

## ARTICLES

**Simulation of Defects in Energetic Materials. 3. The Structure and Properties of RDX Crystals with Vacancy Complexes****Maija M. Kuklja\* and A. Barry Kunz***Department of Electrical Engineering, Michigan Technological University, Houghton, Michigan 49931**Received: January 27, 1999; In Final Form: July 29, 1999*

Hartree–Fock calculations of a cyclotrimethylene trinitramine  $C_3H_6N_6O_6$  (RDX) crystal containing vacancy dimers were performed using a periodic defect model and large supercells. Positive binding energies of the divacancies indicate that single vacancies attract each other in RDX crystals, thus forming defect complexes. One- and two-step processes of vacancy pair formation have been simulated. The density of states and band structure analysis show that the defect pairs narrow the fundamental optical gap. Mutual orientation within vacancy dimers considerably effects the electronic properties. A detailed comparison of perfect RDX, that containing a single vacancy, and that with a divacancy is presented. The role of these defects in the “hot spot” formation and shock initiation of explosions is discussed.

**I. Introduction**

Unstable energetic substances have remained of interest for a very long time. These materials are successfully used as explosives and fuels in many different ways: for land clearing, railroad and highway construction, mining, etc. Recently, they have found a new application as airbag inflators. The distinctive feature of explosive materials is their fast decomposition caused by shock or impact. Despite many theoretical and experimental advances in understanding the macroscopic properties of detonation in explosives over the last 50 years,<sup>1–2</sup> much work remains to be done in order to clarify their microscale shock-induced chemistry and physics. The molecular structures of organic explosives are closely related to their sensitivities in a response to various external stimuli such as heat, shock, or impact. A widely spread idea is that the initiation of combustion in energetic materials is associated with “hot spots”.<sup>3</sup> These are very localized regions where the combustion begins. The main point of this idea is that initiation of combustion requires an intense stimulus, and the average applied stimulus is too small. Thus, the applied stimulus must be localized at intense “hot spots.” It is believed that mechanical mechanisms provide the required localization. These mechanisms involve crystal defects or deformations in the hot spots, leading to chemical chain reactions of decompositions.

Many types of defects such as vacancies, impurities, voids, pores, dislocations, and others are always present in real crystals. It is still not established which of these are responsible for the sensitivity of an explosive to the initiation of combustion. Thus, although the hot spot hypothesis was proposed by Bowden and Yoffe<sup>3</sup> long ago, the structures and natures of hot spots remain puzzling. Because of their importance in understanding energetic materials, knowledge of the nature of hot spots is of great importance.

The basic point defect in molecular crystals appears to be the monovacancy.<sup>4,5,6</sup> Point defects may associate into pairs, or

larger clusters, either through chemical bonding or because the elastic lattice strains around them favor such an association. The possibility of divacancy formation follows from minimization of the number of broken chemical bonds in insulating crystals or metals (or van der Waals interaction energies in organic crystals). More complex aggregations may occur in the form of planar trivacancies, tetrahedrons, voids, or dislocation loops.<sup>7</sup> However, which properties of a crystal are controlled by defect formation is unknown.<sup>8</sup>

For unstable substances, the relationship between defects and “hot spot” formation has special interest. The interaction of strong shock waves with voids leading to local decomposition of the explosive material has been observed experimentally.<sup>9</sup> The luminescence and brightness temperature of the detonation fronts in a mixture of trinitrotoluol (TNT) and RDX has been recorded by a two-wave optical pyrometer.<sup>10</sup> The existence of micropores containing air in the solid high explosive has also been demonstrated. The observation of fracto-emission from PETN and HMX molecular crystals<sup>11</sup> implies that crack propagation in such materials can break intramolecular bonds. It triggers subsequent chemical reactions that lead to a particle emission, which continues for several minutes. An X-ray topographic study of defects in an RDX crystal<sup>12</sup> has indicated that a combination of restricted slip systems and cracking is responsible for significant anisotropy and the triggering of dislocation pile-up collapse. An atomic force microscope was employed very recently to study the structure of defects in RDX.<sup>13</sup> The latter is found to behave like a very fragile crystal in which numerous imperfections show up at the level of the stimuli, far below that necessary for the start of chemical reactions.

Most theoretical work with respect to vacancies or voids has been done by means of molecular dynamics.<sup>14–16</sup> There are indications, based on theoretical estimates, that the formation of small linear multivacancies in molecular crystals is energeti-

cally unfavored.<sup>5,6</sup> To our knowledge, the electronic structures of vacancy dimers in energetic materials have not been studied, either experimentally or theoretically.

In our previous papers, we considered the simplest stable defect—a single vacancy in crystalline RDX<sup>17</sup>—and the isotropic compression of both perfect and defective solids<sup>18</sup> using the ab initio Hartree–Fock technique. It was concluded that applied external pressure as well as the presence of a single vacancy reduces the fundamental optical gap of RDX. Thus, monovacancies in the solid decrease the insulator–metal phase transition pressure. This characterizes transformation of the propagating shock wave into a detonation front. This paper is devoted to simulations of vacancy dimers.

## II. Method

We use the standard Hartree–Fock (HF) technique to calculate the band structure as implemented in the CRYSTAL95<sup>19</sup> computer code. Defects such as vacancies and di-vacancies were modeled using a periodic defect and a supercell method. We used modified 6-21G split valence basis sets. The scaling factor for outer (most diffuse) Gaussian basis vectors was 1.10 for all atoms. As has been established earlier, this basis set reproduces quite accurately the perfect RDX crystalline structure.<sup>20</sup> The same basis set has been used for molecular vacancy simulation in RDX.<sup>17</sup>

Since the standard HF approximation ignores the dynamic interactions of electrons, electron correlation corrections based on second-order many-body perturbation theory (MBPT) are included in the calculations. For this, we have explored the LOPAS computer code<sup>21</sup> based on the local orbitals approach.<sup>22</sup> Thus, the optical band gap value obtained for the HF approximation was then corrected by means of the MBPT. This provided quite accurate direct comparison with the relevant experimental data.

The vacancy dimer formation energy is defined as

$$E_{\text{divac}} = (E_{\text{defect}} + 2E_{\text{molecule}}) - E_{\text{perfect}} \quad (1)$$

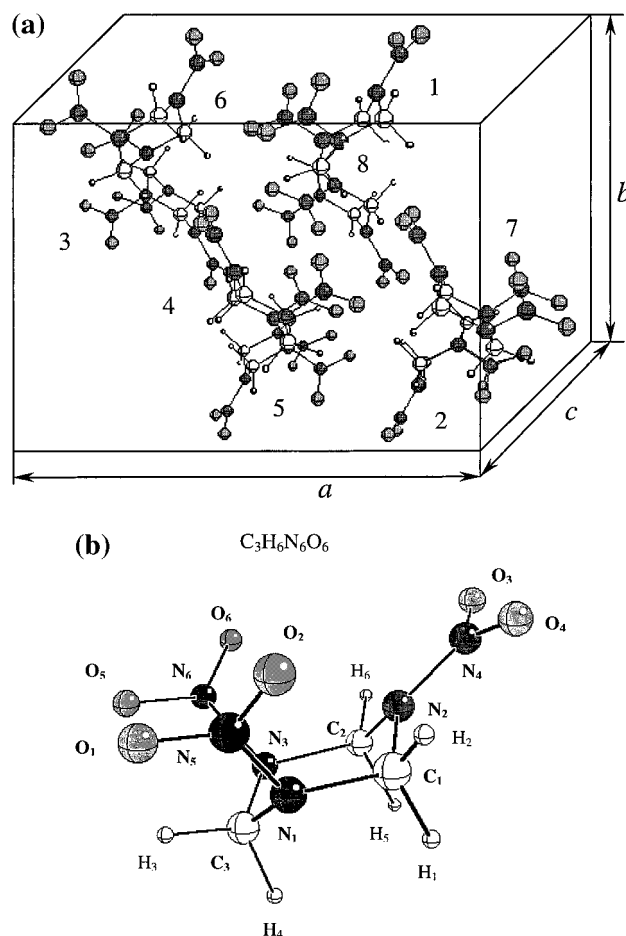
where  $E_{\text{defect}}$  is the total energy of the system containing a divacancy,  $E_{\text{molecule}}$  is the energy of the RDX molecule, and  $E_{\text{perfect}}$  is the total energy of the perfect material. We define of the another energetic quantity,  $E'_{\text{divac}}$  as

$$E'_{\text{divac}} = (E_{\text{defect}} + E_{\text{molecule}}) - E_{\text{vacancy}} \quad (2)$$

which uses the total energy of a crystal with a single vacancy instead of the total energy of the perfect crystal. This value could be interpreted as the energy required to create a vacancy in the crystal next to a pre-existing single vacancy. In other words, the  $E_{\text{divac}}$  describes the divacancy creation in a perfect crystal as a one-step process, whereas the  $E'_{\text{divac}}$  corresponds to a two-step action in sequential formation of two single vacancies near each other. Comparing the divacancy formation energy with two single vacancy formation energies, the binding energy for the vacancy dimer can be obtained as

$$E_{\text{binding}} = 2E_{\text{vac}} - E_{\text{divac}} \quad (3)$$

The single vacancy formation energy ( $E_{\text{vac}}$ ) was derived from eq 1, where  $E_{\text{defect}}$  was the total energy of the crystal with monovacancies. For determination of the RDX gas-phase molecule parameters and energy, we again employed the HF method as realized in the GAUSSIAN94 computer package<sup>23</sup> with an automated geometry optimization procedure.

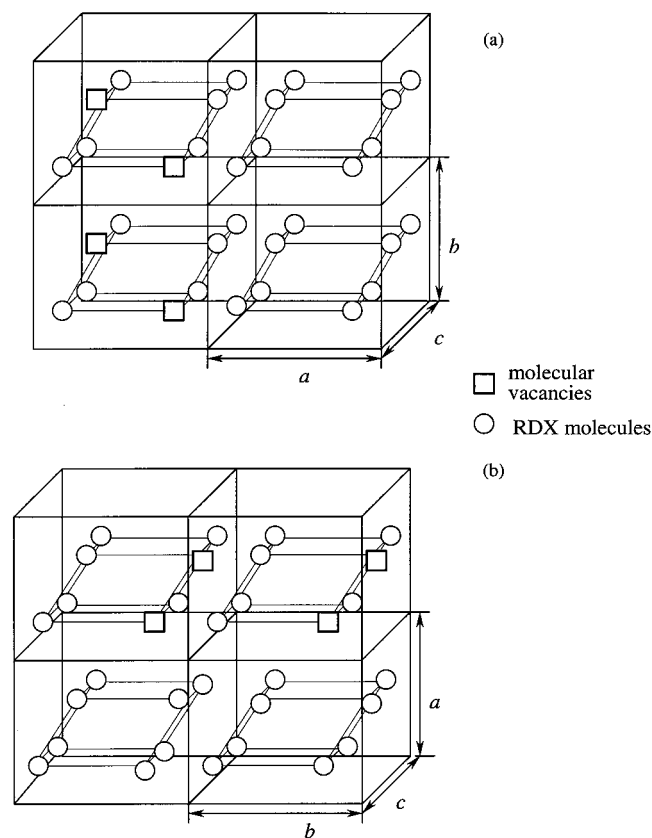


**Figure 1.** (a) RDX crystal with eight molecules per unit cell and (b) structure of a single molecule.

Experimentally, RDX crystals are known to have *Pbca* structures with the lengths of the three lattice constants  $a = 13.192 \text{ \AA}$ ,  $b = 11.574 \text{ \AA}$ , and  $c = 10.709 \text{ \AA}$ , respectively, and eight molecules per unit cell,<sup>24</sup> as is shown in Figure 1. The structure of a perfect crystal was modeled in our previous papers.<sup>17,18</sup> The internal structural parameters of the RDX molecules such as atomic coordinates, bond lengths and angles, were taken from experiment<sup>24</sup> and fixed in the optimization of the crystal geometry. The intermolecular disposition has been determined by the minimization of energy in periodic calculations of the defect-free crystal structure.

To simulate a vacancy dimer, the model of periodic defects (PD)<sup>25</sup> in the form of large supercells (SC) was used. Two entire molecules situated at the nearest neighbor lattice positions were removed from a given SC that was represented by two adjacent orthorhombic RDX cells with a total of 16 molecules. Particular attention was paid to keeping the local nature of the defect, preventing its transformation into a straight through crack due to periodic translations. This was a limitation used as a criterion in the choice of a SC for each pair of vacancies studied. Thus, for the nearest-neighbor (1NN) divacancy calculations, (112) extended unit cells have been used (i.e., the unit cell was doubled along the  $c$  direction and kept the same size along the  $a$  and  $b$  vectors). For the second-nearest-neighbor (2NN) vacancies, both (112) and (211) SCs appear to be appropriate. The third-neighbors (3NN) vacancy dimer was modeled in the (211) SC. Sketches of the supercell models used in our calculations are shown in Figure 2.

Using suitable configurations of the unit cells constituting the SC, one can simulate all possible combinations of divacan-



**Figure 2.** (211) supercell for nearest-neighbor (a) and second-neighbor (b) vacancy dimers. The RDX molecules (with 21 atoms per molecule) in regular lattice positions are indicated by open circles. The atomic structure of the individual RDX molecule is not shown, but all orbitals of all atoms were included in the calculations. Vacancies are represented by open squares.  $a$ ,  $b$ ,  $c$  denoting the original translation vectors of the  $Pbca$  crystal structure. The crystal is composed of SC, each of them is represented by two adjacent minimal unit cells, i.e., four unit cells (two SCs) are seen.

cies. To illustrate the complexity of our calculations, consider a pure RDX crystal. The single unit cell contains eight molecules which equals 168 atoms and a total of 912 electrons, of which only 240 are core electrons. In most of the simulations discussed in this study, two unit cells have been included in each run. Thus, the fragment of the crystal with the defect (SC with a divacancy) consists of 294 atoms, corresponding to 1596 electrons, of which 420 are core electrons. A split valence basis set (6-21G), as used here, consists of 2058 atomic orbitals. Moreover, a point defect reduces the crystal symmetry from eight operations ( $Pbca$  group) to a single operation ( $P1$  group). Thus, a single CRYSTAL95 calculation on the Multiprocessor SUN Enterprise 4000 system (with 12 Ultra Sparc II processors (250 MHz) in a parallel version with four processors) runs for 4–5 days, which demands significant disk memory resources. In some respects, therefore, our calculations are *state-of-the-art* for large-scale defect simulations in solids.

### III. Results and Discussion

This study is aimed mainly at finding out the effect of small vacancy aggregates on the optical gaps of explosive crystals. The electronic properties of the defects under study are collected in Table 1. One can see that *both* the HOMO (the highest occupied molecular orbital) and the LUMO (the lowest unoccupied molecular orbital) energies are sensitive to defect (vacancy and dimer) formation. All examined defects lead to some narrowing of the optical gap. However, this effect is

**TABLE 1: Electronic Properties of Crystalline RDX with a Vacancy Dimer<sup>a</sup>**

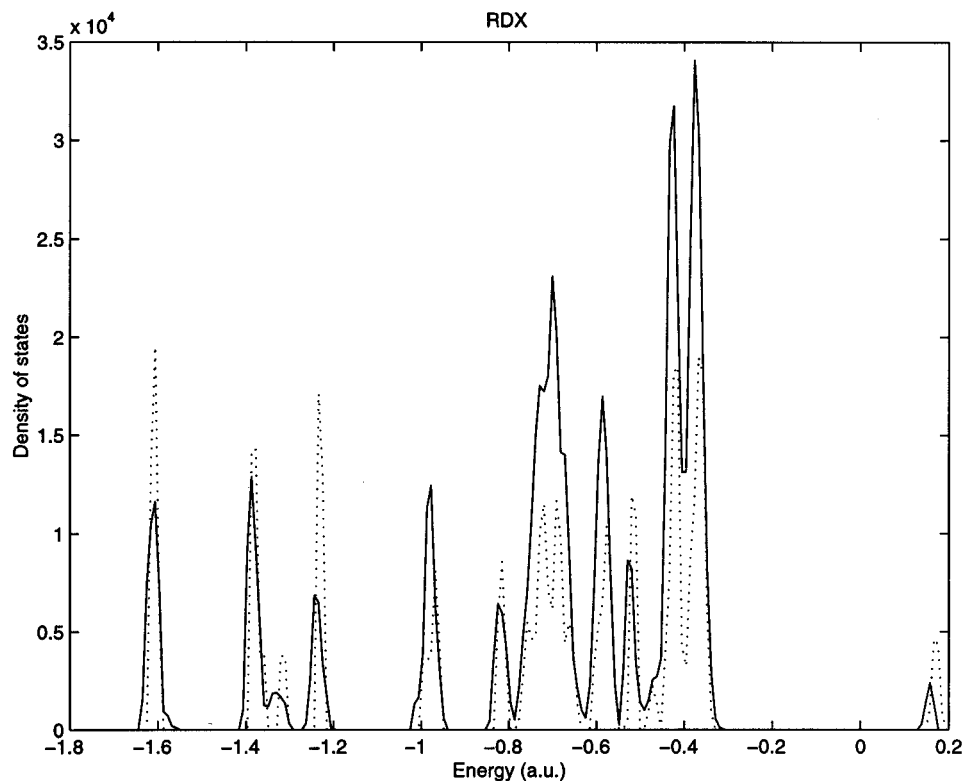
model		HOMO (au)	LUMO (au)	GAP (eV) HF	GAP (eV) MBPT	$\Delta$ GAP (eV)
NN	SC					
1NN	112	-0.3258	0.1513	12.98	4.56	0.7
2NN	211	-0.3427	0.1530	13.49	5.07	0.2
2NN	112	-0.3456	0.1524	13.55	5.13	0.1
3NN	211	-0.3274	0.1423	12.78	4.36	0.9
mono- vacancy	211	-0.3289	0.1468	12.94	4.52	0.7
perfect crystal	single unit cell	-0.3395	0.1630	13.67	5.25	0.0

<sup>a</sup> HOMO (au) is one-electron energy of the highest occupied state of the system. LUMO (au) is one-electron energy of the lowest unoccupied state of the system. GAP HF (eV) is the optical crystal gap, determined as the difference between HOMO and LUMO energies in a Hartree–Fock calculation scheme. GAP MBPT (eV) is the optical gap obtained in the HF method with correction for the electron polarization using the many-body perturbation theory. (These values can be directly compared to the experimental optical spectrum of RDX crystal).  $\Delta$ GAP (eV) is the gap reduction caused by the defects.

different for the studied dimers. This can be understood in terms of the RDX crystal structure and cohesion. The RDX crystal lattice is built of pairs of inverted interlocked molecules as shown in Figure 1. One of the oxygens of the axial N–NO<sub>2</sub> groups is situated in the molecular “pocket”<sup>26</sup> of the neighboring molecule and attractively interacts with all three nitrogen atoms of the nitro groups. Other oxygen atoms attract neighboring pairs of molecules by interacting with the nitro nitrogen of the equatorial N–NO<sub>2</sub> group. Thus, the cohesion arises from interaction of the RDX molecule pairs because of the oxygen affinity. A qualitative difference of the two kinds of simulated vacancy pairs lies in their *mutual* orientation within the unit cell. We denote the nearest divacancy as 1NN (first nearest neighbor), thus stressing the shortest distance between the two RDX molecules constituting this pair. Dimers consisting of first (1NN) and third-neighbors (3NN) (Figure 2) are defects separated by a normal RDX unit cell, thus transforming the perfect crystal into a porous structure. In contrast, 2NN vacancies are placed obliquely in the same unit cell. Hence, both second-neighbor dimer models (112 and 211 SCs) introduce closed zigzag-like pores into the solid structure oriented nearly parallel to the  $b$  direction (see Figure 2) and separated from each other by  $|c|$  and  $|a|$  in (112 SC) and (211 SC), respectively. The 1NN and the 3NN dimers reduce the gap by 0.7–0.9 eV, thus affecting the crystal almost like a single vacancy, whereas the 2NN pair causes almost no change of the gap.

The total electronic density of states for a 3NN dimer is compared with that for the perfect crystal in Figure 3. It is seen that this divacancy affects the *valence band* of the wide-gap RDX crystal. The qualitative picture is close to the effect caused by a monovacancy.<sup>17</sup> What is of special interest is how the spatial arrangement of the vacancy dimers reflects the high anisotropy of the material.

Experimental data indicates that solid RDX usually contains a high concentration of various defects.<sup>13</sup> We have modeled the crystal with a concentration of monovacancies as high as 12.5%. The calculations of divacancies correspond to the same defect concentration but permit us to analyze different sizes of voids and their distribution throughout a crystal. Both systems could serve as good models for porous RDX, which is indeed studied experimentally<sup>27,28</sup> and is a more sensitive explosive than crystalline RDX. It is obvious that defects in the real material



**Figure 3.** Total electronic density of states for crystalline RDX with vacancy dimers (solid line) and for a perfect crystal (dotted line).

**TABLE 2: Energetic Properties of a Molecular Vacancy Dimer in an RDX Crystal<sup>a</sup>**

model		<i>E</i> (au)	<i>E</i> <sub>div</sub> (eV)	<i>E'</i> <sub>div</sub> (eV)	<i>E</i> <sub>binding</sub> (eV)
NN	SC				
1NN	112	-12473.81329	8.06	3.95	0.16
2NN	211	-12473.82786	7.66	3.55	0.56
2NN	112	-12473.83035	7.59	3.53	0.63
3NN	211	-12473.81743	7.94	4.05	0.28

<sup>a</sup> *E* (au) is the total energy of the calculated system (per supercell), energy of the supercell (211) with a single vacancy is -13364.88444 (au), and energy of the unit cell (eight molecules) of the perfect RDX is -7127.980696 au. *E*<sub>div</sub> (eV) is the divacancy formation energy, *E'*<sub>div</sub> (eV) is the energy required to create a second vacancy as the nearest neighbor of an existing vacancy, and *E*<sub>binding</sub> (eV) is the bivacancy binding energy.

could be inhomogeneously distributed, unlike the uniform distribution assumed in our calculations.

From Table 2, which shows the energetics of the defects, the 2NN (112) vacancy pair formation is favored over other dimers. The creation of any of these dimers in one-step costs much higher energy (7.59–8.06 eV) than monovacancy formation (4.1 eV<sup>29</sup>), but less than the formation energy of two well-separated vacancies (8.2 eV). Thus, a second vacancy arising near a pre-existing one demands less energy than a single vacancy in a perfect crystal. This could be expected, considering the number of broken bonds in the crystal. To remove an RDX molecule situated close to a vacancy, it is necessary to break at least one bond fewer than in the single vacancy case. This is also illustrated by dimer binding energies, indicating that defects attract each other and trend to aggregate. Also, from the Table 2, the attraction energy depends strongly on the relative positions of vacancies. An association of two vacancies into a dimer is accompanied by an energy gain. Therefore, this defect should be present in RDX in considerable concentrations.

Experimentally, the shape and critical size of voids and pores able to start initiation are very different and depend strongly

upon the physics and chemistry of the particular material<sup>30</sup> as well as upon an external impulse.<sup>28</sup> Despite the existence of plenty of papers dealing with the relation between micropore size and detonation, a rigorous prediction of the particular parameters of voids which is necessary for starting the reaction is still absent because the microstructures of voids are not known. A combination of experimentally established trends and first-principles calculations seems to be able to provide necessary information. Thus, based on our theoretical results demonstrating that the vacancy aggregation is strongly related to both the energy balance and the electronic structure of the high explosive RDX, one may attempt to predict and analyze the shape and sizes of the large vacancy associates in the solids.

It should be noted that elastic deformations due to defect–crystal interactions have been neglected because of computational limitations and the complexity of the RDX structure. Therefore, the energetics (such as defect formation energy) should be considered as upper bounds. The values would be lowered by taking lattice relaxation into account. Our previous paper estimates the relaxation energy for removing an RDX molecule from an internal lattice site to a large distance outside the crystal<sup>17,18</sup> to be ~1 eV. The single vacancy formation energy obtained in the molecular cluster model is 1.7 eV, which is close to the expected heat of sublimation for RDX, 0.48–1.35 eV. Preliminary calculations of the lattice relaxation around a vacancy show that little relaxation is expected. At most, the molecular relaxation energy should be comparable to the lattice relaxation energy. It is reasonable to expect that the lattice distortion around a 1NN vacancy pair is the superposition of the distortions around two isolated monovacancies, but we do not expect strong changes in the energies.

As to the divacancy binding energy, the calculated value would not be sensitive to the relaxation energies of the defects but only to the difference between the two relaxation energies. For a single vacancy and divacancy, this is expected to be small. Thus, this neglected effect could be smaller for the dimer binding



energies than for the defect formation energies. On the basis of the defect dimer simulation, one can see that 1NN and 3NN dimers introduce significant polarization in the solid while the 2NN pair barely affects the electronic structure. Therefore, it could be expected that the lattice relaxation around former defects would be greater than that around the latter one. This can somewhat change the ratio of the binding energies of dimers by increasing the binding energy of the 1NN and 3NN pairs. However, the binding energies of all the considered dimers are positive. Other qualitative trends derived here will remain valid, indicating that the stability of the dimers will lead to associations into larger aggregates.

#### IV. Conclusions

The structure and properties of molecular vacancy dimers in the high explosive RDX crystal are simulated for the first time by ab initio Hartree–Fock and MBPT techniques. The three nearest-neighbor vacancy dimers have positive binding energies, indicating that vacancy interactions are attractive. Higher vacancy associations may also be energetically favored. We show that high RDX anisotropy is manifested in the different binding energies and optical gap narrowing for the different mutual orientations of vacancy dimers. The results presented here may help to explain how interactions between impact waves and density discontinuities lead to hot spots in which fast chemical reactions are triggered. Further research on vacancy aggregates, large structural voids, and extended defects such as dislocations is highly desirable for developing a reliable model of detonation initiation.

#### References and Notes

- (1) Zel'dovich, Ya. B.; Kompaneets, A. S. *Theory of Detonation*; Academic Press: New York, 1960 and references therein.
- (2) Fickett, W.; Davis, W. C. *Detonation*; University of California Press: Berkeley, 1979. Fickett, W. *Introduction to Detonation Theory*; University of California Press: Berkeley, 1985 and references therein.
- (3) Bowden, F. P.; Yoffe, Y. D. *Initiation and Growth of Explosion in Liquids and Solids*; Cambridge University Press: London, 1952; pp 64–65.
- (4) Chadwick, A. V.; Sherwood, J. N. Point Defects in Molecular Solids. In *Point Defects in Solids*; Crawford, J. H., Jr., Slifkin, L. M., Eds.; Plenum Press: New York, 1975.
- (5) Silinsh, E. A. In *Organic Molecular Crystals. Their Electronic States*; Cardona, M., Fulde, P., Queisser, H.-J., Eds.; Springer Series in Solid-State Sciences 16; Springer-Verlag: Berlin, Heidelberg, New York, 1980.
- (6) Craig, D. P.; Ogilvie, J. F.; Reynolds, P. A. *J. Chem. Soc., Faraday Trans. 2* **1976**, 72, 1603–1612.
- (7) Orlov, A. N. *Introduction to Theory of Defects in Crystals*; Higher School Publ. House: Moscow, 1983 (in Russian).
- (8) van Bueren, H. G. *Imperfections in Crystals*; North-Holland Publishing Company: Amsterdam, 1960.
- (9) Campbell, A. W.; Davis, W. C.; Ramsay, J. B.; Travis, J. R. *Phys. Fluids* **1961**, 4, 511.
- (10) Tarasov, M. D.; Tolshmyakov, A. I.; Kuznetsov, F. O.; Petrushin, O. N.; Petushkov, V. S.; Savel'ev, Yu. A.; Tarakanov, M. Yu.; Til'kunov, V. A. *Proc. SPIE* **1997**, 2869, 894–899.
- (11) Miles, M. H.; Dickinson, J. T. *Appl. Phys. Lett.* **1982**, 41 (10), 924–926.
- (12) Elban, W. L.; Armstrong, R. W.; Yoo, K. C.; Rosemeier, R. G.; Yee, R. Y. *J. Mater. Sci.* **1989**, 24 (4), 1273–1280.
- (13) Sharma, J.; Hoover, S. M.; Coffey, C. S.; Tompa, A. S.; Sandusky, H. W.; Armstrong, R. W.; Elban, W. L. In *Structure of crystal defects in damaged RDX as revealed by an AFM in Shock Compression of Condensed Matter, 1997*; Schmidt, S. C., Dandekar, D. P., Forbes, J. W., Eds.; American Institute of Physics: Woodbury, NY, 1998.
- (14) White, C. T.; Barrettm, J. J. C.; Mintmire, J. W.; Elert, M. L.; Robertson, D. H. In *Decomposition, Combustion and Detonation Chemistry of Energetic Materials, MRS Symposium Proceedings*; Brill, T. B., Russell, T. P., Tao, W. C., Wardle, R. B., Eds.; Materials Research Society: Pittsburgh, PA, 1996; Vol. 418, pp 277–280.
- (15) Tsai, D. H. In *Structure of crystal defects in damaged RDX as revealed by an AFM in Shock Compression of Condensed Matter, 1997*; Schmidt, S. C., Dandekar, D. P., Forbes, J. W., Eds.; American Institute of Physics: Woodbury, NY, 1998; pp 281–286. Tsai, D. H. In *Structure and Properties of Energetic Materials, MRS Symposium Proceedings*; Liedenberg, D. H., Armstrong, R. W., Gilman, J. J., Eds.; Materials Research Society: Pittsburgh, PA, 1993; Vol. 296, pp 113–120.
- (16) Phillips, L.; Oran, E. S. In *Shock Compression of Condensed Matter, Proceedings of the American Physical Society Topical Conference*; Schmidt, S. C., Dick, R. D., Forbes, J. W., Tasker, D. G., Eds.; North-Holland: Amsterdam, 1992; pp 143–146, 1082.
- (17) Kuklja, M. M.; Kunz, A. B. Ab initio simulation of defects in energetic materials. I. The molecular vacancy structure in RDX crystal. *J. Phys. Chem. Solids*, in press.
- (18) Kuklja, M. M.; Kunz, A. B. Ab initio simulation of defects in energetic materials. II. Hydrostatic compression of cyclotrimethylene trinitramine. *J. Appl. Phys.*, in press.
- (19) Dovesi, R.; Saunders, V. R.; Roetti, C.; Causà, M.; Harrison, N. M.; Orlando, R.; Aprà, E. *CRYSTAL95 User's Manual*; University of Torino: Torino, 1996.
- (20) Kunz, A. B. *Phys. Rev. B* **1996**, 53 (15), 9733–9738.
- (21) Kunz, A. B. *J. Phys. Condens. Matter* **1994**, 6, 1233.
- (22) Kunz, A. B. *Theor. Chem. Acta* **1993**, 84, 353.
- (23) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, revision D.1; Gaussian Inc.: Pittsburgh, PA, 1995.
- (24) Choi, C. S.; Prince, E. *Acta Crystallogr. B* **1972**, 28, 2857.
- (25) Evarestov, R. A.; Kotomin, E. A.; Ermoshkin, A. N. *Molecular Models of Point Defects in Wide-gap Solids*; Zinatne: Riga, 1983. Evarestov, R. A. *Quantum-Chemical Methods in the Solid State Theory*; Leningrad University: Leningrad, 1982.
- (26) Karpowicz, R. J.; Brill, T. B. *J. Phys. Chem.* **1983**, 87, 2109–2112.
- (27) Dremine, A. N.; Savrov, S. D.; Trofimov, V. S.; Shvedov, K. K. *Detonation waves in condensed matter*; Publ. House Nauka: Moscow, 1970.
- (28) Kanel, G. I.; Razorenov, S. V.; Utkin, A. V.; Fortov, V. E. *Impact-wave phenomena in condensed matter*; Yanus-K: Moscow, 1996.
- (29) The single vacancy formation energy is slightly different than in our previous papers (see refs 17 and 18), possibly due to both increased tolerances of Coulomb and exchange integrals calculated in Hartree–Fock scheme and correlation corrections for total energies used in this research.
- (30) Dremine, A. N. *Chem. Phys. Rep.* **1995**, 14 (12), 1852–1870.