Slip asymmetry in the molecular crystal cyclotrimethylenetrinitramine

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ABSTRACT

Slip asymmetry is a common occurrence in some monatomic crystals where it is due to complex core structures or specific packing of slip planes. Here we present another mechanism, based on molecular steric hindrance, which leads to asymmetric dislocation motion in cyclotrimethylenetrinitramine (RDX) molecular crystal. Dislocations move at different critical stresses when shear is applied in the positive and negative directions of the Burgers vector in the slip system that contributes most to plastic deformation.

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1. Introduction

Plastic deformation of crystalline materials takes place by the motion of dislocations on specific slip systems. Isolated dislocations move once the applied shear stress resolved in the Burgers vector direction becomes larger than the Peierls stress. Dislocation motion usually requires higher stresses if multiple interacting dislocations are present.

A dislocation in a monatomic face centered cubic (FCC) crystal moves with similar ease in both directions perpendicular to its line. This is a consequence of the mirror symmetry of the crystal relative to the glide plane, which leads to the Peierls stress being identical whether the neighboring atomic planes shift relative to each other in the positive or negative directions of the Burgers vector. As a consequence, the γ-surface is symmetric with respect to zero. The situation is different in body centered cubic (BCC) materials, in which one observes anomalous flow and strong slip asymmetries. Slip in the main {1 1 0}<1 1 1> system is symmetric (although asymmetries have been reported at low temperatures [1]), while in the twinning and anti-twinning directions of the {1 1 2}<1 1 1> system, it is strongly asymmetric [2]. This is due to the nature of the packing of {1 1 2} planes.

Asymmetries can also be due to the interaction of dislocations, an example being the Bauschinger effect. Most dislocation junctions have asymmetric strength, being stronger in one direction of the resolved shear stress and weaker if the stress direction is reversed [3]. In crystals with complex, non-planar cores (e.g., in BCC), an apparent asymmetry may be introduced by the effect of the non-resolved components of the stress tensor on the Peierls stress (non-Schmid effects).

In this Letter we present another mechanism leading to asymmetric slip which operates in complex molecular crystals. The discussion is focused on cyclotrimethylenetrinitramine (RDX), but similar effects are expected in other materials. This has important implications for dislocation mechanics and ultimately for plasticity in these systems.

Molecular crystals are composed from molecules arranged regularly, in a lattice. They find a wide variety of applications which include pharmaceuticals [4], explosives [5], and molecular electronics [6]. Plastic deformation in molecular crystals plays an important role in these applications. For example, the active ingredient in a pharmaceutical tablet, which is usually a molecular crystal, may respond poorly to milling and compacting, resulting in poor tablet formation [4]. Plastic deformation and associated dislocation motion in the explosive powder have been proposed as mechanisms leading to hot-spot formation and detonation [7]. Despite the acknowledged importance of plastic deformation in these applications, a fundamental understanding of deformation mechanisms in molecular crystals is still lacking.

Molecular crystals are held together by weak inter-molecular forces, mostly van der Waals and electrostatic, while the intra-molecular bonding is strong. Therefore, they are rather brittle, have low melting points and are elastically compliant. In addition, due to the topological interactions of the molecules, close packing is difficult and the resulting crystals have low symmetry and complicated structures. The low symmetry leads to a small number of effective glide systems which, in turn, determines how brittle the material is. The complex packing leads, in certain cases, to overlap between molecular side groups when neighboring atomic planes are shifted relative to each other.

RDX is an important secondary energetic material widely used in both military and civilian applications. It is composed from molecules with formula $C_3N_6H_6O_6$, which contain a triazine ring and three nitro side groups. The ring is in a chair configuration, denoted by C. The position of the nitro side group with respect to the normal of the ring is denoted as 'e' or 'a', which stand for equatorial and axial, respectively. An angle of approximately 90° corresponds

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to an equatorial position, while angles close to 0° and 180° correspond to axial positions. Under ambient conditions, the crystal is composed from molecules in the Caae state. Conformational changes in the crystal are difficult due to close packing, but have been observed in molecular simulations in presence of voids [5], in shock fronts [8] and under large strains [9,10].

The RDX crystal is orthorhombic (α state) with a unit cell of dimensions 13.36, 11.34 and 10.35 Å at 0 K and atmospheric pressure. The unit cell is shown in Figure 1 in the [001] projection. Very few aspects of dislocation-mediated plastic deformation of this crystal are understood at present.

Experimental investigations using X-ray diffraction [11], micro-indentation [12], nano-indentation [13] and etch-pitting [14] techniques have been used to correlate deformation features with possible slip systems in the RDX crystal. Independent experimental studies [12,13] have proposed the (010) plane to be the primary slip plane, while {011} and {021} are considered as additional potential slip planes. [100] was suggested as a cross-slip direction since it is shared by the (010), {021} and {011} planes. Non-equilibrium molecular dynamics simulations of an RDX crystal shocked normal to (100) have demonstrated the nucleation and evolution of shear bands at 45° relative to the shock direction, in the (010) plane [8]. Anomalous response of (111) shocked RDX crystal was studied using molecular dynamics simulations in Ref. [15]. Munday et al. [16] investigated the competition between ductile and brittle fracture for various crystal planes in RDX using Rice's criterion and concluded that the (010), (011), (021) and (001) planes may possess active slip systems. They also indicate that (010) [100] is the most easily activated system.

2. Methodology

To demonstrate the slip asymmetry we use molecular simulations. The material is described using the Smith–Bharadwaj potential developed for condensed phase nitramines [17]. The potential has been reported to accurately reproduce elastic and thermal properties of RDX [18]. Non-bonded interactions are explicitly considered up to a cut-off radius of 10 Å and long range interactions are calculated using the Particle–Particle Particle–Mesh (PPPM) algorithm. The simulation cell is of size $100 \times 100 \times 2$ unit cells in the [100], [010] and [001] directions, respectively, and consists of 3,360,000 atoms. The size of the model influences the Peierls stress values, but has no effect on the trends and effects discussed here. Based on a separate analysis of the size effect we established
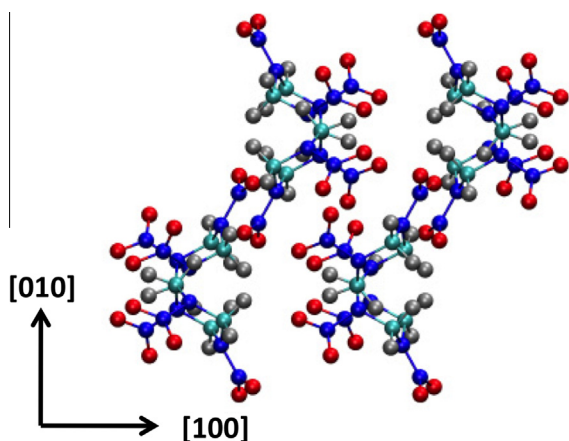

Figure 1. Unit cell of the α-RDX crystal. Molecules are in the Caae configuration. Legend: carbon-cyan, hydrogen-white, nitrogen-blue, oxygen-red. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

that the model of size $100 \times 100 \times 2$ unit cells provides Peierls stress estimates within 15% of the size effect-free values. The initial structure was created using neutron-diffraction data from Choi and Prince [19] and was allowed to relax at 0 K and atmospheric pressure.

In the analysis we consider the (010) [100] slip system for the reasons discussed before. Being the highest mobility system, it is expected to contribute most significantly to plastic deformation. The γ-surface of this plane indicates the existence of a minimum at the $b/2$ position [16]. Hence, a full dislocation would split in two partials of the same type, but with half Burgers vector length. In a separate study of the same slip system and using the same potential [22] we confirmed the expectation that the dislocation with the full Burgers vector, $b = [100]$, is unstable and dissociates in two partials with $b = \frac{1}{2}[100]$. A dipole of edge dislocations with $b = \frac{1}{2}[100]$ 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 displacement field. Since periodic boundary conditions are applied in the two principal crystal directions defining the glide plane ([100] and [001]), the arrangement represents a periodic planar array of dipoles. The initial distance between the two dislocations in the dipole is selected in conjunction with the size of the model, such that the net force on each defect vanishes. The dislocation lines are parallel to the [001] axis. A vacuum pad is used in the [010] direction, perpendicular to the glide plane. The model is deformed by imposing displacement boundary conditions amounting to the application of a resolved shear stress in the Burgers vector direction, which pushes the dislocations towards each other. The Peierls stress is evaluated as the resolved shear stress leading to the advance of the dislocation by at least one lattice spacing, plus the contribution of the stacking fault.

To move the dislocations in the opposite direction and in the same plane, we simply switch their signs and the sign of the applied far-field, while keeping all other details of the model unchanged. The dislocations move toward each other in all cases. Hence, in order to compare motion of given dislocation in opposite directions relative to the crystal, one has to look at dislocations of identical sign in the two cases. This is shown schematically in Figure 2b, where one configuration is shown with continuous red lines, while the other with dashed green lines. Dislocations A and A′ are identical and move in opposite directions relative to the crystal.

All simulations were performed using LAMMPS [20], a molecular simulation code from Sandia National Labs, and 1024 processors of the Blue-Gene/L at the Computational Center for Nanotechnology Innovations (CCNI) at Rensselaer Polytechnic Institute. Visualizations of molecular and crystal structure were created using Visual Molecular Dynamics Software [21].

3. Results

Figure 2a shows a close-up view of the crystal in the [001] projection. The glide planes of interest are horizontal in this view. Molecules are shown by lines connecting the atomic positions, while spheres represent the positions of the COM of the molecules. It is clear from the COM representation that there are two distinct slip planes of the (010) type, which differ in inter-molecular bonding across the glide plane. These planes are denoted as P1 and P2. The interface between the red and blue layers is the P1 slip plane and the interface between the orange and blue layers is the P2 plane. Additional considerations arise when one takes into account the structure of the molecules and the orientation of the side groups relative to the glide plane. Across the P1 plane the nitro group of the molecules below is oriented in the first trigonometric
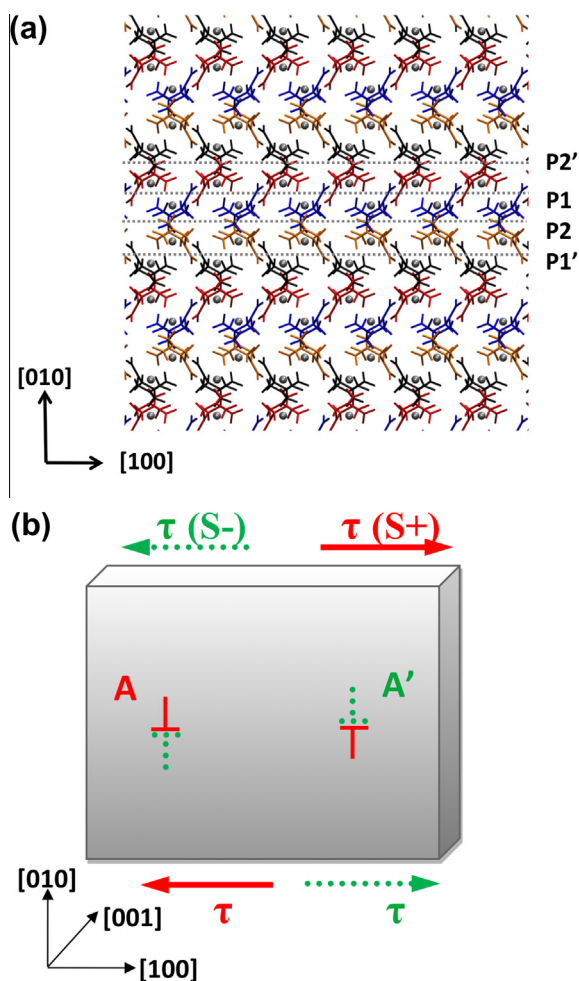
(a)

(b)

Figure 2. (a) [001] projection of the RDX crystal. The red-blue and blue-orange interfaces define planes P1 and P2, respectively. (b) Schematic representation of the model indicating the two configurations (red continuous line and green dashed line) used to evaluate the Peierls stresses for motion of dislocations in opposite directions relative to the crystal. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

quadrant. However, it is observed that the P1 plane below the P2 plane indicated in the figure is not identical to the P1 plane above P2. In this case, the nitro groups are pointing in the second quadrant. Therefore, one has two types of P1 planes which are denoted as P1 and P1' (Figure 2a). A similar situation exists for the other plane and two variants, P2 and P2' are defined in Figure 2a. Based exclusively on the relative positions of the molecular COM, planes P1 and P1' are identical. Same is true for P2 and P2'.

The simple inspection of the crystal geometry is sufficient to suggest the existence of the slip asymmetry discussed in this article. To quantify the effect, we compute the Peierls stress for dislocations moving in the two directions for all these (010) planes. The [100] direction pointing to the right in Figure 2b is denoted as S+ and the opposite direction is denoted as S−. Motion in S+ requires moving the upper molecular planes to the right relative to the lower planes, in this figure. The resolved shear stress required for motion in the S+ and S− directions in the P1 plane is 0.157 and 0.332 GPa, respectively, with an uncertainty of 0.017 GPa. Here the uncertainty represents the magnitude of the loading step in the simulation. The Peierls stress results by adding the contribution of the stacking fault separating the two dislocations in the dipole to the Peach–Koehler force. The stacking fault energy in the P1 plane was evaluated form a separate model and is 153.7 mJ/m².

Therefore, the Peierls stress values for the two directions are 0.387 and 0.562 GPa, and are significantly different. This indicates that dislocation motion in these planes is asymmetric if the applied stress level is below the largest values of the Peierls stress. The similar analysis performed for the two directions of dislocation motion in the P2 plane leads to a smaller Peierls stress and a smaller asymmetry. Specifically, we obtain 0.201 and 0.263 GPa with an uncertainty of 0.012 GPa, for the S+ and S− directions, respectively. The stacking fault energy of the P2 plane is 101 mJ/m² [16]. It is noted that the largest value of these Peierls stresses is smaller or comparable with the Peierls stress for other slip systems in RDX computed using the same model. The full analysis of critical stresses, including the ranking of the slip systems is presented in a separate publication [22].

The effect described above is presented in a more suggestive way in Figure 3 which shows the relative shift of the molecular planes across the glide plane, u(x), as one traverses the core. The red (upper) and green (lower) curves correspond to dislocations A and A' in Figure 2b, respectively. The profile u(x) for A' is shown reversed for easier comparison with that corresponding to A. The shift is measured in the Burgers vector direction. The filled symbols correspond to the relaxed stress-free core structure, while the open symbols indicate the structure after a resolved shear stress of 0.209 GPa was applied. The core of the A dislocation shifts several inter-molecular distances since the applied stress is above the Peierls stress computed for this glide direction. The other core distorts, but is stationary. This provides visualization of the slip asymmetry.

Dislocation motion requires not only significant distortions of the core, but also significant conformational changes of the molecules. Figure 4 shows a detailed view of the core of dislocation A moving in the S+ direction on plane P1. The molecules in the core are color coded to indicate their conformation state. C_{aaa} (red) and C_{aee} (blue) conformations are observed in the core, while molecules further away but in the stacking fault region undergo a transformation (purple) in which the nitro groups situated across the glide plane, which are initially in an equatorial position, rotate to an axial position. The molecular conformation remains C_{aee} owing
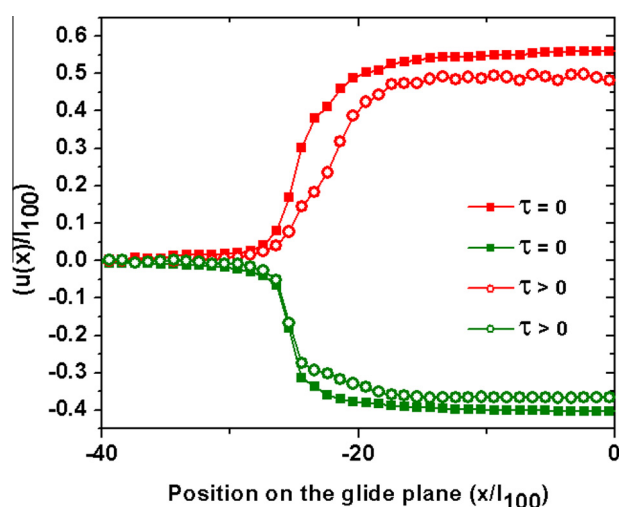

Figure 3. Relative shift of atomic planes across the glide plane, u(x), and across the cores of dislocations A (upper, red) and A' (lower, green). Both axes are normalized by the lattice parameter in the [100] direction, $l_{[100]}$. The filled symbols indicate the unloaded state, $\tau = 0$. The open symbols correspond to $\tau = 0.2093$ GPa, i.e., smaller than the critical stress for motion in S−, but larger than that for motion in S+. Dislocation A moves by several lattice spacings, while the core of A' distorts without moving. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
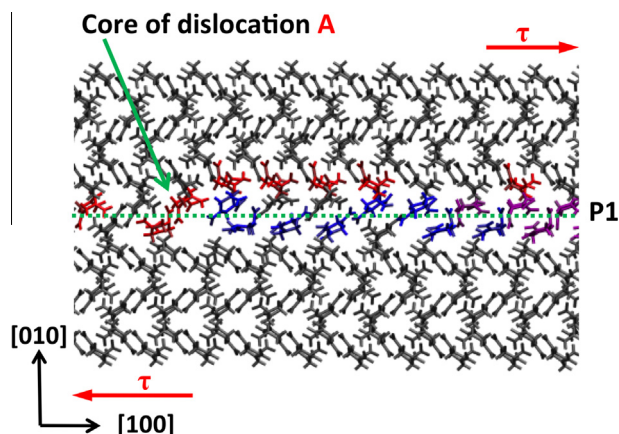
Figure 4. Core structure and molecular conformations for the unloaded dislocation A (Figure 2b). The molecules are colored according to their conformational state: red-Caaa, blue-Caee. Purple indicates molecules undergoing the transformation described in text. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

to a complementing rotation of one of the other nitro-groups, which was originally in an axial position, to the equatorial position. Stable populations of Caee conformations have been reported in shear bands formed under shock loading [8] and in crystals under uniaxial tension applied in the [001] direction [10]. Motion of the edge dislocation in the opposite direction results in an increased steric repulsion as the respective nitro groups would need to undergo further deformation and bend onto the ring of the molecule. This applies to the P1′ plane as well, but for the opposite direction.

4. Conclusions

The asymmetry induced by steric hindrance discussed here adds to the asymmetry potentially introduced by the packing of the molecular planes. The first mechanism is specific to molecular crystals, while the second operates in monatomic systems as well (e.g., in BCC). Both mechanisms can be considered 'core effects' and are different from those leading to slip asymmetry due to the interaction of dislocations.

We expect that this steric hindrance-based mechanism is active in other slip systems in RDX and in other molecular crystals. As discussed above, an asymmetry in the Peierls stress is suggested by a simple inspection of molecular packing. Alternately, one may analyze the γ-surface whose asymmetry is directly related (e.g., through the Peierls–Nabarro model) to the Peierls stress asymmetry. For example, Munday et al. [16] reported asymmetric γ surfaces for the (011) [100] and (001) [010] systems in RDX. Previous studies have indicated that both these slip systems may contribute to plastic deformation in these crystals [15,16].

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