

Theoretical study on crystalline structures of TATB at different pressures

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Abstract

Crystalline structures of TATB including molecule structures, lattice parameters, band structures, XRD spectrums, total densities of states (DOS) and spatial distributions of charge densities at high pressures such as 0.1 GPa, 1 GPa, 10 GPa, 100 GPa, 1000 GPa are investigated by CASTEP in Material Studio, and the results show that: (1) TATB crystal cell mainly changes on c-axis orientation, and the energetic band structure of crystal and TATB molecular structure change a little when the pressure changes from 0.1 GPa to 10 GPa. (2) TATB can be compressed to get a density over 2.5 g/cm³ at tens GPa, and the total energy of the crystal doesn't increase much more. (3) TATB crystal exists as semiconductor at 0.1-100 GPa, and a transition from semiconductor to conductor is predicted at hundreds GPa, and TATB molecular structure must be destroyed at same pressure.

1. Introduction

TATB (1,3,5-triamino-2,4,6-trinitrobenzene) is one of the most widely used explosives for its good insensitivity and a certain detonation properties, and it's the only insensitive explosive that authorized by Department of Energy, United States¹⁾. At present, structure of crystalline TATB is investigated theoretically and experimentally. Ji et al²⁾ draw a conclusion that TATB crystal is between insulator and semiconductor judged from its band gaps of about 4.1eV, and the heat of sublimation is predicted to be 136.25 kJ/mol, which is in good agreement with the experimental result by period DFT method. Band-gap closure is found to begin near 47% uniaxial strain, and lower bound for the metalization pressure is predicted at 120 GPa by Wu et al³⁾, far above the detonation pressure of TATB. Gee et al⁴⁾ suggest that crystal fracture induced by the anisotropic volume expansion of TATB is the root cause for the permanent growth in that nonreversible growth is displayed when crystal fracture is incorporated in their model. An experiment for verifying the semiconductor model of detonation is described by Grebenkin et al⁵⁾, within this model, the electron thermal conductivity is the decisive parameter in the initiation of detonation of TATB. Crystalline structure determines crystalline properties, and people are interested in what are the crystalline structures of TATB at these pressure for there are usually high pressure occurred as TATB explodes, even under other extreme circumstances. This paper will answer this question by theoretical simulation.

2. Methods and computational details

The CASTEP code⁶⁾ which employs the Density Functional Theory (DFT) plane-wave pseudopotential method is adopted to study the structure of crystalline TATB at high pressure such as 0.1, 1.0, 10, 100, 1000 GPa. And effect of pressure on geometry optimization is treated by Winkler's method⁷⁾. Meanwhile, three hypotheses are taken to simulate: (1) All structures are of 0 °C; (2) TATB has crystal structure at high pressure; (3) there are two TATB molecules in simple crystal cell and the space groups of crystals are not constrained. We adopt experimental structure from Literature⁸⁾ (cell parameters are: a -9.010 Å, b -9.028 Å, c -6.812 Å, α -108.59 deg., β -91.82 deg., γ -119.97 deg. and density is 1.937 g/cm³) as initial structure, and Ultrasoft pseudopotential⁹⁾ (USP, reciprocal space) and BFGS method¹⁰⁾ and LDA/CA-PZ functional to optimize TATB crystal structure, and get the properties such as molecule structure, lattice parameter, band structure, XRD spectrum, total density of states (DOS) and spatial distribution of charge density, to investigate the TATB crystal structure at high pressure. Moreover, the energy cutoff and k-points are adopted at 500eV and 9 (3×3×3) respectively, and convergence tolerances are showed as following: energy-2.0e⁻⁵ eV/atom, Max.force-0.05 eV, Max.stress-0.1 GPa, Max.displacement- 0.002 Å, k-points separation-0.05 Å. It must be explained that all these methods have been verified by tentative calculations and contrast with experiment.

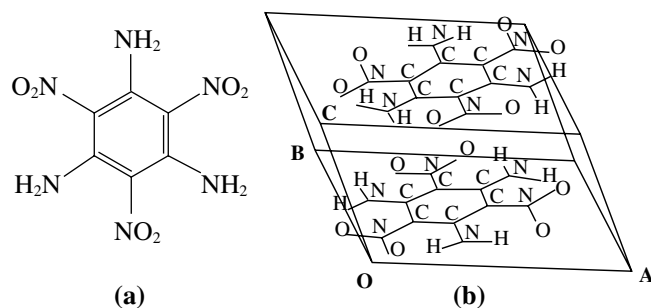


Fig. 1 (a)-TATB molecule, (b)-unit crystal cell of TATB.

3. Results and discussion

3.1 Lattice parameters and densities of crystals

The percentage variations of the lattice parameters and densities of optimized TATB cell at high pressure comparing to the experimental values of common pressure are listed in Table 1. From Table 1, we can see that all parameters change a little under the lower pressure, but three axes change more and the *c*-axis decreases most among them when the pressure increases more than 10 GPa. Accordingly, the densities of crystals increase very fast at higher pressure. All these results must be attributed to layered and graphite-like structure of TATB crystal. There are strong interactions due to formation of hydrogen bond among the neighbor TATB molecules in the same layer, and weaker interaction, that is, van der Waals force between layers nearby. When the pressure increases, the crystal must be most easily and mainly compressed along *c*-axis in that there is the smallest internal stress along this orientation. When the pressure is lower than 1 GPa, the internal stress of TATB crystal can match the external stress, with a result, there are a little change of lattice parameters; and much change take place in that the internal stress is unmatched with the external over several GPa. So, from 0.1 GPa to 1 GPa, the density of TATB crystal increases a little, 0.05 percent, and it has increased 33.30 percent at 10 GPa, 95.57 percent at 100 GPa and 280 percent at 1000 GPa. Also, we

can induce that the most change amplitude of density must be from 100 GPa to 1000 GPa, and there is a special and noticeable pressure at hundreds GPa.

3.2 Total energy

Table 2 contains the total energies of optimized TATB crystal structures at different pressures. From the table, we can find that TATB crystal has the lowest total energy at about 0.1 GPa (-10527.6451 eV), and the total energy changes only about 1 eV from 0.1 to 10 GPa and only about 26 eV from 0.1 GPa to 100 GPa, and there is higher total energy when there is higher external pressure. Moreover, TATB crystal's total energy changes a bit from 0.1 GPa to 10 GPa, from this point of view and Table 1: we can compress TATB crystal and get its crystal density above 2.5 g/cm³ at several 10 GPa. In addition, that the total energy of TATB crystal jumps sharply from -10501.5272 eV to -10258.4103 eV corresponding to 100 GPa and 1000 GPa respectively, shows again that there is a noticeable structural change at hundreds GPa.

3.3 Molecular structure

We mainly analyze the changes of bond length and maximal dihedral angle on benzene ring (D_{\max} , the more D_{\max} , the more TATB destroyed) listed in Table 3 and Table 4 to investigate the TATB molecular structure in crystal cell at high pressure. From Table 3 and Table 4, we can see that the higher pressure it is, the shorter bond lengths and the bigger D_{\max} TATB molecules have (by the way, in Table 3, that the smallest N-H bond length of experiment is 0.798 Å unreasonably due to experimental error). But from 0.1 to 100 GPa, the bond lengths and D_{\max} change a little, and all these must be due to relatively small internal stress along the *c*-axis: when external pressure increases, the crystal will be contracted mainly along the *c*-axis, i.e., the distance between the neighbor layers decrease, and the size and shape of TATB molecules change a little. However, there are sharp and great changes of the bond lengths and D_{\max} at 1000 GPa. As above-mentioned, we can induce that there is a critical pressure which destroys TATB molecules in crystal at hundreds GPa.

Table 1 Percentage variation of lattice parameters and densities of TATB crystals at different pressures.

Pressure (GPa)	Cell parameters						Density
	<i>a</i>	<i>b</i>	<i>c</i>	α	β	γ	
0.1	-0.17	-0.10	0.04	0.03	-0.13	-0.03	0.15
1	0.07	-0.17	-0.01	-0.07	-0.09	0.04	0.05
10	-4.30	-4.30	-15.40	3.06	-0.03	0.04	33.30
100	-11.84	-11.98	-30.28	6.23	-0.76	-0.02	97.57
1000	-26.23	-26.64	-43.89	12.05	-2.07	-0.03	281.21

Table 2 Total energy (*E*, eV) of crystal cell of TATB at different pressure (*P*, GPa).

<i>P</i>	Exp.	0.1	1	10	100	1000
<i>E</i>	-10516.7997	-10527.6451	-10527.5899	-10526.6535	-10501.5272	-10258.4103

Table 3 Bond lengths of TATB molecules in crystal cells (\AA) at different pressures (P , GPa).

P	Exp.	0.1	1	10	100	1000
R_{C-C}	1.433~1.448	1.435~1.438	1.435~1.438	1.429~1.432	1.368~1.373	1.250~1.284
$R_{C-N(NH_2)}$	1.311~1.323	1.314~1.316	1.313~1.317	1.307~1.310	1.259~1.263	1.202~1.224
$R_{C-N(NO_2)}$	1.419~1.426	1.393~1.396	1.395~1.396	1.385~1.388	1.311~1.318	1.198~1.263
R_{N-H}	0.798~1.067	1.044~1.045	1.042~1.046	1.040~1.044	1.029~1.034	0.948~1.027
R_{N-O}	1.234~1.253	1.267~1.275	1.267~1.274	1.267~1.273	1.255~1.268	1.155~1.250

 Table 4 D_{\max} (degree) in crystal cells at different pressures (P , GPa).

P	Exp.	0.1	1	10	100	1000
D_{\max}	4.55	3.57	4.91	6.34	7.92	73.57

3.4 XRD spectrums

Figure 2 shows the calculated XRD spectrums of TATB crystal under different pressure. From Exp. to 1000 GPa, the 2-theta of peaks are 28.41 and 14.09, 28.47, 28.35, 30.68, 29.03, 29.49 and 44.12 and 41.99 respectively. These calculated spectrums reflect the characteristics of TATB crystal and must be constructive for absence of experimental values at these pressures.

3.5 Band structure and density of states

The Fermi energies obtained by calculating are 1.0996 eV, 1.1029 eV, 3.9422 eV, 9.4930 eV and 26.5760 eV respectively corresponding to five different pressures in increasing order. The Fermi energies (showed with dashed) are transformed to zero, and the energy band structures and the total DOS of optimized TATB crystal

structures are showed in Fig. 3 and Fig. 4. The band structures seem very similar when the pressures are 0.1, 1, 10 GPa: the energy distributions of electron are about from -25.0 eV to 7.7 eV and mainly centralize from -7.3 eV to 0.0 eV, the energy gaps (E_g) are about 2.2 eV, 2.2 eV, 1.72 eV respectively similar to that of semiconductor. The ranges of electronic energy distribution increase from -27.83 eV to 8.21 eV and from -41.49 eV to 6.53 eV, and the E_g decrease to 0.94 eV and 0.0eV respectively when the pressures are 100 GPa and 1000 GPa. Meanwhile, the electrons are delocalized in the structures and the higher pressure is, the more electrons are delocalized. So it can be concluded that the Fermi energy and the range of electronic energy distribution and delocalization-ability increase, but E_g decreases and there will be a transition from semiconductor to conductor when the pressure increases.

Figure 4 shows that there are same peak numbers and positions of electron distribution at 0.1 GPa, 1 GPa and 10 GPa, and very differently at 100 GPa and 1000 GPa. At same time, electrons are delocalized most at 1000 GPa. These results are consistent with the above analyses of band structures. As a matter of fact, when c-axis of TATB crystal cell changes in a certain range according to differ-

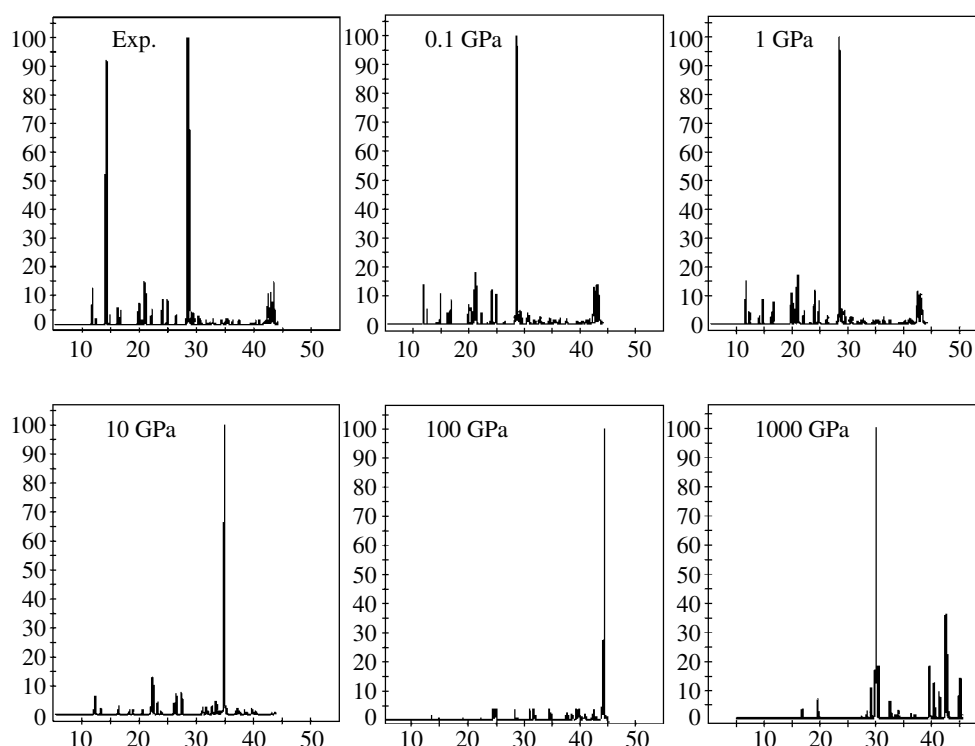


Fig. 2 Calculated XRD spectrums of TATB crystals at different pressures (abscissa-2theta, ordinate-intensity).

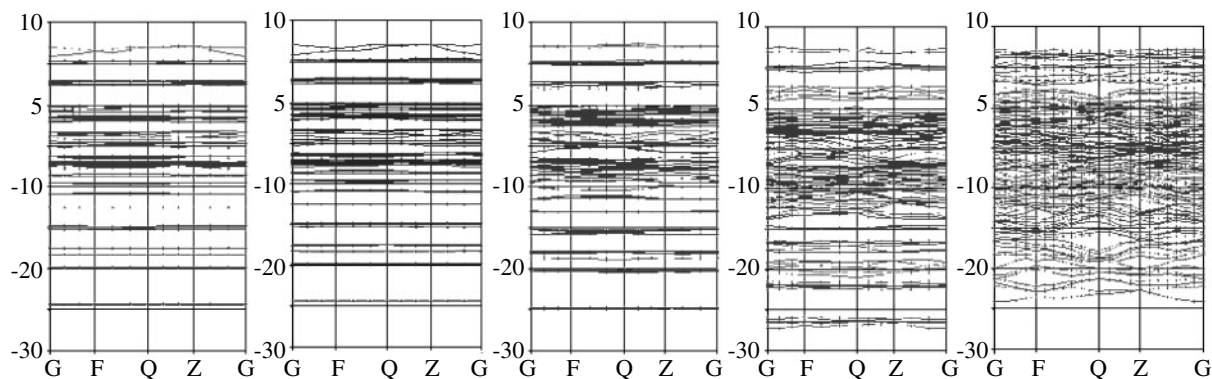


Fig. 3 Energy band structures of TATB crystals at different pressures (ordinate-energy, eV).

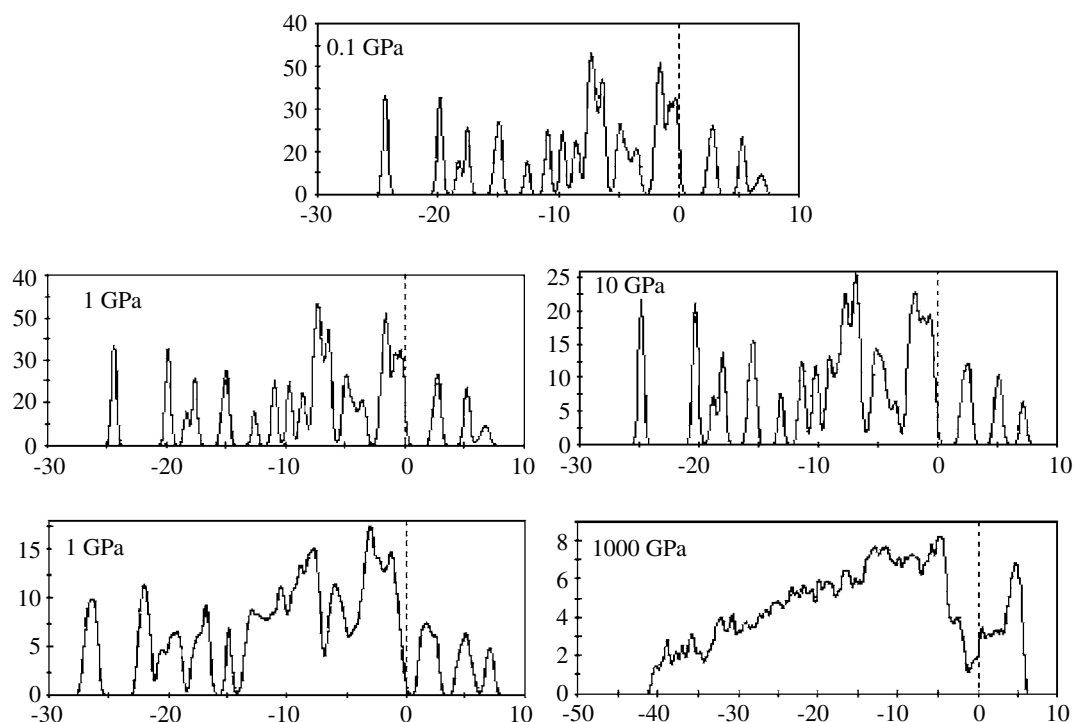


Fig. 4 Total DOS of TATB crystals at different pressures (abscissa-energy, eV, ordinate-DOS, electrons/eV).

ent pressures, i.e. change the distance between the neighbor layers in a certain extent, the energy distribution of electrons in the cell changes little in that TATB is a layered molecular crystal, and there are few effects on electronic structures when the distance changes. But when the pressure increases to hundreds GPa, TATB must turn into conductor according to Fig. 3 and Fig. 4. The result is consistent with Wu's prediction³⁾.

3.6 Density of charge

We cut two slices (one is on the plane of the benzene ring of TATB, the other is on (200) face) to investigate TATB molecular structures and charge density changing when the *c*-axis changes at high pressure. From Fig. 5 that contains two group slices, we can find that TATB approximately keeps a plane structure when the external pressure changes from 0.1 GPa to 100 GPa, but charge density changes much

little. The complete TATB molecule can be seen distinctly in the Fig. 5 (a) from 0.1 GPa to 100 GPa except 1000 GPa. It shows again that TATB molecular structure changes little when the pressure ranges in a certain extent. Figure 5 (b) shows tiny change of atomic distance along the *c*-axis: the bigger pressure, the smaller distance between layers nearby. At 1000 GPa, charge densities on two slices have a great change. It shows again there are an essential change of crystal structure and so-called critical state at hundreds GPa.

4. Conclusions

- (1) TATB crystal cell mainly changes on *c*-axis orientation, and the energetic band structure of crystal and TATB molecular structure change a little when the pressure changes from 0.1 GPa to 10 GPa.
- (2) TATB can be compressed to get a density over 2.5 g/cm³ at tens GPa, and the total energy of the crystal

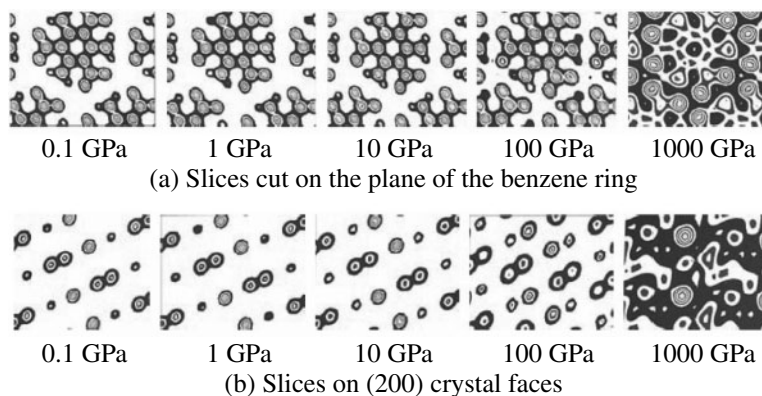


Fig. 5 Charge densities of TATB crystal at different pressure.

doesn't increase much more.

- (3) TATB crystal exists as semiconductor at 0.1-100 GPa, and a transition from semiconductor to conductor is predicted at hundreds GPa, and TATB molecular structure must be destroyed at same pressure.

Acknowledgements

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