESSION:  
FIRST-PRINCIPLES DENSITY FUNCTIONAL THEORY  
STUDIES

Ivan I. Oleynik *, Mike Conroy *, Sergey V. Zybin f, and Carter T. White g

*Department of Physics
University of South Florida, Tampa, FL 33620

f Materials and Process Simulation Center, California Institute of Technology,  
Pasadena, CA 91125

g Naval Research Laboratory
Washington, DC 20375-5320

Abstract. In this paper we present results of systematic investigation of two important  
energetic molecular crystals, pentaerythritol tetranitrate (PETN, C(CH2ONO2)4) and  
cyclotetramethylene tetranitramine (HMX, [CH2NNO2]4) at high compression using  
first-principles density functional theory. The lattice parameters of PETN-I, and  
β-HMX, the ground state structures at ambient conditions, were obtained and compared  
with experiment. The isothermal equations of state have been obtained at a wide range  
of compressions. In addition to accurate simulation of isotropic hydrostatic  
compression we have performed a series of uniaxial compressions in order to simulate  
the anisotropic response of EM under conditions close to those achieved in shock  
compressed EMs. The isothermal hydrostatic equation of state for PETN-I was  
predicted by DFT in a reasonable agreement with experiment. However, the  
hydrostatic EOS for β-HMX as calculated by DFT using GGA-PW shows substantial  
deviation from experiment. The uniaxial compression of both PETN-I and β-HMX  
show interesting anisotropic behavior of the shear stresses. We found that the [100]  
direction, the least sensitive direction in PETN-I, has non-equal \( \tau_{xy} \) and \( \tau_{xz} \) shear  
stresses in contrast to the behavior of shear stresses seen from two other directions,  
[110] and [001], which exhibit greater sensitivity. In addition, for the [100] direction,  
one of the shear stresses, \( \tau_{xy} \), exhibits non-monotonic dependence on the uniaxial  
strain. This may be the reason that the [100] direction is less sensitive to shock  
initiation than all other crystallographic directions. For β-HMX, the shear stresses  
exhibit non-monotonic behavior for all three directions.

INTRODUCTION

An important problem in energetic materials (EMs) research is the understanding of the  
mechanisms of sensitivity of explosives upon impact and other stimuli 1-3. The ultimate goal is to  
aid in developing safe explosives that will minimize both transportation costs and accidental damage to  
both persons and property. One of the important steps in developing predictive capabilities is the
generation of a knowledge base of fundamental materials properties from first principles based upon underlying atomic scale structure. Special attention is being focused on obtaining accurate equations of state (EOS) for several important classes of EMs. Due to the dominant role of shock-induced phenomena in developing the initial stages of detonation\textsuperscript{7}, such properties should be extended beyond traditional isotropic dependence of pressure upon volume to include stress-dependent relationships that describe the anisotropic materials response upon dynamical loading.

In this paper we present results of first-principles density functional theory investigation of two important energetic molecular crystals, pentaerythritol tetranitrate (PETN, C\textsubscript{5}H\textsubscript{12}N\textsubscript{4}O\textsubscript{12})\textsuperscript{5} and cycloketronemethylenetetranitramine (HMX, \textsubscript{[}CH\textsubscript{2}NNO\textsubscript{2}\textsubscript{]}\textsubscript{4})\textsuperscript{5}. These systems have been already studied both experimentally\textsuperscript{6-9} and theoretically\textsuperscript{10-14}. In particular, isothermal compression of PETN has been investigated by Olinger et al\textsuperscript{4} in 1975, but accurate experimental results on isothermal hydrostatic compression of HMX have appeared relatively recently\textsuperscript{5,6}. Interestingly, Dick experimentally discovered the anisotropy in sensitivity to shock initiation present in PETN\textsuperscript{7}. Less sensitivity information is available for HMX energetic crystals\textsuperscript{3}.

Hydrostatic compression of PETN and HMX has been studied theoretically using classical interatomic potentials\textsuperscript{10}, first-principles DFT\textsuperscript{11} and Hartree-Fock methods\textsuperscript{12,13}. In particular, Sorescu, Rice and Thompson investigated both PETN and HMX using a specially developed classical intermolecular potential for nitramines\textsuperscript{10}. A recent study of hydrostatic compression of PETN has been performed using DFT with a Gaussian basis set within an all-electron implementation\textsuperscript{11}. PETN\textsuperscript{12} and HMX\textsuperscript{13} crystals have also been studied by the periodic Hartree-Fock method. Byrd, Scuseria and Chabalowski have recently performed DFT studies of equilibrium crystal structures of several energetic molecular crystals using the plane-wave pseudopotential code VASP\textsuperscript{14}. Their main goal was to evaluate the accuracy of DFT in predicting properties of EM molecular crystals.

This work is concerned with systematic investigation of two classical EM molecular crystals, PETN and HMX, at high compression using first-principles density functional theory as implemented in the plane-wave pseudopotential framework\textsuperscript{15}. In contrast to previous theoretical studies, isothermal equations of state have been obtained at a wide range of compressions. More importantly, in addition to accurate simulation of isotropic hydrostatic compression we have performed a series of uniaxial compressions in order to simulate the anisotropic response of EM under conditions close to those achieved in shock compressed EMs. We discuss the importance of shear stresses developed upon uniaxial compression for understanding the anisotropic sensitivity of EMs.

**COMPUTATIONAL DETAILS**

First-principles density functional calculations were performed by using CASTEP, a plane-wave pseudopotential code\textsuperscript{15}. High quality ultrasoft pseudopotentials were employed to remove the core electrons from calculations, thus making first-principles calculations feasible. The advantage of a plane-wave basis set over the linear combination of atomic orbitals (LCAO) basis is in absence of basis set superposition errors adherent to LCAO methods as well as its ability to control the errors due to the finite size of the basis set. We carefully studied the completeness of the plane wave basis set by optimizing the energy cutoff (a parameter controlling the size of the basis set) to get the convergence in energies, forces and stresses better than 0.01 eV/atom, 0.05 eV/Å and 0.2 GPa respectively. This convergence was checked for both uncompressed, equilibrium structures as well as highly compressed crystals. By performing test calculations at several energy cutoffs (300, 400, 500, 700 and 1000 eV) we found that the optimal cutoff is 500 eV. The Brillouin k-point sampling with a k-point density of 0.08 Å\textsuperscript{-1} at the highest compression was chosen to get the energies, forces and stresses converged to the values cited above. The Monkhorst-Pack k-point grid was kept fixed during the compression simulations to achieve a smooth change of physical properties upon compression.

It is well known that most EM crystals have numerous polymorphs that are exemplified by phase transitions occurring upon compression. In this study we focus our attention on PETN-I and β-HMX, the lowest energy crystal structures at ambient conditions. The PETN-I phase has a tetragonal \textit{P4}_2\textsubscript{1}c unit cell, containing two PETN...
molecules, with 58 atoms in total. The β phase of HMX has a monoclinic $P2_1/c$ structure with two molecules per unit cell, resulting in 56 atoms in total.

EQUILIBRIUM PROPERTIES OF PETN AND HMX MOLECULAR CRYSTALS

The critical issue in employing DFT methods to study molecular crystals is the choice of the density functional. Density functional theory (DFT) has been very successful in recent years in simulating and predicting properties of a wide spectrum of materials from first-principles. However, systems with weak van der Waals interactions, such as energetic molecular crystals, comprise a real challenge for DFT because various density functionals, including the local density approximation (LDA) and the generalized gradient approximation (GGA), face difficulties in describing systems having very small overlap of electronic densities from atoms constituting the system.

In order to assess the performance of different density functionals in describing properties of EM molecular crystals we have investigated the equilibrium properties of PETN-I and β-HMX by employing different flavors of the generalized gradient approximation (GGA) such as the Perdew-Wang (PW) and Perdew-Burke-Ernzerhof (PBE) functionals and the traditional local density approximation (LDA). Our strategy was to choose the density functional that predicts the equilibrium crystal properties closest to experimental values. The lattice parameters (lattice constants and cell angles) were optimized simultaneously with the atomic coordinates to have both zero forces on atoms and zero components of the stress tensor within the tolerances of 0.05 eV/Å and 0.2 GPa respectively.

Tables 1 and 2 compare the DFT results obtained using LDA, GGA-PW and GGA-PBE with experimental values for PETN-I and β-HMX, respectively. As expected, the LDA gives strong overbinding of weak van der Waals forces which results in lattice parameters 5% smaller than experimental values for both PETN and HMX. For the PETN-I crystal, the best results were obtained using GGA-PW (errors less than 2.3%). The LDA calculation for HMX shows the closest match to experiment, yet the absolute value of the percent errors for volume and lattice parameters obtained by LDA, GGA-PW, and GGA-PBE only differ slightly. Because our goal was to analyze the two

<table>
<thead>
<tr>
<th>Table 1. Equilibrium lattice parameters of PETN-I calculated by DFT using several density functionals (LDA, GGA-PW, and GGA-PBE) and compared with experiment.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PETN-I</td>
</tr>
<tr>
<td>Experiment</td>
</tr>
<tr>
<td>LDA</td>
</tr>
<tr>
<td>GGA-PW</td>
</tr>
<tr>
<td>GGA-PBE</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 2. Equilibrium lattice parameters of β-HMX calculated by DFT using several density functionals (LDA, GGA-PW, and GGA-PBE) and compared with experiment.</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-HMX</td>
</tr>
<tr>
<td>Experiment</td>
</tr>
<tr>
<td>LDA</td>
</tr>
<tr>
<td>GGA-PW</td>
</tr>
<tr>
<td>GGA-PBE</td>
</tr>
</tbody>
</table>
structures within the same computational framework, we decided to use GGA-PW for further calculations of hydrostatic and uniaxial compressions. Obviously, the errors are due to well-known problems of DFT to describe properly the van der Waals interactions.

HYDROSTATIC COMPRESSION

The hydrostatic compression of PETN and HMX was simulated using a two-step relaxation process. Starting from the compression ratio $V/V_0 = 1$, the lattice constants were scaled by the appropriate compression ratio, but the fractional atomic coordinates were taken from the structure corresponding to the relaxed cell obtained from the previous stage in the compression. During step one, the atomic coordinates were relaxed, keeping the unit cell fixed. The resulting pressure after relaxation was read and used to form a diagonal, hydrostatic stress tensor. At stage two, all degrees of freedom including atomic coordinates, lattice constants and cell angles were relaxed under the constraint of a fixed stress tensor formed after step

![FIGURE 1. Isothermal hydrostatic equation of state of PETN-I. Left panel – simulation domain, right panel – experimental domain of compression ratios $V/V_0$.](image1)

![FIGURE 2. Lattice parameters of PETN-I as a function of compression ratio $V/V_0$. Left panel – simulation domain, right panel – experimental domain of compression ratios $V/V_0$.](image2)
one within a tolerance of 0.2 GPa. Such a procedure allows fast convergence of relaxation calculations due to gradual changes of several physical parameters of the system. The space symmetry of the crystal structure has also been removed in order to relax symmetry imposed constraints. The compression ratio $V/V_0$ was varied from 1.00 to 0.40 with the step size of 0.025.

We first discuss results for PETN. Isothermal EOS, i.e. the dependence of pressure on volume obtained by DFT (GGA-PW) within the compression ratio interval $0.4 < V/V_0 < 1.0$, is shown in Figure 1 and compared with experimental data by Olinger et al. The pressure range covered by our simulations extends beyond the experimental pressures up to 150 GPa. Our results show very good agreement with experiment when plotted together within the simulation compression interval $0.4 < V/V_0 < 1.0$. However, a closer examination within the range of volume ratios present in the experiment shows less agreement. From the equilibrium structure to a volume ratio of about 0.9, the pressure of the simulated crystal is greater than experiment. Between the volume ratios 0.90 and 0.84, very good agreement is shown. For lower volumes, there is a greater discrepancy between the calculated and experimental pressures. It is worth noting that the curvature of the experimental isotherm at $V/V_0 = 1.0$ is less than the calculated isotherm, which indicates that the theoretical bulk modulus, $B = -V (dP/dV)$ seems to be greater than the experimental value.

The lattice parameters $a$ and $c$ show very good agreement with experiment, see Figure 2. The

![HMX Isothermal EOS](image1)

**FIGURE 3.** Isothermal hydrostatic equation of state of $\beta$-HMX. Left panel – simulation domain, right panel – experimental domain of compression ratios $V/V_0$.

![HMX: Lattice Parameter a](image2)

![HMX: Lattice Parameter b](image3)

![HMX: Lattice Parameter c](image4)

**FIGURE 4.** Lattice parameters of $\beta$-HMX as a function of compression ratio $V/V_0$. Left panel – simulation domain, right panel – experimental domain of compression ratios $V/V_0$. 

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greatest error is observed for the $c$ parameter, which is roughly $2\%$, but the error for $a$ is much smaller. Meanwhile, at compression ratios below what has been observed experimentally, the lattice constants show abrupt changes at $V/V_0 = 0.65$ and also at $V/V_0 = 0.35$ which may indicate the possibility of polymorphic phase transitions of the PETN crystal.

For HMX, the agreement between the calculated and experimental EOS is not so good. This can be easily seen in from the graphs showing both the simulation and experimental domains of volume ratios, see Figure 3. One of the sources of this disagreement is errors in the equilibrium lattice parameters obtained by DFT. The compression simulations begin from an equilibrium structure having $-10\%$ higher volume than the experimental volume. Therefore, the initial volume $V_0$ may affect the curvature of the $\Delta E(V/V_0)$ curve. As far as lattice constants as a function of compression ratio are concerned, the agreement between theory and experiment is good, see Figure 4.

UNIAXIAL COMPRESSIONS OF PETN AND HMX CRYSTALS

We also performed an investigation of uniaxial compression of PETN and HMX crystals. The uniaxially compressed state of the crystal is directly related to the state the crystal experiences upon shock loading. At sufficiently large shock wave intensities, the time scale associated with the initial process of shock compression is on the order of picoseconds. Therefore, the lattice rapidly transforms at the shock wave front to a uniaxially compressed state. By investigating the mechanical properties of a uniaxially compressed crystal including shear stresses we have the possibility to explore the underlying atomic-scale mechanisms of anisotropic sensitivity of EMs.

It is well known that PETN shows interesting sensitivity properties, i.e. a strong anisotropy in the response to shock initiation of detonation. Dick, in his classical experiments, has found that PETN-I is less sensitive in the [100] direction but more sensitive in the [110] direction upon impact initiation. Less is experimentally known about the sensitivity of HMX. The shock loading conditions are characterized by fast uniaxial compression of the crystals along specific crystallographic directions. Therefore, we decided to investigate the uniaxial loading of PETN and HMX along different crystallographic directions with the aim to correlate the anisotropic characteristics with their sensitivity.

The calculations were performed by creating a supercell where both PETN and HMX crystals were rotated to be oriented along a particular direction coinciding with the x-axis of the unit cell, resulting in a non-tetragonal unit cell. Then, the x-dimension of the unit cell was strained by an appropriate scaling of the lattice parameter $a$.

We calculated the stress characteristics of uniaxially-loaded PETN-I in the [100], [110], and [001] directions, see Figure 5. The shear stresses

![Figure 5](image-url) FIGURE 5. Shear stresses in PETN-I upon uniaxial compression along [100], [110], and [001] directions as a function of compression ratio $a/a_0$. 

are our particular interest because they are usually considered to be the driving forces of plastic deformations in crystals. Several interesting observations have appeared. In particular, we have found that for both [110] and [001] directions, the \( \tau_{xy} \) and \( \tau_{xz} \) shear stresses are almost equal for all the states of a uniaxially compressed crystal. In contrast, \( \tau_{xy} \) and \( \tau_{xz} \) are different for the least sensitive direction, [100]. Interestingly, \( \tau_{xz} \) shows non-monotonic dependence as a function of compression ratio \( a/a_0 \).

The shear stresses in the uniaxially-compressed HMX crystal also exhibit anisotropic, non-monotonic behavior for all three directions, [110], [101] and [011], see Figure 6. There is no experimental information on the sensitivity of single crystal HMX. Therefore, more work, both experimental and theoretical, is needed to understand the sensitivity properties of HMX.

**CONCLUSIONS**

We have studied the PETN-I and \( \beta \)-HMX molecular crystals using first-principles DFT implemented in the plane-wave pseudopotential framework. The equilibrium properties of PETN and HMX were studied using different density functionals. It was found that for PETN, GGA-PW gives the smallest error \( \sim 2\% \) for lattice constants and \( \sim 6\% \) for unit cell volume compared to experiment. An obvious reason for this discrepancy is the substantially larger equilibrium volume of the unit cell as calculated by DFT which results in different curvature of the \( \Delta E(V/V_0) \) curve as compared to experiment at the same absolute volume of the crystal.
The uniaxial compression of both PETN-I and $\beta$-HMX show interesting anisotropic behavior of the shear stresses. In PETN-I we found that the [100] direction, the least sensitive direction has non-equal $\tau_{xy}$ and $\tau_{xz}$ shear stresses in contrast to the behavior of shear stresses seen from two other directions, [110] and [001], which exhibit greater sensitivity. In addition, for the [100] direction, one of the shear stresses, $\tau_{yz}$, exhibits non-monotonic dependence on the uniaxial strain. This might be a primary reason why the [100] direction is less sensitive to shock initiation than all other crystallographic directions. For $\beta$-HMX, the shear stresses exhibit non-monotonic behavior for all three directions. Because no experimental information on shock sensitivity is available for this crystal, more work, both theoretical and experimental, is needed to clarify the fundamental mechanisms of shock sensitivity in EMs.

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VI. ANISOTROPIC CONSTITUTIVE RELATIONSHIPS IN ENERGETIC MATERIALS: PETN AND HMX

The following article\textsuperscript{26} was accepted to be published in the proceedings of the 15\textsuperscript{th} American Physical Society Topical Conference on Shock Compression of Condensed Matter, and it has been reproduced here with permissions from the American Institute of Physics and the authors of the article.
ANISOTROPIC CONSTITUTIVE RELATIONSHIPS IN ENERGETIC MATERIALS: PETN AND HMX

M. Conroy, I.I. Oleynik, S.V. Zybin, and C. T. White

1Department of Physics, University of South Florida, Tampa, FL 33620
2Materials and Process Simulation Center, California Institute of Technology, Pasadena, CA 91125
3Naval Research Laboratory, Washington, DC 20375

Abstract. This paper presents results of first-principles density functional calculations of the equation of state (EOS) of PETN-I and β-HMX. The isotropic EOS for hydrostatic compression has been extended to include uniaxial compressions in the [100], [010], [001], [110], [101], [011], and [111] directions up to compression ratio \( V/V_0 = 0.70 \). Equilibrium properties, including lattice parameters and elastic constants, as well as hydrostatic EOS are in good agreement with available experimental data. The shear stresses of uniaxially compressed PETN-I and β-HMX have been evaluated and their behavior as a function of compression ratio has been used to make predictions of shock sensitivity of these EMs. A comparison of predicted sensitivities with available experimental data has also been performed.

Keywords: Energetic materials, PETN-I and β-HMX, density-functional theory, equation of state, shock sensitivity, shear stresses

PACS: 31.15.Ar, 31.15.Ew, 31.70.Ks, 62.50.+p, 64.30.+t

INTRODUCTION

One of the goals of energetic materials (EMs) research is to obtain accurate equations of state (EOS) for several important classes of EMs. Although a number of theoretical and experimental studies have been performed to obtain hydrostatic EOS for several EMs, there is an urgent need to extend isotropic EOS to include a description of the materials response upon uniaxial compression. The uniaxially compressed state of the crystal is directly related to the state that a crystal experiences upon shock loading. The shear stresses upon uniaxial compression are of particular interest because they are usually considered to be the driving forces behind plastic deformations in crystals and the sources of mechano-chemical reactions behind the shock wave front.

Anisotropic response to plane shock wave loading was observed in the experiments on PETN by J. J. Dick. Detonation at relatively low input stresses and run distances was observed for shocks delivered in the [110] and [001] crystallographic directions, yet detonation was not observed for shocks delivered in the [100] and [101] directions.

The goal of this work is to obtain highly accurate hydrostatic EOS for PETN-I and β-HMX and extend them to include uniaxial
compressions in a wide range of compression ratios. We discuss the behavior of the shear stresses upon uniaxial compression and their potential importance in explaining the anisotropic shock sensitivity of PETN-I and β-HMX.

**COMPUTATIONAL DETAILS**

The density functional calculations were performed using the Vienna Ab-Initio Simulation Package (VASP)\(^{12}\). Special attention was paid to ensure high accuracy in the calculations. Test calculations were done to determine the types of density functionals and pseudopotentials, the value of the energy cutoff, and the density of k-point sampling within the Brillouin zone that are adequate to reproduce available experimental data on equilibrium crystal structures. From these tests, the Generalized Gradient Approximation (GGA) density functional theory (DFT) with the Perdew-Burke-Ernzerhof (PBE) functional, the soft projected augmented wavefunction (PAW) pseudopotential with a 400 eV nominal cutoff, and a fixed Monkhorst-Pack grid corresponding to an average of 0.08 Å\(^{-1}\) k-spacing at maximum compression have been chosen. An energy cutoff of 700 eV was used, which yielded convergence better than 0.4 GPa in pressure, 0.0015 eV/atom in energy, and 0.015 eV/Å in forces.

The equilibrium structures of PETN-I and β-HMX were calculated by relaxing all the degrees of freedom of the experimental structures including lattice parameters and atomic coordinates using the quasi-Newton method as implemented in VASP. For all relaxations in this study, the convergence for electronic steps was set to 10\(^{-6}\) eV, and relaxation continued until the maximum force on any atom within the unit cell was less than 0.03 eV/Å.

Hydrostatic compression calculations were performed on single unit cells of PETN-I and β-HMX in the range of V/V\(_0\) = 1.06 to 0.60 in increments of 0.02, where V\(_0\) is the volume at zero pressure. Uniaxial compressions of both PETN and HMX were performed in the [100], [010], [001], [110], [101], [011], and [111] directions. For each compression direction, the calculated equilibrium unit cell was rotated such that the x-axis corresponded to the direction of compression. Subsequently, the x-component of each lattice vector was scaled by 2% up to V/V\(_0\) = 1.06 and down to V/V\(_0\) = 0.70.

**RESULTS AND DISCUSSION**

**PETN-I.** The calculated unit cell parameters were compared to experimental data from Olinger, Halleck, and Cady\(^4\). According to their work, the lattice constants a = b = 9.386 Å and c = 6.715 Å. The lattice constants from this study (and the percent difference from experiment) were 9.617 Å (+2.5%), 9.612 Å (+2.4%), and 6.83 Å (+1.7%) for a, b, and c, respectively. The disagreement between DFT calculations and experiment for molecular crystals has been studied in several works and has been attributed to poor description of van der Waals interactions by DFT.

The isothermal equation of state (EOS) from the hydrostatic compression simulations of this work was compared with the experimental data of Olinger *et al.*, see Figure 1. Pressure, change in energy per atom, and band gap were plotted as a function of absolute volume in the range of V/V\(_0\) = 1.0 to 0.60. Good qualitative agreement was observed between the EOS calculated in this study and experimental data. For PETN-I, the elastic constants C\(_{11}\), C\(_{22}\), and C\(_{33}\) were calculated and compared with experiment\(^15\), see Table 1. Results on isotropic EOS and elastic constants...
TABLE 1. Elastic constants of PETN-I calculated in this work and compared with experiment.\(^{15}\)

<table>
<thead>
<tr>
<th>Study</th>
<th>C(_{11}) (GPa)</th>
<th>C(_{22}) (GPa)</th>
<th>C(_{33}) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp.: Ref. 6</td>
<td>17.22</td>
<td>17.22</td>
<td>12.17</td>
</tr>
<tr>
<td>This work</td>
<td>18.25 (+6.0%)</td>
<td>18.5 (+7.4%)</td>
<td>14.5 (+19%)</td>
</tr>
</tbody>
</table>

have given us confidence that DFT gives a reasonable description of the compressed crystals despite the problem with van der Waals interactions.

In the case of uniaxial compressions of PETN-I, the change in energy per atom, longitudinal stress, band gap, and shear stresses were examined as a function of c/c\(_0\). The shear stresses, which showed the greatest relative variation among the inspected properties, were calculated from the equation

\[
\tau_{yx} = \frac{\sigma_{xx} - \sigma_{yy} + \sigma_{zz}}{2},
\]

where x indicates the direction of compression. Figure 2 shows the values of the shear stresses at uniaxial compression of c/c\(_0\) = 0.7.

From the experiments of J. Dick\(^ {10} \) on PETN-I, the [110] and [001] directions have exhibited a greater sensitivity to detonation via shock, and the [100] and [101] directions have displayed decreased sensitivity. It can be observed from Figure 2 that the shear stresses for the more sensitive directions, [110] and [001], exhibit greater values for both \(\tau_{yx}\) and \(\tau_{zx}\) than the directions of lower sensitivity, [100] and [101]. Reduced values of shear stresses and greater separation between \(\tau_{yx}\) and \(\tau_{zx}\) were observed in the less sensitive directions, [100] and [101]. Therefore, the suggestion\(^ {10} \) that shear stress behavior is linked with sensitivity is supported by these results.

Non-monotonic dependence of shear stress upon strain was also observed for directions of decreased sensitivity. From these calculations and experimental data, we see that greater calculated values of both \(\tau_{yx}\) and \(\tau_{zx}\) upon uniaxial compression correlates positively with increased sensitivity in energetic molecular crystals.

\(\beta\)-HMX. The calculated equilibrium lattice constants of \(\beta\)-HMX were compared with the experimental data from Choi and Boutin\(^ {13} \). Their results were a = 6.54 Å, b = 11.05 Å, and c = 8.70 Å. The calculated values of the lattice constants from this work (and the percent difference from experiment) were 6.701 Å (+2.5%), 11.347 Å (+2.7%), and 8.910 Å (+2.4%) for a, b, and c, respectively. Again, overestimation of the lattice parameters was associated with the inability of DFT functionals to describe the significant intermolecular van der Waals interactions.

The calculated isothermal EOS was compared with the experimental data obtained by Gump and Peiris\(^ {5} \) and Yoo and Cynn\(^ {6} \), see Fig. 3. As observed in PETN-I, DFT provides good qualitative agreement with the EOS data gathered.

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\(\tau_{yx}\) and \(\tau_{zx}\) at uniaxial compression 0.7 in PETN-I.
The shear stresses for the uniaxial compressions performed on HMX at \( c/c_0 = 0.7 \) were plotted in Fig. 4. Greater magnitudes of shear stresses, which corresponded to directions of greater sensitivity in PETN-I, were present in the directions [110] and [010]. Consequently, if the trend found for PETN-I is maintained for \( \beta \)-HMX, then greater sensitivity to initiation is expected in these directions.

**CONCLUSIONS**

The energetic material crystals PETN-I and \( \beta \)-HMX were studied using first-principles density functional theory. Good agreement was observed between available experimental data and calculated equilibrium structures, hydrostatic equations of state, and elastic constants. The errors were attributed to poor description of van der Waals interactions by DFT. The inclusion of van der Waals interactions will be the subject of future work.

The isotropic EOS have also been extended to include uniaxial compressions PETN-I and \( \beta \)-HMX in the [001], [010], [011], [110], and [111]. Upon comparison of the simulated uniaxial compression data with experimental information on the anisotropy in sensitivity to shock-induced detonation for PETN-I, a correlation between shear stresses and sensitivity was suggested. The magnitudes of the calculated shear stresses were greater for the more sensitive directions, [110] and [010], than for the less sensitive directions, [100] and [011]. Extrapolating this trend between calculated shear stresses and known sensitivity in PETN to our calculated results for \( \beta \)-HMX suggests that for \( \beta \)-HMX the [110] and [010] directions could be more sensitive to initiation.

**ACKNOWLEDGEMENTS**

The work at USF was supported by the Office of Naval Research (ONR) through the Naval Research Laboratory (NRL). The work at NRL was also supported by ONR both directly and through NRL. M. Conroy thanks the organizing committee of SCCM 2007 (Ricky Chau) for the travel support to attend SCCM 2007 in Hawaii.

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VII. ANISOTROPIC CONSTITUTIVE RELATIONSHIPS IN ENERGETIC MATERIALS: NITROMETHANE AND RDX

The following article was accepted to be published in the proceedings of the 15th American Physical Society Topical Conference on Shock Compression of Condensed Matter, and it has been reproduced here with permissions from the American Institute of Physics and the authors of the article.
ANISOTROPIC CONSTITUTIVE RELATIONSHIPS IN ENERGETIC MATERIALS: NITROMETHANE AND RDX

I.I. Oleynik¹, M. Conroy¹, and C. T. White²

¹Department of Physics, University of South Florida, Tampa, FL 33620
²Naval Research Laboratory, Washington, DC 20375

Abstract. The anisotropic constitutive relationships in solid nitromethane (NM) and α-RDX were studied using first-principles density functional theory (DFT). In addition to hydrostatic compressions, we performed uniaxial compressions in the [100], [010], [001], [110], [101], [011], and [111] directions up to the compression ratio V/V₀ = 0.70. Equilibrium properties, including lattice parameters and elastic constants, as well as hydrostatic EOS, are in good agreement with available experimental data. The shear stresses of uniaxially compressed NM and α-RDX were used to predict the relative shock sensitivity between different crystallographic directions.

Keywords: Energetic materials, nitromethane and α-RDX, density-functional theory, equation of state, shock sensitivity, shear stresses

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INTRODUCTION

Shock sensitivity of energetic materials is one of the outstanding scientific issues that have been a focus of the energetic materials (EMs) community in the last several decades [1-4]. A number of experiments have investigated shock sensitivity of single crystals of PETN-I [2-4] and β-HMX [5]. In particular, J.J. Dick observed the anisotropic response of PETN to plane shock wave loading: the [110] and [001] crystallographic directions were found to be more sensitive than the [100] and [101] directions [2-4]. Less is known about the relative shock sensitivity of other EMs such as solid nitromethane (NM) and α-RDX. Ultimately, the shock sensitivity must be related to the underlying atomic-scale structure of EMs which governs their constitutive properties.

The goal of this work is to provide such constitutive relationships for NM and α-RDX from first-principles by explicitly treating electrons using density functional theory (DFT). By extending the hydrostatic equations of state (EOS) to include a description of the materials response upon uniaxial compression, we are trying to establish the relationship between the behavior of the shear stresses and the anisotropic shock sensitivity of EMs. Such uniaxially compressed states of the crystal are directly related to the state that a crystal experiences upon shock loading. The shear stresses upon uniaxial compression are usually considered to be the driving forces behind plastic deformations in crystals and the sources of mechano-chemical reactions behind the shock wave front.
COMPUTATIONAL DETAILS

The first-principles calculations of EM crystals NM and RDX were performed using the density functional theory code VASP (Vienna Ab-Initio Simulation Package) [6]. Special attention was paid to ensure the accuracy of the calculations by optimizing parameters such as the types of density functionals and pseudopotentials, the energy cutoff and the density of k-point sampling of the Brillouin zone. We found that the Generalized Gradient Approximation (GGA) DFT with the Perdew-Burke-Ernzerhof (PBE) functional, projected augmented wavefunction (PAW) pseudopotentials, 700 eV energy cutoff and fixed Monkhorst-Pack grid corresponding to an average of 0.08 Å⁻¹ k-spacing at maximum compression are adequate to reproduce available experimental data on equilibrium properties of NM and α-RDX.

The equilibrium structures of NM and α-RDX were calculated by relaxing all degrees of freedom including lattice parameters and atomic coordinates using the quasi-Newton method as implemented in VASP. For all relaxations in this study, the convergence for electronic steps was set to 10⁻⁶ eV, and relaxation continued until the maximum force on any atom within the unit cell was less than 0.03 eV/Å.

Hydrostatic compression calculations were performed on single unit cells of NM and α-RDX in the range of V/V₀ = 1.06 to 0.70 in increments of 0.02. Uniaxial compressions were performed in the [100], [010], [001], [110], [101], [011], and [111] directions up to compression ratio c/c₀ = 0.70. For each compression ratio, the change in energy per atom, longitudinal stress, band gap, and shear stresses were determined. The shear stresses were calculated as τ_(j(z)) = (σ_(xx) - σ_(yz(z)))/2, where σ_(xx) and σ_(yz(z)) are the longitudinal and transverse stresses, respectively. The calculated values of τ_(j(z)) were compared with experimental data.

RESULTS AND DISCUSSION

Nitromethane. The experimental equilibrium unit cell structure of solid nitromethane is orthorhombic, with space group P2₁2₁2₁ and lattice parameters a = 5.183 Å, b = 6.236 Å, c = 8.518 Å [7]. The calculated equilibrium lattice parameters are a = 5.301 Å, b = 6.591 Å, c = 8.838 Å which are within +2.3%, +5.7% and +3.8% of experimental values, respectively. The source of these errors is in the poor description of van der Waals interactions by DFT.

The isothermal equation of state (EOS) for the hydrostatic compression calculated by DFT was compared with the experimental work of Yarger, and Olinger [8], see Figure 1. Pressure, change in energy per atom, and band gap were plotted as a function of absolute volume in the range of V/V₀ = 1.0 to 0.70. Good qualitative agreement was observed between the EOS calculated in this study and experimental data.

The anisotropic properties of NM have been investigated by performing uniaxial compressions in the [100], [010], [001], [110], [101], [011], and [111] directions up to compression ratio c/c₀ = 0.70. For each compression ratio, the change in energy per atom, longitudinal stress, band gap, and shear stresses were determined. The shear stresses were calculated as τ_(j(z)) = (σ_(xx) - σ_(yz(z)))/2, where σ_(xx) and σ_(yz(z)) are the longitudinal and transverse stresses, respectively. The calculated values of τ_(j(z)).
correspond to maximum shear stresses applied at 45° to the compression direction. Figure 2 shows the values of the shear stresses at uniaxial compression \( c/c_0 = 0.7 \).

By inspecting the values of the shear stresses along different crystallographic directions, we found that the [001] compression has the highest values of \( \tau_{yx} \) and \( \tau_{zx} \). In our work on uniaxial compressions of PETN-I [9], we found a positive correlation between directions exhibiting greater sensitivity in shock-compression experiments and the crystallographic directions possessing relatively higher shear stresses in theoretical compression simulations. Similar correlation between the directions of the smallest shear stresses and the less sensitive directions was found. Although there is no anisotropic shock sensitivity data available for NM, by extrapolating the correlation found in PETN-I, suggests that the [001] direction will be the direction of the highest shock sensitivity.

\( \alpha \)-RDX. The experimental crystal structure of \( \alpha \)-RDX possesses the orthorhombic space group Pbc\( a \) with lattice parameters \( a = 13.182 \, \text{Å} \), \( b = 11.574 \, \text{Å} \), \( c = 10.709 \, \text{Å} \) [10]. The DFT results are \( a = 13.522 \, \text{Å} \), \( b = 11.758 \, \text{Å} \), \( c = 11.102 \, \text{Å} \) and the percent difference from experiment are +2.3%, +1.6%, and +3.7% respectively. Again, overestimation of the lattice parameters was associated with the inability of DFT functionals to describe intermolecular van der Waals interactions.

The calculated isothermal EOS for \( \alpha \)-RDX is shown in Figure 3. The only experimental data on the isothermal EOS of \( \alpha \)-RDX were obtained by Olinger, Roof and Cady in 1978 [11] and only pressures up to 4 GPa were reported. Therefore, we do not plot these experimental points.

An important method to test the accuracy of DFT is the comparison of predicted elastic constants with experiment. For \( \alpha \)-RDX, the elastic constants \( C_{11} \), \( C_{22} \), and \( C_{33} \) were calculated and compared with experiment [12], see Table 1. The average error of DFT is 3.2%, which gives us confidence that DFT provides a sufficiently accurate description of the compressed state of EMs despite the problem with van der Waals interactions at small compression.

The shear stresses for the uniaxial compressions of \( \alpha \)-RDX at \( c/c_0 = 0.7 \) are plotted in Figure 4. Greater magnitudes of shear stresses, Table 1.

<table>
<thead>
<tr>
<th>Constants</th>
<th>( C_{11} ) (GPa)</th>
<th>( C_{22} ) (GPa)</th>
<th>( C_{33} ) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>25.5 (0.4%)</td>
<td>20.5 (3.8%)</td>
<td>18.0 (5.3%)</td>
</tr>
<tr>
<td>Exp.: Ref. 12</td>
<td>25.6</td>
<td>21.3</td>
<td>19.0</td>
</tr>
</tbody>
</table>
which could correspond to directions of greater sensitivity, were present in the [100] and [011] directions of α-RDX. Thus, increased sensitivity for these directions could be expected. The [101] direction displayed the smallest shear stresses suggesting that it could be the least sensitivity. Again, these suggestions are made following the establishment of a positive correlation between experimental sensitivity data and shear stress values in PETN-I [9].

CONCLUSIONS

We have studied the energetic materials crystals NM and α-RDX using first-principles density functional theory and found good agreement between available experimental data and calculated equilibrium structures, hydrostatic equations of state, and elastic constants. The errors are probably due to an inadequate description of van der Waals interactions by DFT. The isotropic EOSs have been extended to include uniaxial compressions in the [100], [010], [001], [110], [101], [011], and [111].

Using a correlation found in previous studies of PETN-I, we also made suggestions of relative shock sensitivities of NM and α-RDX based on calculated shear stresses for different crystallographic directions. For NM, the magnitudes of the shear stresses were the greatest for the [001] direction suggesting that it corresponds to the most sensitive direction. In the case of α-RDX, the [100] and [011] directions are expected to be more sensitive, while the [101] direction is expected to be the least sensitive direction. These theoretical predictions, which assume that the positive correlation between calculated shear stress and observed sensitivity in PETN can be extrapolated to NM and α-RDX, require experimental confirmation.

ACKNOWLEDGEMENTS

The work at USF was supported by the Office of Naval Research (ONR) through the Naval Research Laboratory (NRL). The work at NRL was also supported by ONR both directly and through NRL. M. Conroy thanks the organizing committee of SCCM 2007 (Ricky Chau) for the travel support to attend SCCM 2007 in Hawaii.

REFERENCES

VIII. FIRST-PRINCIPLES INVESTIGATION OF ANISOTROPIC CONSTITUTIVE RELATIONSHIPS IN PETN

The following article will be submitted to *Physical Review B*.
FIRST-PRINCIPLES INVESTIGATION OF ANISOTROPIC CONSTITUTIVE RELATIONSHIPS IN PENTAERYTHRITOL TETRANITRATE (PETN)

M. Conroy†, I. I. Oleynik‡, S. V. Zybin§, and C. T. White*

†Department of Physics, University of South Florida, Tampa, FL 33620
‡Materials and Process Simulation Center, California Institute of Technology, Pasadena, CA 91125
*Naval Research Laboratory, Washington, DC 20375

Abstract. First-principles density functional theory (DFT) calculations have been used to obtain the constitutive relationships of the energetic material crystal, pentaerythritol tetranitrate (PETN-I). The isotropic equation of state (EOS) for hydrostatic compression has been extended to include uniaxial compressions in the <100>, <010>, <001>, <110>, <101>, <011>, and <111> crystallographic directions up to a compression ratio of \( V/V_0 = 0.7 \). DFT predicts equilibrium properties such as lattice parameters and elastic constants, as well as hydrostatic EOS in agreement with available experimental data. The hydrostatic EOS has been extended to include the response of EMs upon anisotropic uniaxial compressions. Our results show a substantial anisotropy of various properties of PETN-I upon uniaxial compressions. To characterize the anisotropic properties of PETN, different physical properties of the uniaxially compressed crystal such as the energy per atom, band gap, and stress tensor have been evaluated as a function of compression ratio. The maximum shear stresses were calculated and examined for a correlation with the anisotropy in shock-initiation sensitivity.

I. INTRODUCTION

One of the goals of energetic materials (EMs) research is to investigate the fundamental physical and chemical properties of EM molecular crystals from first-principles based on the underlying atomic scale structure. Accurate equations of state (EOS) are of particular interest because they establish fundamental relationships between thermodynamic variables and provide necessary input for the description of materials at the mesoscopic and continuum levels. Ultimately, these EOS are governed by the interactions at the atomic scale which provides an excellent opportunity for atomic-scale simulation techniques to establish these relationships by linking the microscopic and macroscopic properties of the material.

Most of the theoretical and experimental investigations focus on isotropic EOSs, i.e. relationships between pressure and volume. However, due to the dominant role of shock-induced phenomena during initiation and propagation of detonation, there is an urgent need to extend the isotropic EOS to include the response of EMs upon anisotropic uniaxial compressions.

PETN, an important EM, has attracted considerable interest from the EM community because of the discovery of its anisotropic shock sensitivity by J.J. Dick. Some prior work
on PETN has indicated anomalous behavior upon shock compression. In particular, Halleck and Wackerle\textsuperscript{4} performed shock compressions of up to about 4 GPa on single-crystal samples with planes cut perpendicular to the <110> and <001> directions. For shocks at and above 4 GPa on the <110> crystals, shock-induced decomposition was expected from a rapid increase in stress amplitude approximately 0.3 μs after shock arrival. However, it was J.J. Dick who unambiguously demonstrated in his classic experiments the anisotropy in shock sensitivity. He found that when compressed in its most sensitive direction, <110>, detonation has been observed\textsuperscript{3} in PETN crystals under shock stresses as small as 4.2 GPa (from J. Dick\textsuperscript{3}, \textit{<hkl>} denotes the direction perpendicular to the (hkl) plane). The <001> direction has also been reported as sensitive\textsuperscript{1-3}. However, it is very insensitive to shocks in the <100> direction\textsuperscript{1-3, 5}, and the <101> direction has also been found to be relatively insensitive\textsuperscript{1-3}. Later, the anisotropic shock sensitivity of PETN was also investigated by Soulard\textsuperscript{6, 7}.

There have also been a number of works suggesting mechanisms for the directional dependence of sensitivity in PETN. Dick \textit{et al.}\textsuperscript{1-3} have proposed a model based upon steric hindrance to shear, which suggests that sensitivity is related to the ease by which slip is allowed via the available slip systems under shock compression. Further, Jindal and Dlott\textsuperscript{8} have suggested that anisotropic heating in response to shock compression might be responsible for directional dependence of sensitivity. Gruzdkov and Gupta\textsuperscript{8} have added to the possible mechanisms by arguing that changes in the local polarization of the lattice arise due to conformational changes in PETN molecules under compression, allowing decomposition via ionic reactions.

The macroscopic properties of several energetic materials including PETN, HMX, RDX, and TATB have been studied and described well\textsuperscript{9, 10}. However, the microscopic behavior responsible for the shock initiation observed on the macroscopic scale is not well understood. First-principles simulation of these materials at the atomic and molecular level is therefore providing an excellent opportunity for the investigation of microscopic processes leading to shock initiation. Because of the relatively large unit cells and complex geometries of these energetic materials, first-principles calculations have only been feasible for the last decade due to both advances in computational methodology and the exponential growth in computational power of modern computers. PETN is an exemplary EM for these calculations, as its anomalous anisotropic shock-initiation behavior\textsuperscript{1-3} can be probed at the atomic scale.

The crystal structure of PETN was studied experimentally via x-ray diffraction by Booth and Llewellyn\textsuperscript{11}, whose data was later revised by Trotter\textsuperscript{12}. A tetragonal lattice with space-group symmetry \textit{P42_1c} was determined, with two C(CH\textsubscript{2}ONO\textsubscript{2})\textsubscript{4} molecules (58 atoms) per unit cell\textsuperscript{11}. Importantly, it was noted that weak van der Waals forces play an important role in the intermolecular interactions\textsuperscript{11}. We denote the PETN-I polymorph as PETN, but a second polymorph, PETN-II, has been reported at high temperature\textsuperscript{13} and a third polymorph, PETN-III, has recently been reported near 6 GPa\textsuperscript{14}. In addition, Olinger \textit{et al.}\textsuperscript{15} performed x-ray diffraction experiments of linear and volume compression of PETN up to 10 GPa at room temperature.

Several theoretical studies of energetic materials including PETN may be found in the literature\textsuperscript{16-28}. Of particular importance for comparison with this work are the first-principles studies by Gan \textit{et al.}\textsuperscript{18}, Byrd and Rice\textsuperscript{23}, and Brand\textsuperscript{19}. Gan \textit{et al.}\textsuperscript{18} performed DFT calculations using the Perdew-Burke-Ernzerhof (PBE) functional and a Gaussian basis set to simulate the hydrostatic compression of PETN. Byrd and Rice\textsuperscript{23} have performed a comprehensive study of the accuracy of DFT in application to several EMs. They used DFT with a plane-wave basis set using the Perdew-Wang (PW91), PBE, and local density approximation (LDA) flavors of density functional theory at various cutoff energies. Also, Brand\textsuperscript{19} performed Hartree-Fock
calculations of hydrostatic compression with a Gaussian basis set. Most of the calculations deal with equilibrium properties or hydrostatic compression. Therefore, the goal of this work is to extend the isotropic EOS for PETN to study its anisotropic properties upon high compression. The uniaxial compression studies, motivated by the highly anisotropic shock-sensitivity behavior of the crystal, were performed to investigate relative changes of physical properties upon uniaxial compression along seven low index crystallographic directions, \(<100>\), \(<010>\), \(<001>\), \(<110>\), \(<101>\), \(<011>\), and \(<111>\). We also completed studies of the equilibrium properties and the hydrostatic EOS of PETN-I for the purpose of evaluating the accuracy of DFT as applied to EM crystals and for comparison with previous calculations.

The shear stresses upon uniaxial compression are of particular interest because they are usually considered to be the driving forces of plastic deformations in crystals and the sources of mechano-chemical reactions behind the shock wave front. Therefore, we investigate the behavior of shear stresses in PETN upon uniaxial compression with the specific aim of seeing if there is any correlation with observed anisotropic shock sensitivity.

II. COMPUTATIONAL DETAILS

First-principles DFT\textsuperscript{29} calculations were performed using the Vienna Ab-Initio Simulation Package\textsuperscript{30,31} (VASP). To obtain accurate results, tests were performed to choose appropriate the DFT functional, pseudopotential, k-point set, and energy cutoff – the parameters that control the quality of the calculations. The DFT functionals tested were PW91\textsuperscript{32,33} and PBE\textsuperscript{34,35} of the DFT Generalized Gradient Approximation (GGA).

VASP employs either ultrasoft pseudopotentials\textsuperscript{36,37} (USP) or the projector-augmented wave\textsuperscript{38,39} (PAW) method to eliminate explicit treatment of core electrons during self-consistent electronic structure calculations. Therefore, both PW91 and PBE functionals were tested with PAW and USP potentials. For each, the experimental structure of PETN was relaxed with an energy cutoff of 1,000 eV and a 2x2x2 Monkhorst-Pack\textsuperscript{40} (MP) k-point grid. We found that the PBE functional and the PAW potential produced better agreement than any other combination of functional and potential.

The energy cutoff is a very important parameter that controls the completeness of the plane-wave basis set. Together with the density of k-point sampling of the Brillouin zone, it determines the numerical accuracy of DFT plane-wave calculations. It is also known that the DFT calculations of molecular crystals, which are characterized by a highly inhomogeneous distribution of electron density, require larger basis sets to sample the very small electron density in the intermolecular space of the crystal. Therefore, extensive tests were performed to choose the energy cutoff and k-point density that would provide sufficient accuracy of total energies, atomic forces, and stresses acting on the PETN crystal both at equilibrium and at highly compressed states.

First, total energy calculations without relaxation were performed on both the experimental structure and a half-compressed structure using an energy cutoff of 1,000 eV to test for a sufficient k-point set. The half-compressed structure was made by scaling the lattice parameters by \(0.5^{(1/3)}\), and it was used in this test to be sure that, as the Brillouin zone enlarged during compression, the fixed k-point set would still provide results with sufficient accuracy. We found that the 2x2x2 MP set yielded convergence results better than 0.0007 eV/atom in energy, 0.02 eV/A in forces and 0.05 GPa in pressure, and was chosen for the equilibrium structure and compression calculations. It should be noted here that the k-point spacing in this
grid corresponded to an average k-point spacing of 0.08 Å\(^{-1}\) in each direction when the structure was scaled to half of its experimental volume.

Energy cutoff values of 400, 500, 700, and 1000 eV were then tested on the experimental structure via total energy calculations using the PBE functional, the PAW pseudopotentials, and the 2x2x2 MP grid. The minimum energy cutoff, and thus basis set size, with sufficient accuracy was desired. From this comparison, the 700 eV energy cutoff was chosen to be used for all future calculations, which yielded convergence better than 0.4 GPa in pressure, 0.0015 eV/atom in energy, and 0.015 eV/Å in forces. It should be noted that 700 eV is almost twice the nominal energy cutoff for the PAW potential used, 400eV.

To obtain the theoretical cell parameters for PETN, the experimental structure was relaxed using the parameters above via the quasi-Newton structure minimization method as implemented in VASP. Unit cell size and shape, as well as atomic coordinates, were allowed to simultaneously relax without a constraint on symmetry. The convergence criterion for electronic steps for all calculations was set to 10\(^{-6}\) eV, whereas ionic steps were stopped when the maximum force on any atom was less than 0.01 eV/Å. Hydrostatic compression of PETN was simulated by VASP calculations that compressed the unit cell from \(V/V_0 = 1.00\) to 0.60 in increments of 0.02, where \(V_0\) is the predicted volume at zero pressure. At each step within the compression, the unit cell shape and atomic coordinates were allowed to relax under constant volume without symmetry constraints. The maximum force on any atom was less than 0.03 eV/Å for all compression simulations.

Uniaxial compressions were performed along seven low index crystallographic directions: \(<100>\), \(<010>\), \(<001>\), \(<110>\), \(<101>\), \(<011>\), and \(<111>\). For each compression direction, the Cartesian coordinate system, used to specify components of the lattice vectors, was rotated to orient the x-axis along the specific crystallographic direction to be compressed. Then, the x-component of each lattice vector was scaled by increments of 0.02 up to \(V/V_0 = 1.06\) and down to \(V/V_0 = 0.70\). The uniaxial expansions and compressions near equilibrium were also used to obtain elastic constants of PETN. At each step, only the atomic coordinates were allowed to relax while unit cell was held fixed. To avoid any jumps in physical quantities due to insufficient sampling of the Brillouin zone, the MP k-point set was generated for each uniaxial compression to ensure an average grid spacing of 0.08 Å\(^{-1}\) in each direction\(^{41}\) when the structure was scaled to half of its experimental volume along the corresponding compression direction.

### III. EQUILIBRIUM PROPERTIES AND HYDROSTATIC EOS

The structure of PETN-I at zero pressure was calculated, and the unit cell parameters were compared with the data refined by Trotter\(^{12}\) from the experiments of Booth and Llewellyn\(^{11}\), Table 1. Calculated equilibrium structure of PETN compared with experiment.

<table>
<thead>
<tr>
<th>Work</th>
<th>(a) (Å)</th>
<th>(b) (Å)</th>
<th>(c) (Å)</th>
<th>(V) (Å(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>9.617 (+2.5%)</td>
<td>9.612 (+2.5%)</td>
<td>6.826 (1.9%)</td>
<td>630.99 (+7.0%)</td>
</tr>
</tbody>
</table>
The percent error of our calculations of equilibrium lattice constants is within 2-3%.

As in previous DFT studies of energetic materials\textsuperscript{17, 21}, the prediction of greater lattice constants was believed to be due to an inadequate description of van der Waals dispersive interactions in DFT functionals. Predicted lattice angles, similar to experiment\textsuperscript{11, 12}, were calculated to be 90.0 degrees.

The PETN-I isothermal equation of state was obtained by performing DFT hydrostatic compression simulations at 0 K. Fig. 1. compares the DFT results with the room-temperature experimental data from the work of Olinger, Halleck, and Cady\textsuperscript{15}. The range in volume changes shown is from 60 to 100% of the calculated equilibrium volume, 630.99 Å\textsuperscript{3}. At $V/V_0 = 0.6$, the calculated pressure is approximately 30 GPa, which is also approximately the detonation pressure of PETN\textsuperscript{42}. The calculated pressure at a given volume is higher than the experimental value, which is believed to be due to the inadequate description of weak van der Waals dispersive interactions by DFT\textsuperscript{21}. Meanwhile, the discrepancy between the experimental and calculated isotherms is reduced as volume decreases, which is probably due to increased overlap of electron densities of neighboring molecules leading to a better description of the intermolecular interactions by DFT. This trend has been observed in a number of hydrostatic compression studies of energetic molecular crystals using DFT\textsuperscript{21}.

The lattice constants $a$ and $c$ as a function of pressure are compared with experimental data\textsuperscript{15}, see Fig. 2. As pressure increases, the experimental value of $a$ approaches the calculated value. However, the calculated value of $c$ is greater than the experimental value for all pressures. This trend has been observed previously in the DFT calculations of Brand\textsuperscript{19}.

Bond lengths of a PETN molecule within the crystal were plotted as a function of $V/V_0$ in Fig. 3. As observed in a previous DFT study by Gan, Sewell, and Challacombe\textsuperscript{18}, the C-C bond and the O-N bond experience greater changes than the other bonds. The greatest change in bond length observed was for the proximal O-N bond, which decreased by 0.086 Å.

The bulk modulus, $B_0 = -V(dP/dV)$, and its derivative with respect to pressure $B'_0$ were obtained from fitting the PETN-I EOS data to the Birch-Murnaghan EOS\textsuperscript{18}. 

---

\textbf{Figure 1.} Isothermal hydrostatic EOS of PETN-I.

\textbf{Figure 2.} Lattice parameters of PETN under hydrostatic compression.

\textbf{Figure 3.} Bond lengths of PETN under hydrostatic compression.
\[ P = \frac{3}{2} B_0 (\eta^7 - \eta^5) \left[ 1 + \frac{3}{4} (B'_0 - 4) (\eta^2 - 1) \right], \quad (1) \]

where \( \eta = V/V_0 \), using pressures from about -0.3 to 10.4 GPa (\( V/V_0 = 1.06 \) to 0.72). Following the work of Gan, Sewell, and Challacombe\(^{18} \), we have restricted our fitting to pressures below 10.45 GPa to be consistent with the experimental work of Olinger\(^{15} \). Table 2 shows our data as compared with the Birch-Murnaghan fitting\(^{18} \) of the experimental data obtained by Olinger et al.\(^{15} \) and the bulk modulus obtained via experimental elastic constants\(^{43} \),

\[ B = \frac{C_{33} (C_{11} + C_{12}) - 2C_{13}^2}{(C_{11} + C_{12}) + 2C_{33} - 4C_{13}}, \quad (2) \]

from Winey and Gupta\(^{44} \). Not included in Table 2 are the values of the bulk modulus from the theoretical works of Gan et al.\(^{18} \) (\( B_0 = 14.5 \) GPa, \( B'_0 = 6.7 \)) which were obtained by fitting their EOS data to the Birch-Murnaghan EOS (1) and Brand\(^{45} \) obtained \( B_0 = 9.38 \) GPa by using elastic constants via equation (2).

The bulk modulus can be found by fitting to other equations, such as the Murnaghan equation and the Hugoniot conservation equations used by Gan et al.\(^{18} \). The values of the bulk modulus found by fitting our data set to these equations were within about 10% of the value obtained by fitting to (1), similar to the results obtained by Gan et al.\(^{18} \).

Using the uniaxial compression data discussed below, the energy \( E \) of the crystal as a function of strain \( \varepsilon \) was fit to a fourth-order polynomial \( E(\varepsilon) \). The elastic constants calculated were then found from the relation

\[ C_{ii} = \frac{1}{V_0} \left( \frac{\partial^2 E}{\partial \varepsilon_i^2} \right), \quad (3) \]

where \( i = 1, 2, 3 \). The calculated values for these elastic constants are in good agreement with the experimental data analyzed by Winey and Gupta\(^{44} \), see Table 3.

<table>
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<tr>
<th>Work</th>
<th>( B_0 ) (GPa)</th>
<th>( B'_0 )</th>
</tr>
</thead>
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<td>8.3</td>
</tr>
<tr>
<td>Olinger et al. (Birch-Murnaghan) [Ref. 15]</td>
<td>9.4</td>
<td>11.3</td>
</tr>
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<td>Winey and Gupta [Ref. 44]</td>
<td>9.1</td>
<td>-</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Work</th>
<th>( C_{11} ) (GPa)</th>
<th>( C_{22} ) (GPa)</th>
<th>( C_{33} ) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>18.3</td>
<td>18.5</td>
<td>14.2</td>
</tr>
<tr>
<td>Winey and Gupta [Ref. 44]</td>
<td>17.22</td>
<td>17.22</td>
<td>12.17</td>
</tr>
</tbody>
</table>
IV. UNIAXIAL COMPRESSIONS

The diagonal elements of the stress tensor, $\sigma_{xx}$, $\sigma_{yy}$, and $\sigma_{zz}$, as a function of compression ratio from $V/V_0 = 0.7$ to 1.0 for each uniaxial compression are shown in Figs 4a, 4b, and 4c, respectively. The anisotropic character of constitutive relationships is clearly seen from Fig. 4a, which shows substantial differences in longitudinal stresses between uniaxial compressions along different crystallographic directions as compared with pressure from hydrostatic compressions when $p = \sigma_{xx} = \sigma_{yy} = \sigma_{zz}$. For strains below 15%, the calculations indicate that the crystal is less compressible in the $<011>$ and $<101>$ directions and more compressible in the $<110>$ and $<001>$ directions. However, for strains greater than 25%, the $<001>$ and $<110>$ directions emerge as the least compressible. Based upon the work of Jindal and Dlott\cite{8}, the anisotropic compressibility of PETN could be an important factor for determining if anisotropic heating upon shock compression plays a significant role in its anisotropic detonation sensitivity. However, we do not calculate the Gruneisen parameters necessary for such a prediction\cite{8}. For shocks near 4 GPa in the $<110>$ direction, evidence of detonation has been shown in several experiments\cite{3}. Therefore, it is likely that the anisotropic constitutive relationships can not be probed experimentally when compressed in this direction beyond 4 GPa. However, the $<100>$ direction has been shown to be very insensitive\cite{1,3,5}, and therefore it is most likely that the experimental dependence of shear stress on strain can be obtained for this direction in the compression interval shown in Fig. 4.

The change in energy per atom and the band gap of PETN-I as a function of...
compression for each uniaxial compression and the hydrostatic compression are shown in Figs 5 and 6, respectively. Anisotropic behavior is clearly exhibited in both graphs. The greatest change in energy is experienced when the crystal is compressed in the <101> or <011> directions, and all uniaxial compressions raise the energy of the crystal more than hydrostatic compression because of the constraints of the unit cell in transverse directions. Similarly, the greatest reduction in the band gap is observed for the <101> and <011> uniaxial compressions. The smallest change in band gap is observed for hydrostatic compression, but it should be noted that the most sensitive direction, <110>, experiences only a slightly larger reduction in band gap than the hydrostatic compression.

V. SHEAR STRESSES

The shear stresses could be of paramount importance in understanding the shock-induced anisotropy of EMs. The shock-loading conditions are characterized by fast uniaxial compression of the crystal along a specific crystallographic direction corresponding to the direction of the shock-wave propagation. The shear stresses are the driving forces of shear-induced plastic deformations and mechano-chemical events behind the shock-wave front. Therefore, we calculate the maximum shear stresses for each uniaxial compression, see Figs 7a, and 7b. Under the uniaxial compression, the crystal experiences the maximum shear stresses $\tau_{xy}$ and $\tau_{xz}$ directed at 45° to the compression direction, their values being $\tau_{xy} = (\sigma_{xx} - \sigma_{yy})/2$ and $\tau_{xz} = (\sigma_{xx} - \sigma_{zz})/2$.

The behavior of the shear stresses for each compression is relatively similar for the $\tau_{xy}$ and $\tau_{xz}$ maximum shear stresses. The $\tau_{yz}$ values for each compression are relatively different and significantly smaller than the $\tau_{xy}$ and $\tau_{xz}$. For compressions greater than $V/V_0 = 0.76$, the more sensitive directions, <110> and <001>, show greater magnitude of shear stresses $\tau_{xy}$ and $\tau_{xz}$ than the insensitive directions, <100> and <101>. Based upon the greater shear stresses displayed for compression in the more sensitive directions, we have previously suggested a correlation between sensitivity and shear stress behavior under uniaxial compression. Here, we also examine the shear stress maxima, $\tau_{xy}$ and $\tau_{xz}$, as a function of longitudinal stress, $\sigma_{xx}$, to compare with experiment and examine the possibility of a correlation between sensitivity and shear stresses in PETN, see Figs. 8a and 8b. Note that each curve terminates at $V/V_0 = 0.70$. The calculated longitudinal stress, $\sigma_{xx}$, required to compress PETN to the point

![Figure 7a. Shear stress maximum $\tau_{xy}$ (a) and $\tau_{xz}$ (b).](image)
where <110> and <001> compressions exhibit both shear stresses greater than the sensitive <100> and <101> compressions, varies from ~4 GPa for <100> direction to ~12 GPa for <101> direction. As stated above, <110> compressions have experienced transition to detonation in Dick’s experiment upon compression by longitudinal stresses as low as 4.2 GPa\(^3\). Further, compressions of PETN in the <001> direction have produced detonation at longitudinal stresses just above 12 GPa\(^3\). The values of \(\tau_{xy}\) and \(\tau_{xz}\) for the <001> compression do emerge as the greatest values for the compressions studied beyond 12 GPa, while below this value both shear stress maxima for <101> compression remain the greatest. However, in Dick’s experiment shock in <101> does not lead to detonation for the input stresses up to ~15 GPa, though it exhibits an intermediate velocity transition (abrupt increase of the shock velocity and stress) at 8.8 GPa. Thus, while there are some indications of a correlation between maximum shear stresses and shock sensitivity for the <100>, <110>, and <001> cases, additional analysis needs to be performed. In particular, as suggested in the work of J. Dick\(^1\), it might be helpful to consider the projection of shear stress maxima on available slip systems under uniaxial compression, and this will be the subject of our future work.

**VI. CONCLUSIONS**

First-principles simulations of hydrostatic compression and uniaxial compressions in the <100>, <010>, <001>, <110>, <101>, <011>, and <111> directions of PETN have been performed using DFT with the PBE functional and the PAW potential. The calculated lattice parameters were overestimated by about 3%, which is believed to be due to a poor description of van der Waals dispersive interactions in the functionals of DFT. The calculated bulk modulus and elastic constants are in reasonable agreement with experiment. With the application of hydrostatic pressure, the calculated unit cell volume and lattice parameters of PETN show increasing agreement with experimental data.

The energy per atom, band gap, and stresses were calculated for each uniaxial compression and compared with the calculated results hydrostatic compression. Our results show a substantial anisotropy of various properties of PETN-I upon uniaxial compressions. The maximum shear stresses were calculated and examined for a correlation with the anisotropy in shock-initiation sensitivity. The calculated maximum shear stresses, \(\tau_{xy}\) and \(\tau_{xz}\), upon compression in the sensitive <110> and <001> directions are greater than for the insensitive <100> direction at input longitudinal stresses above 4 GPa, but no clear correlation

\[ \text{Figure 8a. Maximum shear stress } \tau_{xy} \text{ (a) and } \tau_{xz} \text{ (b) as a function of longitudinal stress } \sigma_{xx}. \]
between maximum shear stresses and sensitivity is observed for the <101> direction up to 12 GPa. In the future, we will perform a more detailed analysis of the shear stress behavior under uniaxial compressions by considering slip systems of the PETN crystal available upon compression in specific crystallographic directions, as suggested by the work of J. Dick\textsuperscript{1}, to establish more certain correlations with anisotropic shock sensitivity of PETN.

ACKNOWLEDGEMENTS

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REFERENCES

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Graduate Research Associate  
Materials Simulation Laboratory  
University of South Florida  
lab: (813) 974-6395  
email: mconroy[ at ]shell.cas.usf.edu

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Director, Materials and Process Simulation Center (MSC)
Office: 316 Beckman Institute (BI)
Mail Code (139-74) (400 South Wilson Ave.)
California Institute of Technology
1200 East California Blvd.
Pasadena, California 91125 USA
http://www.wag.caltech.edu
Phone: (626) 395-2731 (wag), 395-2730 (Sec), FAX: (626) 585-0918, Teleconfer: (626)395-3093
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Fx: (703) 767-5535 (Attn: Su Peiris)  
Em: Suhithi.Peiris@dtra.mil

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