DFT Study on Non-reversible Expansion of TATB Crystal

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Abstract: By using DFT method, changing the six parameters of TATB cell and calculating the total energy corresponding to different *volume ratio*, this paper concludes that TATB crystal can only extend irreversibly along the c-axis when heated because the point of experiment is unstable thermodynamically and the ratio of non-reversible expansion must be about 2.6-3.7 per cent theoretically.

Keywords: TATB crystal, non-reversible expansion, DFT

Introduction

TATB (1,3,5-triamino-2,4,6-trinitrobenzene) is one of the most widely used explosives for its good insensitivity and certain detonation properties, and it is the only insensitive explosive authorized by Department of Energy, United States [1]. At present, structure of crystalline TATB is investigated theoretically and experimentally. Ji *et al*. [2] draw a conclusion that TATB crystal is between insulator and semiconductor judged from its band gaps of about 4.1 eV, 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 al.* [3], far above the detonation pressure of TATB. Gee *et al.* [4] suggest that crystal fracture induced by the anisotropic volume expansion of TATB is the root cause for the permanent growth in that non-reversible 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 al.* [5], within this model, the electron thermal conductivity is the decisive parameter in the initiation of detonation of TATB. The non-reversible expansion of TATB crystal is an embarrassed but noticeable phenomenon in armament assembling because it is very important [6, 7], and there some explains but not by Density Function Theory (DFT) for that. Crystalline structure determines crystalline properties, so the non-reversible expansion of TATB crystal must be due to the structure of crystalline TATB. This paper tries to explore the TATB's non-reversible expansion by structural analysis and DFT method.
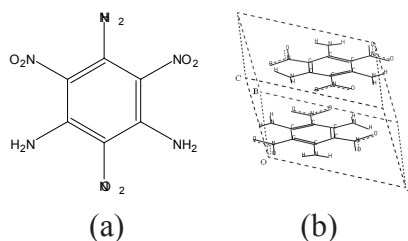
Methods and Computational Details

Figure 1. (a) – TATB molecule, (b) – single crystal cell of TATB

CASTEP [8] which employs DFT and plane-wave pseudopotential method, and Dmol^3 [9], another DFT code, are adopted to study the structure of crystalline TATB. At first, we take structure from Literature [10] (Figure 1) as initial structure, and define a ***volume ratio***, which is the ratio of a volume calculated by changing only one of six TATB cell parameters and that of experiment (a = 9.01 Å, b = 9.03 Å, c = 6.81 Å, α = 108.59°, β = 91.82°, γ = 119.97°). When the volume ratio is less than 1, the crystal is com-

pressed; and more than 1 swells; and 1 is the value of experiment. Secondly, we adopt Ultrasoft (reciprocal space) pseudopotential [11] and BFGS method [12] and LDA/CA-PZ functional to optimize TATB crystal structure (the crystal cell constrained), and get the total energy corresponding to different *volume ratio* and find an explanation for the non-reversible expansion of TATB crystal. Moreover, the energy cut off and k-points are adopted at 500 eV and 9 (3×3×3) respectively and convergence tolerances are showed as following: energy – 2.0 e^{-5} eV/atom, Max. force – 0.05 eV, Max. stress – 0.1 GPa, Max. displacement – 0.002 Å, k-points separation – 0.05 Å. All works have been done by Accelrys' Material Studio on SGI origin 350 station at our institute.
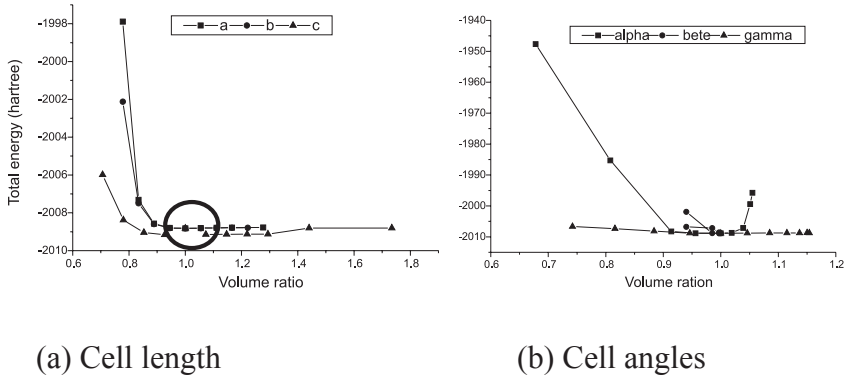
Results and Discussion

(a) Cell length　　　　　　　　　　　　(b) Cell angles

Figure 2. The relationship between total energy and volume ratio when cell parameters of TATB change**.**

We can find that the total energy of TATB crystal has a global minimum (where the volume ratio is 1, that is, the value is of experiment) on five curves but that of c-axis from Figure 2. Now, we can think that TATB crystal extends irreversibly only along c-axis due to local energy maximum being on the curve of c-axis only (to see an ellipse on Figure 1(a)). In order to get more information around the maximum, we do more calculation around it.
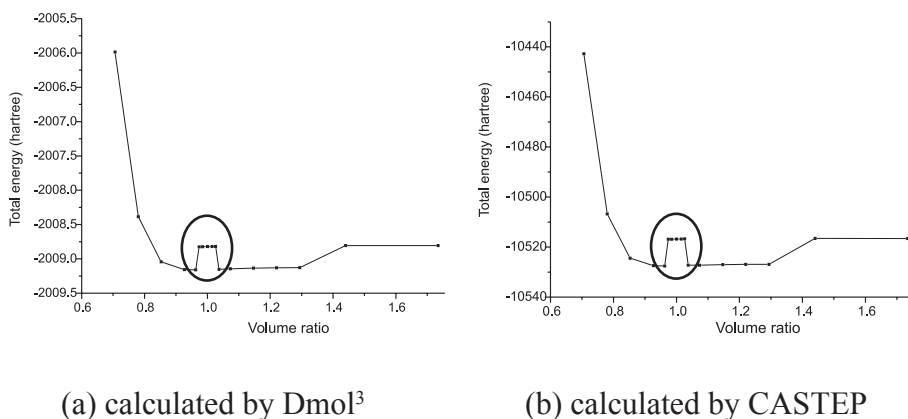
(a) calculated by Dmol³   (b) calculated by CASTEP

Figure 3. The relationship between total energy and volume ratio when
c-axis of TATB cell changes.

We optimize the structures of crystalline TATB and get the total en-
ergies by using Dmol³ (LDA-PWC, Quality-fine) and CASTEP, and the
results around the maximum are displayed on Figure 3 (see two ellipses)
and listed on Table 1. From Figure 3 and Table 1, it can be deduced that
TATB crystal can extend irreversibly along the c-axis when heated be-
cause the point of experiment is unstable thermodynamically (the crystal
must get over an energy barrier when it returns to the former state, so this
expansion is non-reversible). At the same time, it also can be concluded
that expansion can arrive at the point irreversibly where the volume ratio
is 1.037 and total energy is the lowest. The ratio of non-reversible expan-
sion must be about 3.7 per cent theoretically, which is comparable to the
experimental value of a plastic-bonded explosive of TATB and Kel-F800,
1.5-2.0 per cent [13].

Table 1. Total energy and volume ratio when c-axis of TATB cell changes around the maximum

c-axis Length [Ĺ]	Volume ratio	Total energy (hartree) by Dmol³	Total energy (eV) by CASTEP
6.312	0.927	-2009.156	-10527.445
6.562	0.963	-2009.160	-10527.589
6.637	0.974	-2008.826	-10516.900
6.712	0.985	-2008.824	-10516.886
6.812	1.000	-2008.822	-10516.812
6.912	1.015	-2008.820	-10516.771
6.987	1.026	-2008.819	-10516.744
7.062	1.037	-2009.151	-10527.219
7.312	1.073	-2009.145	-10527.218

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 nearby layers. When heated, the crystal must be most easily and mainly expanded along c-axis in that there is the smallest internal stress and the lowest energy point along this orientation. So, this expansion is anisotropic, and the process of energy decreasing partially, with a result that it is non-reversible.

Table 2. Percentage variation of lattice parameters and densities of TATB crystal at high pressure

Pressure(GPa)	a	b	c	α	β	γ
10.000	-4.30	-4.30	-15.40	3.06	0.03	0.04
100.00	-11.84	-11.98	-30.28	6.23	-0.76	-0.02
1000.0	-26.23	-26.64	-43.89	12.10	-2.07	-0.03

In order to verify the force difference between neighbor layers and neighbor molecules, we do other calculations on optimizing TATB crystal structures under different high pressures 10 GPa, 100 GPa and 1000 GPa by using CASTEP. The percentage variations of lattice parameters

comparing to the experimental values are listed in Table 2. From the table, we can see that parameters such as a, b, α, β and γ decrease less than c under the different high pressures. All this result must be owing to layered and graphite-like structure of TATB crystal mentioned above. 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.

In a word, we obtain the non-reversible expansion extent of TATB by static calculation, in contrast with Gee [4], by dynamic method, but not get the extent. This must be our characteristics.

Conclusion

The non-reversible expansion of TATB crystal takes place on its c-axis, and ratio of that must be theoretically 2.6-3.7 per cent, which is comparable to experimental value 1.5-2 per cent.

Acknowledgement

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