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

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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 \( \beta \)-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 \( \beta \)-HMX as calculated by DFT using GGA-PW shows substantial deviation from experiment. The uniaxial compression of both PETN-I and \( \beta \)-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, \( \tau_{xx} \), 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 \( \beta \)-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. 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, 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\(_4\)H\(_{12}\)N\(_{10}\)O\(_{34}\)) and cyclotetramethylene tetranitramine (HMX, C\(_4\)H\(_{10}\)N\(_{10}\)O\(_{34}\)). These systems have been already studied both experimentally and theoretically. In particular, isothermal compression of PETN has been investigated by Olinger et al. in 1975, but accurate experimental results on isothermal hydrostatic compression of HMX have appeared relatively recently. Interestingly, Dick experimentally discovered the anisotropy in sensitivity to shock initiation present in PETN. Less sensitivity information is available for HMX energetic crystals.

Hydrostatic compression of PETN and HMX has been studied theoretically using classical interatomic potentials, first-principles DFT, and Hartree-Fock methods. In particular, Soreescu, Rice and Thompson investigated both PETN and HMX using a specially developed classical intermolecular potential for nitramines. A recent study of hydrostatic compression of PETN has been performed using DFT with a Gaussian basis set within an all-electron implementation. PETN and HMX 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. 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. 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. 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\(^{-1}\) 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 \(P\overline{4}2_1c\) 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 1. Equilibrium lattice parameters of PETN-I calculated by DFT using several density functionals (LDA, GGA-PW, and GGA-PBE) and compared with experiment. |
|---|---|---|---|
| PETN-I | a=b, Å (error, %) | c, Å (error, %) | c/a (error, %) | Cell Volume, Å |
| Experiment | 9.38 | 6.71 | 0.71 | 589.5 |
| LDA | 8.891 (-5.2%) | 6.453 (-3.8%) | 0.726 (+2.3%) | 510.1 (-13.5%) |
| GGA-PW | 9.600 (+2.3%) | 6.796 (+1.3%) | 0.708 (-0.3%) | 626.3 (+6.2%) |
| GGA-PBE | 9.820 (+4.7%) | 6.950 (+3.6%) | 0.708 (-0.3%) | 670.2 (+13.7%) |

| 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. |
|---|---|---|---|---|---|
| β-HMX | a, Å (error, %) | b, Å (error, %) | c, Å (error, %) | $\alpha = \beta$ | $\gamma$ | Cell Volume, Å |
| Experiment | 6.54 | 11.05 | 8.70 | 90 | 124.3 | 519.4 |
| LDA | 6.375 (-2.5%) | 10.474 (-5.2%) | 8.375 (-3.7%) | 90 | 123.7 | 465.4 (-10.4%) |
| GGA-PW | 6.755 (+3.3%) | 11.497 (+5.2%) | 9.096 (+4.6%) | 90 | 124.7 | 580.9 (+11.8%) |
| GGA-PBE | 6.760 (+3.4%) | 11.505 (+4.1%) | 9.095 (+4.6%) | 90 | 124.8 | 581.1 (+11.9%) |
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 $V/V_0$.](image)

![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 $V/V_0$.](image)
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
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

![Graphs showing shear stresses in PETN-I upon uniaxial compression along [100], [110], and [001] directions as a function of compression ratio $a/a_0$.](image)

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 non-monotonic behavior of shear stresses has been observed in other classes of shock-compressed material. For example, we have recently found that covalently bonded materials such as diamond and silicon exhibit an anomalous elastic response upon shock wave propagation: the weaker wave has both elastic and plastic regions of material behind the shock wave front, but at larger shock intensities the plastic deformations disappear. We related such unusual behavior with the non-monotonic behavior of the shear stresses: the crystal undergoes all the stages of compression quickly until it reaches the final compression corresponding to very low values of the shear stresses. Because the shear stresses are the driving forces of plastic deformations, the compressions corresponding to the lowest values of shear stresses may be characterized by the absence of the plastic deformations. This might be the reason of the absence of the initiation for the [100] crystallographic direction at the same level of compression (shock wave intensity) as for crystals compressed in [110] and [001] directions.

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, whereas the lattice parameters of \( \beta \)-HMX exhibit larger errors \( \sim 5\% \) for all the DFT functionals.

The isothermal hydrostatic equation of state for PETN-I was predicted by DFT in a reasonable agreement with experiment. However, the hydrostatic EOS for \( \beta \)-HMX as calculated by DFT using GGA-PW shows substantial deviation from 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 β-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, $\tau_{xz}$, 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 β-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.

REFERENCES

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