

Rotational defects in cyclotrimethylene trinitramine (RDX) crystals

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Cyclotrimethylene trinitramine (RDX) crystalizes in the orthorhombic α -phase at the ambient pressure and temperature. In principle, the point defects commonly found in monatomic crystals, such as vacancies and interstitials, may exist in RDX as well. However, in molecular crystals one encounters additional point defects associated with the distortion of the molecules. A set of rotational defects are described in this article. These are molecules which are located in the proper positions in the crystal but are rotated relative to the molecules in the perfect crystal, and their ring is slightly puckered. The energetic barriers for defect formation and for their annealing back to the perfect crystal configuration are computed using an atomistic model. It is shown that the formation energy of rotational defects is smaller than the vacancy formation energy. Such defects are identified in the cores of dislocations in RDX and hence their concentration in the crystal is expected to increase during plastic deformation. The importance of such point defects is related to their role in phonon scattering and in dislocation-mediated plastic deformation. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4862997]

I. INTRODUCTION

Molecular crystals are a common occurrence in everyday life, for example, in the form of ice and various pharmaceuticals.¹ Other examples are organic electronic² and energetic materials.³ Mechanics is important in many cases; in the case of pharmaceuticals for example, the mechanical behavior of crystals controls the ability to compact the powder in tablets, as well as the phase stability of the active compound. In energetic materials the deformation of the crystal controls the susceptibility of the material to the initiation of the chemical reaction leading to detonation.

Plastic deformation of molecular crystals takes place by the formation and propagation of various types of defects – dislocations and twins – just like in all other crystalline solids. In monatomic crystals, point defects such as vacancies, interstitials, and substitutional atoms are important in plastic deformation and are used routinely to modify the properties of engineering materials. A broader class of point defects exists in molecular crystals. These include the point defects usually encountered in monatomic systems and specific defects produced by the distortion of molecules.

Let us classify point defects in molecular crystals in three categories: (a) vacancies and interstitials, (b) conformational defects, and (c) rotational defects. Of these, the last two are specific to molecular crystals. Conformational defects are those in which the side groups are oriented in different directions relative to the ground state of the respective crystal, while the respective molecule is not rotated of translated. In the case of rotational defects, the molecules are both distorted and rotated relative to the ground state configuration, while the positions of their centers of mass are largely unperturbed. Large shifts of the center of mass, corresponding to the creation of self-interstitials, are generally prohibited on energetic grounds, as the molecules are too large to be accommodated interstitially at reasonable energy levels.

RDX is one of the most studied energetic materials. It is a secondary explosive with chemical composition $C_3N_6H_6O_6$. The molecule is composed from a triazine ring and three nitro side groups. The ring may assume chair (denoted by C), twist (denoted by T) or boat (denoted by B) configurations. The side groups take positions that make angles ranging from approximately 35° to 135° with respect to the normal of the ring. An angle of approximately 90° corresponds to an equatorial position (denoted by "e"), while angles close to the extremes of the indicated range correspond to axial positions (denoted by "a"). The ground state of the α RDX crystal has molecules in the Caae configuration. Ab initio studies have confirmed the conformational isomerism of the isolated RDX molecule^{4,5} indicating the existence of Caaa, Caae, Caee, and Ceee conformers. A conformer with a twist configuration for the ring was also observed. Conformational changes have been reported in molecular dynamics studies of RDX crystals, but only in presence of voids,³ stacking faults,⁶ and in shock wave fronts.⁷ The energetic barriers for conformation changes were reported in Ref. 8 where it was also shown that certain strain states favor the existence of conformational changes. The transition between two conformational states involves a transient in the internal energy of the respective molecules, which may play a role in up-pumping, i.e., the process by which the kinetic energy of the inter-molecular vibration modes is transferred to the intra-molecular modes.⁸

Rotational defects have not been described so far for RDX. The ability of molecules to rotate has been discussed in relation with other molecular crystals. Small molecules, such as water, which do not have strong steric interactions in the ice crystal, are free to rotate.⁹ In cases in which packing is more pronounced, molecules may rotate only by switching between discrete orientations.¹⁰

Rotational defects require that the molecule is rotated relative to the usual position in the crystal, while the system is in a local energy minimum configuration. These defects introduce a perturbation of the crystal periodicity and hence are expected to act as scattering centers for phonons.¹¹ They are also expected to interact strongly with dislocations. The purpose of the present article is to report the existence of several such rotation defects in RDX and to define their limits of stability. It is further observed that dislocation cores are sites where rotation defects are produced. In the undistorted bulk at ambient and higher temperatures their lifetime is limited. However, their concentration is expected to increase during plastic deformation.

The article begins with a review of the methodology used, followed by the definition of four rotational defects. The associated lattice distortions and the energy barriers defining their stability limits are presented in Sec. III, together with observations of core structures containing various types of distorted molecules. The conclusions are presented in closure.

II. METHODOLOGY

RDX is modeled using the fully flexible potential for condensed phase nitramines developed by Smith and Bharadwaj.¹² The potential was originally developed for cyclotetramethylene tetranitramine (HMX) and was parameterized using quantum chemistry calculations for molecular geometries and conformational energies for HMX and dimethyl dinitro methyldiamine (DDMD). The potential, though not fitted to any physical constants, was reported to reproduce accurately the elastic and thermal properties of RDX.¹³ The potential was used to study high pressure phase stability^{13,14} and phase transformations during shock,¹⁵ as well as the critical stresses for dislocation motion^{16,17} and dislocation nucleation.¹⁸

In the present simulations, the electrostatic interactions are calculated explicitly up to a cut-off radius of 15 Å and long range interactions are calculated using the PPPM method. The van der Waals interactions are also cut-off at 15 Å. The charges are modified to account for the effects of polarization in the condensed phases.^{7,15} In addition to electrostatic interactions, the potential includes van der Waals as well as angle-bending, bond-stretching and dihedral interactions representing the intra-molecular bonds.

The structure of crystalline α -RDX is orthorhombic and belongs to the space group Pbca in ambient conditions. The initial structure was created using crystallographic data¹⁹ and was allowed to relax under atmospheric pressure. The supercell used for simulations of the crystal was composed of $5 \times 5 \times 5$ unit cells and contains 1000 molecules. Larger super-cells, up to $10 \times 10 \times 5$ were used in some simulations of point defects. Periodic boundary conditions were used in all directions. The potential size effect affecting the results was investigated by considering systems of sizes ranging from $3 \times 3 \times 3$ to $10 \times 10 \times 10$ unit cells. The results of this study are reported in Sec. III A.

All simulations were performed with LAMMPS,²⁰ a molecular simulation code from Sandia National Labs. The equations of motion (NVT and NPT ensembles) are those of the Nose-Hoover non-Hamiltonian form,²¹ while the integrators are time-reversible and measure-preserving, as given in

Ref. 22. Viscous damping of 20 Kcal/mole-fs was used to assist minimization.

The computations were performed in parallel using 128 processor cores on the SUR Blue Gene/Q at the Center for Computational Innovations (CCI) at Rensselaer Polytechnic Institute.

III. RESULTS

A. Identification of rotational defects

Stable defects correspond to local minima of the crystal energy. To explore the existence of such preferential configurations, super-cells are considered in which all molecules are in the perfect lattice position and orientation, except one probe molecule which is rotated. The rotation is defined by specifying the orientation of the normal to the mean plane of the ring, **n** (Fig. 1(a)), relative to the three orthogonal principal crystallographic axes of the crystal. The two polar angles, θ and ϕ , define the direction of **n**. Angle θ is measured between **n** and the [001] crystallographic direction, while angle ϕ is measured relative to the [100] direction. The third rotational degree of freedom represented by the rotation of the molecule about vector **n** is not considered since the molecule is chemically trifold symmetric with respect to this degree of freedom, and the final ring structure is often puckered. Note that Euler angles are broadly used to define the orientation of molecular segments in studies of DNA and proteins.^{23,24}

Random values are selected for the rotation angles and the molecule is placed in the new configuration without



FIG. 1. (a) Schematic representation of the mean plane of the ring with normal **n**. Blue indicates N, red indicates C, yellow H, and cyan O. (b) Polar map of molecular orientations. The two angles, θ and ϕ , are measured between **n** and the crystal axes [001] and [100], respectively. Attractors A to D represent rotated states, while E represents the proper orientation of the molecule in the perfect crystal.

distorting the ring. In order to avoid the steric hindrance due to the neighboring molecules, a small dilatation strain centered at the defect is applied. The strain is graded such that it vanishes at the boundary of the model. Periodic boundary conditions are used in all cases.

Once the probe molecule is rotated, it is rigidly fixed and the surrounding region is relaxed by performing a molecular dynamics run in the NVT ensemble at $300 \,^{\circ}$ K, for 10 ps. The rotated molecule is then freed and the entire system is allowed to relax during an NPT run, for 50 ps at $300 \,^{\circ}$ K, under a pressure of 1 atm. Subsequently, the potential energy is minimized and the system is brought to the athermal, $0 \,^{\circ}$ K state.

Sixty randomly selected rotated states of the probe molecule are considered. Figure 1(b) shows the initial and final positions of these molecules in the plane of the two polar coordinates. The initial point of each arrow corresponds to the initial state, which was selected at random. The other end of each arrow corresponds to the state in which the molecule relaxes. The actual trajectory of the molecule in the $\theta - \phi$ plane during relaxation is not rectilinear. The final states cluster at five points (labeled A to E in Fig. 1(b)) which are attractors for this fictitious dynamics. The state labeled E is the expected orientation of the molecule at that lattice site of the perfect crystal. The other four configurations represent rotational defects. These are subjected to repeated relaxations following small random perturbations to test their stability. It results that all four are indeed stable to local intra- and inter-molecular perturbations. Note that the $\theta - \phi$ plane is only a projection of the real phase space of the rotating molecule. Therefore, the basins of the five attractors overlap in this projection and the trajectories of the relaxing molecules intersect at multiple points.

The structure of defects A to D is shown in Fig. 2 and is described in Table I. Defect A retains the chair conformation but the mean plane is tilted 135° equatorially (about the [001] axis) from the orientation in the perfect crystal; as a result, the position of the nitro groups relative to the ring is changed but is still approximately of AAE type. Defect B has a twist boat conformation of the ring with a mean plane tilted 55° relative to conformation E, with the two axial nitro groups pointing in opposite directions. These are indicated as A and \overline{A} in Table I. Defect C has a boat conformation with the mean plane close to that of E and all nitro groups oriented axially, while defect D has the similar twist-boat shape and nitro angles of defect B, albeit with a different mean plane normal.

The twist configuration of the ring was detected in MD simulations of isolated molecules performed with a different potential at temperatures above 400 K,^{4,25} and was stabilized in *ab initio* simulations under similar conditions. Here, ring twists are induced by the steric interaction with neighboring molecules and are intrinsic to the structure of the described rotational defects.

It is useful to characterize the lattice distortion in the vicinity of a rotational defect. To this end, the displacement of the molecular centers of mass relative to the perfect crystal state is computed. The magnitude of this displacement for defect C is shown in Fig. 3 as a function of the distance from the center of mass of the rotational defect, r. The other defects lead to similar results. The displacements represent the lattice



FIG. 2. Rotational defects A to D in the RDX crystal. Configuration E represents the perfect crystal. The orientation of the coordinate system shown is common to all configurations.

distortion and include a smaller contribution due to molecular distortions. The data are rather scattered due to this intramolecular distortion contribution, but may be described approximately by a power function, i.e., the displacement scales as $r^{-\gamma}$, with $\gamma = 1.7$ (slope of the line added to Fig. 3). The strain induced by the defect in the surrounding lattice scales as $r^{-\gamma - 1}$. In a previous study,²⁶ it was shown that the strain field associated with any point defect can be decomposed in a Laurent series, each term of which is associated with a point source of elastic field. Specifically, in three dimensions, the r^{-2} term corresponds to a point force, the r^{-3} term corresponds to centers of dilatation and/or rotation, while higher order terms correspond to higher dipoles and multipoles of

TABLE I. Structure of rotational defects A to D. The position of the nitro groups is indicated in the right column, where A and E stand for the axial and equatorial positions, respectively. A bar on A indicates that the group is oriented axially, but in the opposite direction.

Defect type	ϕ	θ	Ring	Nitro-groups
E (default)	136.6	100.8	Chair	AAE
А	2.81	127.1	Chair	AAE
В	81.8	125.9	Twist-boat	$A\bar{A}E$
С	115.0	106.2	Boat	$AAar{A}$
D	143.4	153.4	Twist-boat	$A\bar{A}E$



FIG. 3. Magnitude of the displacement of the center of mass of molecules surrounding the rotational defect C relative to their position in the perfect crystal, function of the distance from the center of mass of the rotated molecule, *r*. The best fit line has slope -1.7.

centers of dilatation and/or rotation. The observation that the displacement field decays faster than r^{-1} (strain decays faster than r^{-2}) indicates that the rotational defect may be approximated with a center of dilatation or rotation and that the field is short-ranged. Specifically, relative center of mass displacements decrease below 0.03 Å at r > 15 Å. Let us observe that 15 Å is also the cut-off distance of short range electrostatic and van der Waals interactions. This implies further that using a unit cell of size $5 \times 5 \times 5$ precludes significant elastic and electrostatic interaction of the defect studied with its images induced by the periodic boundary conditions.

The potential size effect affecting these results was studied by considering models of sizes $3 \times 3 \times 3$ and $10 \times 10 \times 10$ unit cells. The defect energy did not change significantly when the system size is increased to $10 \times 10 \times 10$ unit cells. As discussed above, this is expected given the short range of the lattice distortion associated with the defect. The observation indicates that the results reported here are size effect-free.

B. Energetic characterization of rotational defects

The energetic barriers stabilizing these defects are evaluated using the Nudged Elastic Band method.^{27–29} The algorithm works by minimizing the energy of a set of configurations (images) interpolating between the initial and final states of the system. The resulting Minimum Energy Path (MEP) traces the path the system takes when transiting from one state to the other and provides the activation energy to be overcome for the transition to occur. The barriers are defined in Fig. 4, where the reference energy is the energy of the perfect crystal. The barrier for the formation of the defect, ΔE_2 (path pointing to the left), is always larger than the barrier for the annealing process, ΔE_1 (path pointing to the right). In ambient conditions, $\Delta E_2 \sim 1.5 \,\text{eV}$, while $\Delta E_1 \leq 0.3 \,\text{eV}$ for all these defects. Defect A has the largest ΔE_2 , of 1.8 eV, while defect C has the smallest $\Delta E_2 = 1.36 \text{ eV}$. Defect C has the largest ΔE_1 of 0.34 eV, while defect A has the smallest $\Delta E_1 = 0.08$ eV.

Figure 4 shows the variation of the two barriers with the pressure. To compute these values, each defect configuration is stabilized at given target pressure and perfect crystal structures with identical pressure are created. Transition pathways obtained at ambient conditions are scaled to these volumes

which are then provided to the Nudged Elastic Band method in LAMMPS as initial reaction paths. Since the volume is kept fixed during the NEB runs, the pressure along the pathway fluctuates to within 10% of the target pressure in all these cases. As the pressure increases, the barrier for formation, ΔE_2 , increases rapidly becoming larger than 2 eV at applied pressures above 1 GPa. Barrier ΔE_1 has a more gradual variation, remaining in the vicinity of 0.4 eV even at pressures as high as 2 GPa. This indicates that the formation of such defects is not favored under shock conditions, but their annealing is slowed down.

It is useful to evaluate the contribution to the formation energy of the various types of interactions, i.e., the electrostatic, van der Waals, and intra-molecular. The results are shown in Fig. 5 for the four types of defects at 0° K and 20 MPa pressure. The intra-molecular interactions help stabilize defects C and D (have a negative contribution), while the van der Waals interactions have the largest positive contribution. This is expected since molecular rotation perturbs the packing and should lead to large excluded volume energy penalty. All contributions are positive in the case of the highest energy defect, A, while defects C and D have lower formation energy due to some degree of intra-molecular relaxation.

Furthermore, it is interesting to inquire if the point defects tend to cluster. To investigate this issue, it is necessary to place in the super-cell two defects separated by a vector, r; the length of this vector is kept as a parameter. The difference between the energy of this structure and that of the crystal with the same defects separated by "an infinite" distance represents the interaction energy. An exhaustive study of this effect would require considering all combinations of defect types and all possible orientations of \mathbf{r} relative to the crystal axes. In this work we limit our attention to the lowest energy defect, C, and consider that **r** is parallel to the [100] axis of the crystal. The interaction energy is shown in Fig. 6 versus the separation distance, $|\mathbf{r}|$, for systems at 0 °K and 20 MPa compressive hydrostatic stress. The first data point corresponds to be case in which both rotated molecules are placed in the same lattice unit cell. The points appear staggered since, as $|\mathbf{r}|$ increases, it is only approximately parallel to [100]. The approximation improves as the separation distance $|\mathbf{r}|$ increases. This is due to the fact that the actual molecular arrangement is such that only every second molecule is located exactly on the [100] axis.

The interaction is attractive and the range is comparable with that of the perturbation elastic field shown in Fig. 3. This is expected since the point defects interact in the longrange through the elastic field and electrostatic interactions. The maximum binding energy is rather small, below 0.1 eV, which indicates that clustering is likely to be eliminated by thermal fluctuations at sufficiently high temperatures.

C. Molecular distortion in dislocation cores

Conformational changes of molecules in the cores of dislocations in RDX have been reported previously.^{17,30} The large strain field at such locations promotes conformational transitions, but the exact conditions promoting the transition



FIG. 4. Variation of barriers ΔE_1 and ΔE_2 for annealing of rotational defects and their formation, respectively, and of the defect formation energy, $\Delta \mathbf{H}$, with the pressure. The barriers are defined in the schematic of the transition path shown.

have not been fully defined so far. Here we observe that rotational defects as well as molecules with highly distorted rings can also be found in certain cores.

Dislocations are simulated using the procedure employed in Refs. 16 and 17. Simulation cells of size $100 \times 2 \times 100$ lattice unit cells are considered, with the smaller dimension in the direction of the dislocation line. A dislocation dipole was created by imposing the Volterra displacement field on the Center of Mass (COMs) of the molecules, which ensures that the molecular bonds and angles are not distorted by the applied displacements. The individual dislocations of the dipole are arranged on the same glide plane in such a way that a periodic array of dipoles results (on the glide plane) upon application of periodic boundary conditions. The distances between the dislocations in the unit cell and between these and their images are equal. This ensures that the Peach-Koehler force acting on each dislocation due to the interaction with others in the periodic array vanishes. The glide plane is (010). Two cases are considered in this study: arrays of edge dislocations with Burgers vector $\frac{1}{2}(010)[100]$ and arrays of screw dislocations of same Burgers vector. After imposing the Volterra field, periodic boundary conditions are applied in the [100]



FIG. 5. Contribution of the electrostatic, van der Waals and intra-molecular interactions to defining the formation energy of the four types of defects.

and [001] directions, while the boundaries perpendicular to the [010] direction are kept traction free. The core structure is examined after relaxation. No far field stress is applied and the temperature if 0° K.

Figures 7(a) and 7(b) depict the molecular arrangement close to the cores of edge and screw dislocations with Burgers vector $\frac{1}{2}(010)[100]$, respectively. In RDX these dislocations dissociate in two partials with $\frac{1}{2}$ Burgers vector length. Therefore, the two partials in each pair are separated by a stacking fault. The stacking fault stretches to the left of the core, as indicated in the figure. These dislocations are the most mobile in RDX as they have the smallest Peierls stress.¹⁶

The observation relevant for this discussion is that distorted molecules exist in the stacking fault and core regions. In the case of the edge dislocation (Fig. 7(a)), molecules with a twist boat configuration are located along the stacking fault. These molecules are not rotated. Rotated molecules are seen near the core. In the case of the screw dislocation (Fig. 7(b)), rotated and distorted molecules are seen along the dislocation line. The molecules along the stacking fault are not distorted.

As discussed in Ref. 16, the flexibility of the molecules plays an important role. If molecules are forced to remain rigid, the dislocation cores are less compact and of higher energy, while the Peierls stress increases dramatically, the dis-



FIG. 6. Interaction energy of two rotational defects of type C separated by an imposed distance along the [100] crystal axis.



FIG. 7. Core structure of $\frac{1}{2}(010)[100]$ (a) edge and (b) screw dislocations. The molecules colored in orange are not rotated but their rings are in the twist boat configuration. The molecules colored in red are rotated. These occur very close to the core in both cases.

location becoming sessile. Molecular rotation in the cores is also expected to play a similar role. It is not possible to test this conjecture directly since preventing molecules from rotating while allowing them to remain flexible is not feasible in simulations. However, since rotated molecules are observed in these low energy states, preventing molecular re-orientation is expected to lead to higher energy configurations which would reflect in a higher Peierls stress.

IV. DISCUSSION

To discuss the findings reported in Sec. III in perspective, it is useful to compute the formation energy of a point defect which is considered fundamental for the mechanics of most materials – the vacancy. The vacancy formation energy is computed by removing a molecule and evaluating the system energy after relaxation. This value is compared with the cohesive energy of the perfect crystal composed from the same number of molecules at the same pressure. In RDX, the vacancy formation energy results 1.68 eV at atmospheric pressure, 1.7 eV at 10 MPa (98.7 atm) and 1.8 eV at 50 MPa (493.4 atm) and 0 °K.

Interestingly, the vacancy formation energy is comparable with the formation energy of the four rotational defects discussed. Hence, these are at least as prevalent in crystals as vacancies. Nevertheless, the concentration of thermal rotational defects is small. Let us write the balance of the flux of defects being formed and that of defects annealing out as

$$N_0 \exp\left(-\Delta E_2/kT\right) = N_d \exp\left(-\Delta E_1/kT\right), \qquad (1)$$

where N_0 and N_d are the number of lattice sites occupied by molecules in the perfect crystal and the number of sites occupied by rotational defects, respectively. The concentration of defects results

$$c_d = \frac{N_d}{N_d + N_0} = \frac{1}{1 + \exp\left(\frac{\Delta E_2 - \Delta E_1}{kT}\right)}.$$
 (2)

With the values reported above for the energetic barriers, one may evaluate that in ambient conditions the concentration of defect C is highest, but only 4.9×10^{-18} . All other defects have thermal concentrations in ambient conditions below 10^{-20} . As the pressure increases, the concentrations decrease. The concentration of thermal vacancies under the same conditions is on the order of 10^{-29} . Clearly, the concentrations of defects produced by thermal means are very small and they are likely inconsequential for the plastic deformation of RDX, for phonon scattering and up-pumping.

The presence of conformational and rotational defects in dislocation cores leads to a different perspective on their role in the mechanics of the crystal. These defects form under the action of the high gradient strain field close to the core. As the dislocation moves away, they are left behind in a perfect, strain-free crystal. Subsequently, thermal fluctuations anneal them out. The rate of this process is controlled by the annealing barrier, ΔE_1 . Specifically, let us consider the attempt frequency to be equal to the smallest eigenfrequency of the wagging motion of the nitro side groups. This was estimated from the Fourier spectrum of the trajectory of one of the nitro groups (angle relative to the ring normal) and was found to be on the order of $v_0 = 10^{12}$ Hz. The characteristic time of the annealing process becomes $\exp(\Delta E_1/kT)/\nu_0$. With the value of ΔE_1 reported above, this gives $2.04 \times 10^{-5} \ \mu s$, 0.87 $\times 10^{-3} \mu s$, 0.82 μs , 0.29 μs for the four types of defects, A to D, respectively. These times are to be compared with the inverse of the frequency at which a site is visited by dislocations, Δt_w . The strain rate of plastic deformation is given by the Orowan equation: $\dot{\varepsilon} = \rho bv$, where ρ is the dislocation density, b is the magnitude of the Burgers vector, and v is the mean velocity of dislocations. The return time Δt_w is related to v through $\Delta t_w = 1/v\sqrt{\rho}$, where the average distance between dislocations was taken equal to $1/\sqrt{\rho}$. Then, one can write $\dot{\varepsilon} = \sqrt{\rho}b/\Delta t_w$. With $\rho \sim 10^{12} \text{ m}^{-2}$ and $b \sim 10^{-9}$ m, one estimates $\Delta t_w \sim 1 \mu s$ for impact conditions with $\dot{\varepsilon} \sim 10^3 \text{ s}^{-1}$. Hence the two characteristic times are of the same order of magnitude, which indicates that one may consider that during plastic deformation the average density of rotational defects in the crystal is equal to the density of dislocations times the number of such point defects per core (which is on the order of one per unit length of dislocation line). This is not a negligible quantity and the presence of such defects may play a role in phonon scattering and as obstacles for dislocation motion.

The discussion above indicates that, despite the weak inter-molecular interactions in molecular crystals, the expected concentration of thermal point defects is very small. The central reason for this situation is the contribution of the

TABLE II. Values of the formation energy for the four rotational defects, A, B, C, and D and for vacancies at 0° K and 20 MPa pressure. The formation energy for Caae conformational defects from Ref. 8 is included.

Point defect type	Formation energy (eV)	
А	1.7	
В	1.48	
С	1.08	
D	1.29	
Vacancy	1.72	
Caee conformational defect	0.026	

intra-molecular deformation modes to the total energy of such defect. This view is qualitatively in line with the perspective formulated by Kaprowicz and Brill³¹ who pointed out that in α -RDX, the crystal symmetry is determined largely by geometric constraints produced by molecular packing which do not favor any deviation from the original geometry of the molecule. As proposed in the Introduction, the point defects in molecular crystals are divided in vacancies, conformational defects and rotational defects. Table II shows the formation energies, ΔH , for the four rotational defects and the vacancy at 0 °K and 20 MPa pressure. It also reports the formation energy for conformational defects (Caae in a lattice in which all other molecules are in the Caae state) in α -RDX, from Ref. 8. Conformational defects are observed only in presence of tensile strains and this value is obtained for 0.5% uniaxial strain applied in the [001] direction. These are not stable under compression. It was also reported that Caee conformation defects form only in presence of voids,³ stacking faults,⁶ and due to the passage of shock waves.⁷ Rotational defects are stable at the atmospheric pressure. The values in the table and the observation of such defects in dislocation cores indicate that rotational defects are expected to be much more prevalent in the RDX crystal than vacancies.

The relatively small annealing rates of rotational defects (annealing rates of rotational defects are much smaller than those of conformational defects) lead to a transient dynamic population which is expected to occur during plastic deformation. This indicates that under shock conditions dislocations do not move in a perfect crystal, rather they encounter point defects of various kinds which act as obstacles to their motion. These point defects also act as phonon scattering centers, therefore possibly modifying the way in which inter-molecular vibration energy is transferred to the intra-molecular modes during up-pumping. The data presented in this article are brought in support of the conjecture that, although point defects are not important in thermodynamic equilibrium, they become important under far-fromequilibrium conditions such as during plastic deformation induced by shock.

V. CONCLUSIONS

A new class of point defects in the molecular crystal RDX is described in this article. These are molecules which are rotated (but not displaced) relative to their position in the perfect crystal. Four such stable configurations are described.

The formation energy of these defects is sufficiently large to preclude the formation of large populations under thermodynamic equilibrium conditions. However, stable rotated states are observed in dislocation cores. It is conjectured that rotational defects are left behind when dislocations move away under stress, and anneal out at a rate controlled by an energetic barrier on the order of 0.3 eV. Therefore, a transient population of rotation defects, with lifetimes close to 1 μ s, is expected to exist in non-equilibrium conditions.

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