

Electronic Structure Modifications Induced by Nanosize Lattice Imperfections in Molecular Crystals

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ABSTRACT

A first-principles theoretical modeling of basic defects such as a molecular vacancy, a vacancy dimer, an edge dislocation, and a nano-crack in organic molecular crystals, particularly solid RDX ($C_3H_6N_6O_6$) and PETN ($C_5H_8N_4O_{12}$), is presented. It is established that shock compression changes the optical properties of both the defect-free crystal and the crystal with defects by narrowing the optical band gap. The lattice defects (especially dislocations) are identified with the so-called "hot spots" in triggering the explosive detonation. We found that the edge dislocations produce local electronic states in the gap whereas the external pressure moves these states deep within the band gap. This creates favorable conditions for the critical chemical bond rupture due to exciton formation. Relation between defects, hot spot formations, the sensitivity of solids to initiation, and particular applications of the obtained results are briefly discussed.

Keywords: electronic structure, defects, organic crystals, shock compression, explosions, metallization.

1 INTRODUCTION

Molecular crystals are solids composed of poly-atomic molecules having a complicated structure. Many of these materials have important technological applications. We selected for this study cyclotrimethylene trinitramine [$(CH_2NNO_2)_3$] also known as RDX) and pentaerythritol tetranitrate [$C(CH_2ONO_2)_4$] also known as PETN), often used as high explosives and propellants.

Nanotechnology arises from the exploitation of physical, chemical and biological properties of systems that are intermediate in size between isolated atoms/molecules and bulk materials, where phenomena length scales become comparable to the size of the structure. A critical issue for nanotechnology is the ability to understand, model, and simulate the behavior of the small structures and to make the connection between structure, properties, and functions. Most nanosystems are too small for direct measurements, too large to be described by current rigorous first principles in theoretical and in computational methods, exhibit too many fluctuations to be treated monolithically in time and space, and are too few to be described by a statistical ensemble [1].

There have been many theoretical and experimental advances in the understanding the macroscopic properties

of energetic materials in gas and liquid phases. Atomic and electronic level processes taking place in solid state are much less understood. This is partly due to the complexity of the structure of the materials and partly due to the fast initiation of chemistry in detonation fronts (fs range).

A great deal of information is currently available regarding the influence of the external impulse (impact/shock, laser, accelerator, etc.) on the detonation front parameters for various explosive materials. However, the spectral and time resolution of modern techniques is still insufficient for a complete understanding of the initial stages of chemical decomposition. Hence, large-scale theoretical and computer simulations of the structure and properties of the materials are highly desirable.

Although the molecular composition and crystal structure play a significant role in determining sensitivity, energetic considerations have led to the hypothesis of "hot spot" regions in the crystal. It is assumed that these "hot spots" are regions of the system containing significant defect or impurity concentrations. They localize the energy of the impact wave and start the chemical reaction. There is no general agreement as to what constitutes a "hot spot." Often dislocations or micro-cracks are blamed for initiation, where the initiation of explosives could be interpreted in terms of redistribution of dislocations [2]. The idea was suggested long ago, and has been discussed many times in many different aspects but still has never been proved.

There are several different realistic mechanisms for "hot spots" formation and detonation initiation. The question of what kind of defects are responsible for sensitivity of the explosives to detonation still remains open. The existing models are able to explain experimental observations of shock front only fragmentally. The main problem in the development of the modern detonation theory lies in the lack of detailed information about the micro-structure of the explosive materials, atomic/electronic level processes, and various lattice defects, their interactions, and their influence on crystal properties [3]. Besides a fundamental significance, the obtaining of this information is of great practical importance for safety issues.

The defect- and compression-induced effects on the optical band-gap of a solid RDX and PETN were investigated by means of a first-principle, quantum-chemical method. The *ab initio* Hartree-Fock (HF) calculation scheme combined with the *many-body perturbation-theory* (MBPT) were used to simulate the atomic and electronic structure of a series of lattice defects in the materials such as a molecular vacancy [4], a vacancy dimer [5], an edge dislocation [6], a nano-crack [7], and a

free surface [8]. As a result, we can predict how a presence of nanosize imperfections in the crystal will modify its macro-behavior such as electronic (optical) properties. Experimental facts supporting the theoretically obtained results are discussed in some detail.

2 METHODOLOGY

The method is based on standard Hartree-Fock technique as implemented in the CRYSTAL95/98 program package [9]. Electron correlation corrections based on the second-order MBPT are included in the calculations of optical gaps. For this purpose, we used the LOPAS computer code [10] based on the local orbital approach [11]. Thus, optical band gaps obtained in this study can be directly compared to relevant experimental data.

In this work, we used the 6-21G split valence set with the modified scaling factor of 1.10 for outer Gaussian basis vector on all atoms. In all calculations the internal geometry parameters of the RDX [12] and PETN [13] molecules such as bond lengths, angles, and torsion angles were taken from experimental data (see Fig. 1). They were fixed while the lattice constants were theoretically optimized.

To simulate a molecular vacancy in RDX, we remove one of the eight molecules from the orthorhombic RDX unit cell. Use of periodic boundary conditions (supercell model) results in a model crystal with a concentration of defects as high as 12.5%. The molecular cluster model was also used for calculations of the vacancy formation energy. A combination of these two approaches could serve as a good model for a porous RDX material. General trends obtained can be compared to the samples investigated experimentally [17]. By doubling the size of the supercell and varying positions of vacancies, we were able to study the effect of defect distribution, in particular the formation of vacancy dimers, on the electronic and optical properties of the solid. In a similar manner we modeled two-dimensional defects, such as fine nano-cracks, placed close to each other.

The modeling of dislocations is more challenging. In accordance with Halfpenny et al [14, 15], the most likely configuration for an edge dislocation in PETN is determined by [001] Burgers vector and (110) slip plane. In order to theoretically simulate the corresponding distortion of the crystal, the lattice is assumed to be composed of parallel three-dimensional layers sliced perpendicularly to the (110) surface. For the perfect material, this is the same as choosing just different unit cell for the PETN crystal keeping the right structure. Using appropriate translations we still can reproduce the initial bulk crystal. To create the dislocation, one should slip one part of the crystal with respect to another as if we insert an extra half-plane of the PETN molecules, thus producing the plastic deformation in the material. The boundary between the slipped and unslipped regions is the edge dislocation. The relevant unit cell of the crystal in polymer model is sketched in Fig. 2. In similar manner we modeled the [001](010) edge dislocation in RDX. The corresponding crystal unit cell consisted of 10

RDX molecules [6]. In our calculations we modeled the dislocation core by a one-dimensional (polymer) model applying the periodic translation only along the dislocation line d . Thus, we simulate a single dislocation per crystal avoiding strong dislocation interactions. That is, we can find out how this local lattice deformation (shear stress), induced by a single defect, modifies the optical absorption spectrum.

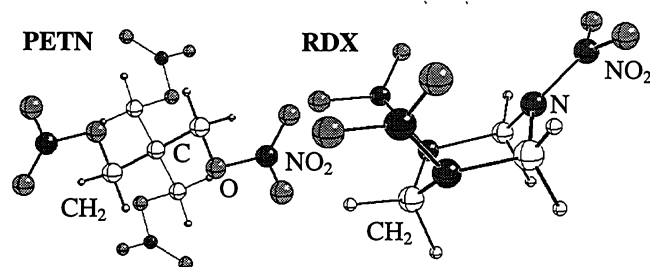


Figure 1. The structure of individual PETN and RDX molecules.

The effect of shock compression on the ideal and defective crystals was modeled in the rigid molecule approximation. Thus, isotropic compressibility of the crystal in terms of Volume-Energy dependence was investigated by proportionally decreasing all lattice constants and keeping the structure of the molecules in the crystal unaltered. The pressure was calculated using the low-temperature formula $P = -dU/dV$. The pressure-volume plot for the defect-free solid RDX [16] is in good qualitative agreement with the experimental impact adiabatic curves [17].

The lattice relaxation induced by defects was neglected in this study since it was estimated to be small and to reduce computational costs.

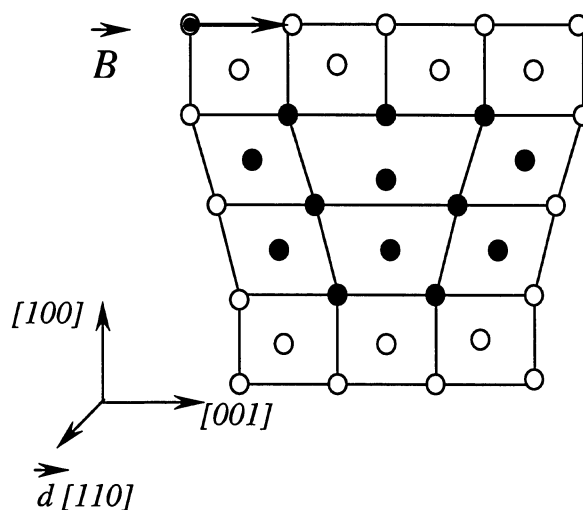


Figure 2. The edge dislocation with the Burgers vector [001] and the slip plane (110) in the polymer model (PETN crystal). Open circles correspond to the PETN molecules with the structure shown in Fig. 1.

3 RESULTS AND DISCUSSION

Our main objective was to study the changes in the electronic structure of the molecular crystals, PETN and RDX, which were induced by small deformations of the crystalline lattices. In particular, we were looking for an effect of lattice defects such as a single molecular vacancy [4], a vacancy dimer [5], chains of vacancies [7], and edge dislocations [6, 23] on the optical band gap of the solids. Our calculations have been performed for the crystal structures both in equilibrium and under external hydrostatic compression [16]. The band gap as a function of the RDX crystal compression V/V_0 is shown in Fig.3. This allows us to make two important observations. First, most studied defects induce a reduction of the band-gap, even at zero pressure. The band-gap is most sensitive to the presence of dislocations due to a strong internal stress. Second, volumetric contraction usually leads to the additional narrowing of the gap. This effect strongly depends on the nature and spatial orientation of defects in the solid. For instance, in crystals containing nano-cracks in the form of linear vacancy chains (crack (2NN) line in Fig.3) the gap weakly depends on the pressure, while in crystals with edge dislocations the gap drops to 1.5eV at the relatively small compression, about 92% of a normal crystal volume V_0 .

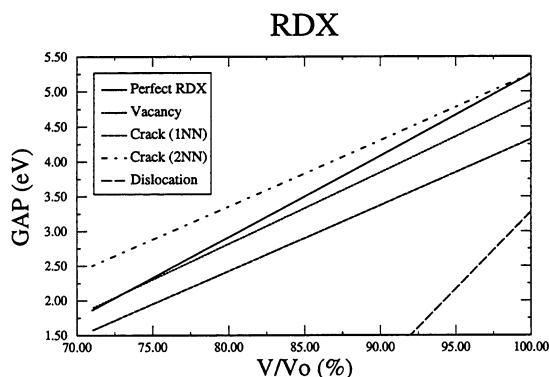


Figure 3. The optical gap vs to volume compression V/V_0 .

It is well known that strong hydrostatic compression of solids leads to the electronic *insulator-metal phase transition*, which is characterized by a critical pressure (Herzfeld-Mott metallization). According to the detonation theory, an impact shock wave, propagating through the crystal, is characterized by high temperature and pressure. Following J. Gilman et al [18], the origin of the large pressure spike at the detonation front is associated with the valence electrons being suddenly able to expand in the antibonding electronic states. At this moment, as was suggested, the explosive substance is undergoing the phase transition. At constant volume this produces pressure in the 10^{11} Pa-range [18]. Our theoretical estimates fall in this range. The calculated pressure corresponding to the zero-band gap for defect free RDX comes out to be about 180

GPa [16]. Vacancies presented in RDX decrease this pressure down by about 30%, i.e. 120 GPa. This theoretical simulation along with further modeling of large vacancy aggregates and free surfaces can help for better understanding of the accumulation mechanism of detonation initiation and for the model based on the collapse of pores. For now, it should be concluded that metallization hardly occurs on very initial stages of detonation since the corresponding experimental pressures, which cause detonation, are much smaller, from 0.2 GPa [19] to 4 GPa [3].

Our calculations demonstrate that edge dislocations strongly affect the optical properties of both RDX and PETN solids. A significant distortion in the electronic structure of RDX caused by a local deformation in the lattice (which represents an element of a dislocation) has been described earlier [20] by a simplified model. The HF embedded-cluster calculations show an increased molecular polarization (up to 20%) along different directions, resulting in a scenario where some of the molecules tend to attract each other while others tend to repel. It is explicitly shown here that the interactions among molecules inside the dislocation core produce local electronic states in the band gap, even at zero pressure [6]. When applying an external pressure to this already stressed crystal, a further reduction of the band gap takes place [23]. From our results one may also conclude that edge dislocations decrease the metallization pressure much stronger than other defects. This is caused by a dramatic narrowing of the optical gap, which is related to the splitting off of local levels from both the top of the valence band and the bottom of the conduction band. An eigenvectors analysis proves that these local states are related to the weakest chemical bond in a molecule located near the dislocation core and have bonding and antibonding character, respectively. Thus, the local states in the gap of solid PETN are formed by the molecular orbitals of the O-NO₂ group while they are formed by the molecular orbitals of the N-NO₂ group in RDX.

From this observation two very important conclusions follow. First, the band gap reduction increases the probability of the electronic transitions across the gap. And the second, the lowest-energy electronic excitation, i.e. promotion of an electron from HOMO (highest occupied molecular orbital) to LUMO (lowest unoccupied molecular orbital), can lead to the breaking of the critical chemical bond in the crystal, N-NO₂ in RDX and O-NO₂ in PETN. If this excited state lives longer than a characteristic time of atomic vibrations, then dissociation can occur. The nature of the HOMO to LUMO excitation in RDX and its relation to the molecular decomposition has been established in earlier theoretical [21] and experimental [22] studies. In particular, it was found that the strong intramolecular absorption at wavelengths below 340 nm (3.4 eV) leads to the formation of the NO₂ radicals, i.e. products of the bond rupture. The calculated in our study band gap for perfect RDX is 5.25 eV, which is visibly higher than the

experimental data. The edge dislocation reduces the band gap to 3.3 eV in RDX [23], yielding an amazing agreement with the experimental value. The similar situation is observed for PETN crystals. A new broad optical absorption band, predicted in our simulations [6], was recently found experimentally to be centered around 400 nm (3.1 eV) for shocked solid PETN [24]. A detailed and careful discussion of these results and their possible applications is provided [6]. Based on these simulations, a new *mechanism of detonation initiation* in molecular solids is proposed [25].

4 CONCLUSIONS AND APPLICATIONS

An *ab initio* study of the electronic structure of the molecular crystals, RDX and PETN, containing various crystalline defects was performed by means of the Hartree-Fock periodic method combined with the many-body perturbation theory. It was shown that the edge dislocations, unlike other defects, produce local electronic states in the band gap of the material. These states are formed mainly by molecular orbitals of N-NO₂ group in RDX and of O-NO₂ group in PETN, which are critical chemical bonds responsible for the stability of the materials. The induced gap states are very sensitive to the motion of molecules. New optical absorption peaks associated with these electronic states appear in the density of states plot. Optical absorption measurements described in the literature yield good agreement with our theoretically predicted results. The dislocation-related band structure deformation contributes strongly to mechanical and electronic (optical) properties of the explosive crystals.

The possible mechanism involving electronic excited states may have application in explaining the initiation and detonation behavior of explosive solids. Dislocations can serve as hot spots, which are characterized by a local internal stress and by a reduced optical gap. The impact wave propagating through the crystal stimulates a further dramatic gap reduction increasing the probability of electron excitation. This, in turn causes molecular dissociation via an excitonic mechanism and start a chain reaction and explosion.

The obtained results are of great *practical importance* for safety issues. Our conclusions provide useful insights for the control of sensitivity of explosive crystals to detonation initiation, for storage and handling of energetic materials, for prevention of accidental explosions and fires, and also for manufacturing efficient and safe explosive sensors. It is also to be mentioned here a significance of the *fundamental aspect* of this research. In this investigation, we have applied a traditional approach of solid state chemistry, which is well developed for semiconductors and ionic crystals, to the absolutely new class of problems - the electronic structure of complicated organic solids, and changes of that due to nano-size lattice deformations. This resulted in a discovery of a very new perspective for the development of the modern initiation and detonation theory.

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