New Shock-Induced Phase Transformation in RDX

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The response of crystalline solids to shock loading is complex and often involves extensive plastic deformation [1] and/or military phase transformations [2] in order to reduce the overall elastic strain energy in the material. A previously unknown shock-induced phase transformation has been identified in the secondary explosive RDX (cyclotrimethylene trinitramine) using large-scale molecular dynamics (MD) simulations. RDX is a molecular crystal that adopts an orthorhombic unit cell (α-polymorph, spacegroup *Pbca*) in ambient conditions [3].

The phase transformation was first observed in MD simulations of the collapse of cylindrical voids during shock loading normal to the (210) plane (see Fig. 1). The ordering of the molecular centers of mass was found noticeably different from that of the parent α phase in volumes around the collapsing void. However, a coherent interface is found between parent and product phases. A sample of the new phase was "cut out" of the larger void collapse simulation block for further study and comparison with the α phase.

Molecular dynamics simulations of the new phase showed that it also belongs to spacegroup *Pbca* but with relative translations of the molecules with respect to the parent structure (Figs. 2a and 2b). The molecular translations that give rise to the transformation result in a decrease in the *b* lattice parameter and an increase in the *c* lattice parameter by around 3.4% while the *a* lattice parameter remains almost unchanged. The transformation to the new phase results in an increase in volume by around 0.4%. Calculations of the enthalpy difference between the two phases under hydrostatic compression shows that α-RDX is more stable than the new phase by about 40 meV per molecule in the sampled pressure range of 1.5 GPa to 5.0 GPa. The new phase is unstable rather than metastable at hydrostatic pressures below 1.5 GPa.

Small volumes of the new phase were able to form in MD simulations of void collapse when the shock direction was normal to (210) because of compressive stresses exerted along [010] as the void collapses. The free surfaces at the void allow the expansion of the lattice parallel to [001] to be accommodated via extrusion of the material into the void. On the basis of these results, we were able to predict that this military phase transformation will take place in RDX single crystals shocked sufficiently strongly along [010]. The Hugoniot for shock loading along [010] was calculated using MD simulations (Fig. 3). Changes in gradient of the $U_s - U_p$ Hugoniot correlate very closely with the onset of the phase transformation. Experimental studies are currently underway to evaluate these theoretical predictions.

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[1] B.L. Holian and P.S. Lomdahl, *Science* **280**, 2085 (1998).
[2] K. Kadau, et al., *Science* **296**, 1681 (2002).
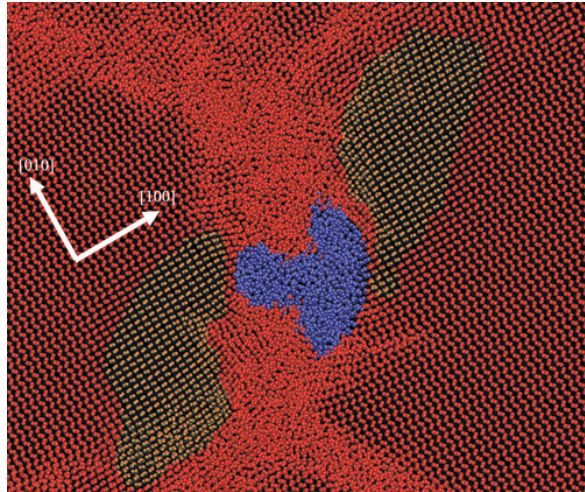[3] C.S. Choi, and E. Prince, *Acta Cryst.* **B28**, 2857 (1972).

Fig. 1.
Snapshot of the molecular centers of mass during the collapse of a 200-Å diameter cylindrical void after shock loading normal to (210) at a particle velocity of 630 ms⁻¹. Color scheme: blue correspond to molecules that were on the surface of the void; yellow to molecules comprising the new shock-induced phase, and red to the α-RDX structure and defects induced in the bulk during the simulation.
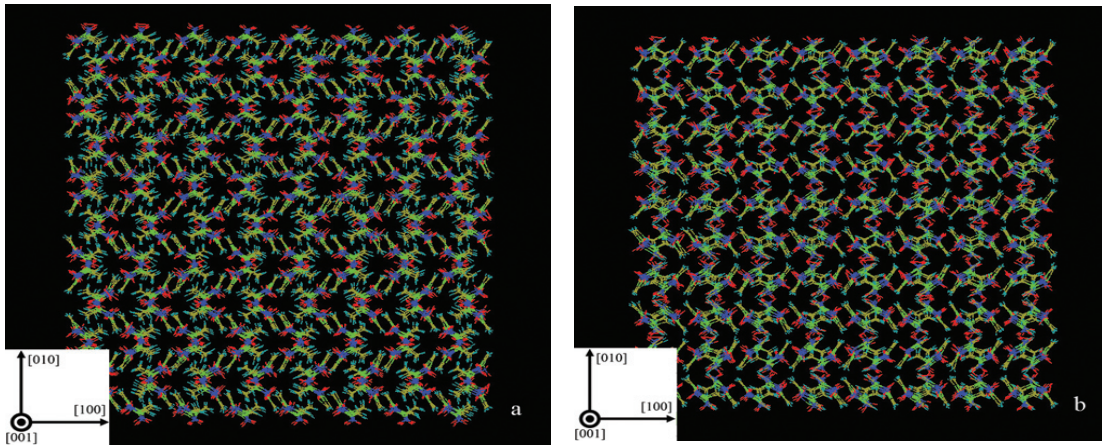

Fig. 2.
Left–A projection along [001] of the molecular structure of 4 x 4 unit cells of α-RDX at a hydrostatic pressure of 1.5 GPa. Right–A projection along [001] of the molecular structure of 4 x 4 unit cells of the predicted new phase of RDX at a hydrostatic pressure of 1.5 GPa.
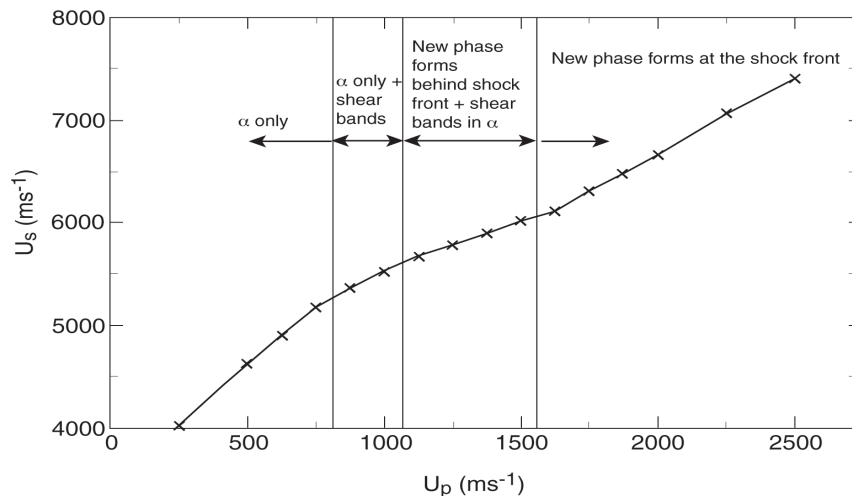

Fig. 3.
Hugoniot for shock loading parallel to [010] in single-crystal RDX calculated using MD simulations.