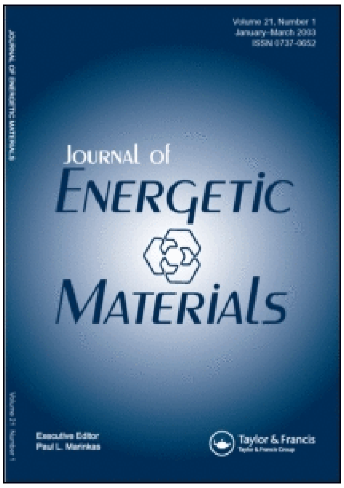

Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

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To cite this Article Ramaswamy, Alba Lalitha(2006) 'Mesoscopic Approach to Energetic Material Sensitivity', Journal of Energetic Materials, 24: 1, 35 — 65

To link to this Article: DOI: 10.1080/07370650500374342

URL: http://dx.doi.org/10.1080/07370650500374342

Journal of Energetic Materials, 24: 35–65, 2006

ISSN: 0737-0652 print/1545-8822 online
DOI: 10.1080/07370650500374342

Mesoscopic Approach to Energetic Material Sensitivity

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A background of some of the earliest mesoscopic phenomena observed in energetic material initiation is described together with newer results, an understanding of which provides a mesoscopic approach to energetic material sensitivity. Mesoscopic phenomena and observations include the formation of "initiation sites" at the atomic and molecular levels, and their propagation to form submicron "reaction sites," which expand and coalesce to produce micron-scale "hot spots." A physiochemical atomistic understanding for the observed phenomena is outlined and described.

Keywords: initiation, "hot spots," "reaction sites," mesoscopic approach, deflagration, detonation

Introduction

Mesoscopic physics refers to the physics of condensed structures of sizes ranging from a few atomic radii or single molecules to several microns. The prefix *meso-* derives from the Greek *mesos* signifying middle or intermediate, and *scopic* comes from the Greek *skopeo*, meaning "to look at." The ability "to look at" or the experimental "observation" of several atoms or molecules of an energetic material or explosive up to a few

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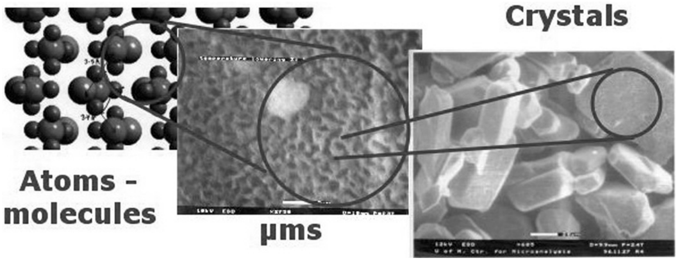


Figure 1. Spatial range of mesoscopic phenomena observed in energetic materials.

microns has revealed structures or ''nuclei'' of decomposition that originate at the atomic or molecular scale and rapidly expand there from. This forms the basis for a series of mesoscopic phenomena occurring in energetic materials, which include the development of ''hot spots'' at the micron scale, the formation of ''reaction sites'' at the submicron level, and the triggering of the energetic reactions at atomic or molecular scale ''initiation sites.'' The spatial range of the observed mesoscopic phenomena typical of energetic materials is depicted in Figure 1.

A background of some of the earliest results in the area, together with a description of newer observations, is provided in this paper. Furthermore an analysis of the range of observed mesoscopic phenomena, as described in this paper, is deepening the understanding into the underlying mechanisms of energetic material initiation and an in-depth mesoscopic approach to explosive sensitivity.

Background

The mechanisms by which the mechanical energy in an impact can initiate an explosive reaction have intrigued scientists for many years. A classic series of experiments performed by Bowden et al. [1,2] in the 1940s first shed light on some of the main processes, which resulted in the development of the thermal ''hot spot'' theory for explosive initiation, a fundamental in the science of the energetic material. The overriding impetus behind the early work by Bowden et al. was the need, for the times, to develop standard explosive sensitivity tests, which would serve as a practical guide for safety in the manufacture and operation of the energetic materials [1].

Liquid explosives were utilized in the initial experiments because they were considered as homogeneous. Factors such as the crystal size, crystalline form, and density of packing, which typically lead to a variation in the sensitivity for solid explosives, are absent. It was found that an enormous increase in the impact sensitivity of the explosives occurs when tiny gas spaces are introduced into the liquid [1,2]. These minute bubbles can be as small as $10^{-11}\,\text{cm}^3$ at atmospheric pressure. Experiments performed in vacuum and with various gases revealed that the bubbles heat up by adiabatic compression to form small nuclei of hot gases and act as the source for the explosion reactions. Some viscous heating of the explosive due to the very rapid flow of the liquid as it escapes through a narrowing gap of the impacting striker also was detected but found to be of secondary importance. A ‘‘moving-film’’ camera recorded the initiation and caught the very first visible reaction as a tiny pinpoint of flame from a bubble surface [1,2], the first observation of which was shortly thereafter termed or coined ‘‘hot spot’’ initiation.

The impact experiments next were extended to solid explosives [3]. The artificial introduction of small, hard high-melting-point foreign particles (grit) was found, in a similar fashion, to sensitize greatly the explosive initiation [4]. The melting point of the grit is the determining factor in the sensitization. In fact, all the grits, with melting points above a threshold value between 400 and 550°C, sensitize the explosives. When an explosive in either the liquid state or solid form was placed between two sliding surfaces, initiation always was found to coincide with the formation of frictional ‘‘hot spots.’’ The explosion of nitroglycerine, for example, is triggered by frictional ‘‘hot spots’’ with a temperature of 480°C.

In the 1930s Bowden and Ridler [5] had shown that surfaces that are rubbed together develop very high localized temperature rises at the points of sliding contact. These hot points or "hot spots" become visible as small stars of light when they reach a temperature of 520–570°C and readily occur on the surfaces of nonconductors. The origin of the term "hot spot," as applied to energetic material initiation, thus can be traced to these early frictional studies. The investigations by Bowden et al. further revealed that liquid and solid explosives bear a striking similarity during the initiation process. The point of initiation always is located at a localized source or sources: for example, a hot wire, an electric spark, an impacted grit particle, or at a gas pocket suddenly compressed during the impact. The localized areas of initiation or "hot spots" appear on the micron scale and can be visualized by high-speed photography [6]. They are observable because of a pinpoint of flame arising from the initiation reaction at the "hot spot" and/or from the self-luminescence of the heat. Whatever the form of the input energy, be it impact, frictional, or electric, initiation is found to take place when the energy is degraded into heat and "localized" or concentrated to form one or more "hot spots," with a temperature greater than the decomposition temperature of the explosive. A series of physical mechanisms thus was established to explain how the input energy, be it mechanical, electrical, or electromagnetic (radiation), can be degraded into localized areas of heat to initiate the explosive reactions [7].

A critical component of the initiation reaction is the time factor, that is, the time necessary for the hot source or "hot spot" to trigger an explosion. Rideal and Robertson [8], in 1948 applied a theoretical treatment of the thermal theory of explosion for gaseous systems to condensed high explosives. The theory is governed by the simple physical consideration that if the rate of evolution of heat by chemical reaction within a small volume is greater than the rate at which it is lost to the surroundings by conduction and other means, it will grow. If not, it will die away. The gaseous state thermal initiation theory first was developed by van't Hoff in 1884 [9] and reexamined by Frank-Kamenetski in 1939 [10], Rice in 1940 [11], and Dainton in 1942 [12]. The calculations of Rideal and Robertson [8] showed that for a self-supported propagation of the reaction or explosion, the "hot spot" must have a minimum critical dimension, which is dictated by its time or duration. Thus for typical frictional "hot spots" with a temperature of about 400–500°C and a duration of 10^{-5} to 10^{-3} s, the calculations reveal that they must vary in size from 10^{-3} to 10^{-5} cm, which is much larger than the molecular dimensions. The computed results are in agreement with the experiments of Bowden and Gurton [4].

The "hot spot" theory alone, however, could not account for a number of energetic phenomena such as the explosion of ozone during its cooling or liquefaction to form oxygen, the spontaneous detonation of crystals of lead azide as they grow in solution, and the application of gas pressure to 300 atm on nitrogen iodide, which causes its spontaneous detonation [13]. Furthermore when the velocity of detonations is taken into consideration, thermal or heat transfer processes are too slow to account for the observed velocities, even when combined with the pressure increase due to the momentum transfer of the gaseous decomposition products. Thus, some underlying phenomenon/a of the initiation process still appeared to be missing.

Early experiments by Von Kallmann and Shrankler [14] in 1933 had shown that TNT, mercury fulminate, and azides could be exploded when bombarded with an intense beam of hydrogen, argon, or mercury ions. The analysis appeared to pinpoint the dimension of the first nucleus for self-supporting decomposition to a size corresponding to the projectile cross section, or of the order of several energetic molecules. This was in contrast with the "hot spot" theory and Rideal's calculations, which predicted sizes much larger than the molecular dimensions. On the other hand, Muraour [15] and Garner et al. [16,17] argued that the minimum critical dimension for the nucleus of decomposition must correspond to the size of several adjacent energetic molecules.

Bowden and Singh [6] reproduced analogous experiments by bombarding a series of solid explosives with electrons, neutrons, fission products, and X-rays. Explosion was achieved in every case with an intense electron beam, but for all other projectiles, although interesting changes within the crystal were observed, explosion was not triggered except for the case of nitrogen iodide. An intense electron beam produces large amounts of heat, and the observed explosions are thus in agreement with a thermal ‘‘hot spot’’ theory of initiation. In the case of lead azide, it was realized that only projectiles with a cross section that could activate neighboring molecules such as ions of mercury and argon would cause initiation; projectiles with a smaller cross section such as alpha particles could not. The interpretation of the results for the remaining explosives appeared to support the thermal ‘‘hot spot’’ theory, though there was still some discrepancy with the views of Von Kallman, Muraour, and Garner.

The experiments performed by Bowden and colleagues extended into the 1950s and corresponded in time with the development of the scanning electron microscope in 1955 in the Engineering Laboratory, Cambridge, just down the road. This formidable analytical tool allowed the examination of the decomposition of energetic crystals at high magnification heated either by a hot-stage or by the electron beam itself, over and above the resolutions typical of optical microscopes. Experiments on sodium and thallous azide clearly revealed that the main decomposition occurs at the surface of the crystal rather than in the bulk, forming a decomposing interface, which moves into the parent crystal along specific crystallographic directions [18]. A similar phenomenon also was observed in lead azide [19]. The rate of the reaction seemed to be dictated by the surface area of the decomposing surface. Furthermore the decomposition appeared to be in the reverse direction to that of the crystal growth. Not all crystallographic surfaces were found to be of equal importance. In fact, Evans and Yoffe [20] observed that in sodium azide the minor morphological facets are more sensitive to photochemical decomposition than the major ones.

In all cases a ‘‘porous’’ or structured residue results on the surface, with crystallographic features depending on the energetic material type [18,19]. Some of these features were resolved as having sizes down to 100 Å. The surface appears to have been ‘‘etched away,’’ leaving pits in the locations where the decomposition gases are released. Smaller crystals require higher temperatures for the surface decomposition to accelerate into an explosion of the crystal [19], which is in agreement with the ''hot spot'' theory because the sizes of the crystals, which explode, are comparable with the critical ''hot spot'' size computed using Rideal and Robertson's formulation [8]. It also demonstrates that unless the defect population of the crystals is also size dependent, the results obtained cannot be explained in terms of reactions occurring preferentially at internal defects within the crystal [19]. Smaller crystals also tend to split up and crack along specific crystallographic planes, when heated, sometimes opening violently [19], which again seems to suggest that the rate of decomposition is a maximum along preferred planes in the crystal.

Experiments performed by Boggs and Kraeutle [21] in 1969 and Herley, Jacobs, and Levy [22] in 1970 also revealed that scanning electron micrographs of the surface of decomposed AP crystals show reactions to have started at sites with crystallographic form. The sites were termed ''nucleation sites'' since they were believed, at the time, to have formed by nucleation around a dislocation. More recent experiments in the 1990s have shown [13,23] that the localization is evidence for the fact that these ''reaction sites'' begin at the atomic/molecular level, where bond formation as well as rupture is important. The crystallographic shape shows that their formation depends on the precise position of the atoms in the crystal lattice relative to the surrounding atoms. Dislocations facilitate the formation of the sites but are not a prerequisite. The experiments further reveal that the formation of pits or surface structure observed on the crystals can be related to localized energetic decompositions forming at the ''reaction sites.'' The latter have crystallographic shapes, and their formation is a characteristic attributable to energetic materials in general, both primary and secondary, as further described in this paper.

Real-time observations or ''filming'' of the whole initiation process at high magnifications via the environmental scanning electron microscope [23–25] show that these tiny ''reaction sites'' appear at submicron dimensions and tend to expand along specific crystallographic directions both laterally and inward into the bulk of the crystal, coalescing to form larger sites of

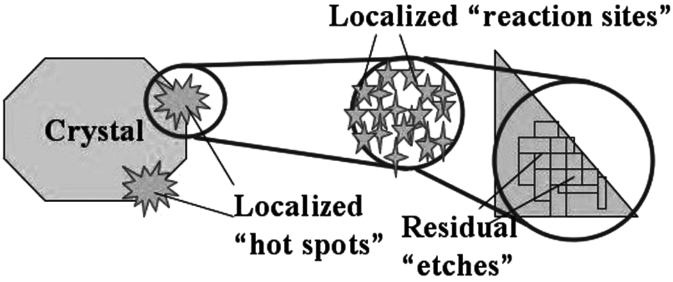


Figure 2. Formation of "reaction sites" observed as residual etches.

the dimension of a "hot spot." Under the appropriate conditions the reactions can accelerate into an explosion or propagation of a detonation wave. The formation of "hot spots" and "reaction sites" on energetic crystals is depicted in Figure 2.

The basis for the crystallographic dependency of the observed experimental results appears to be due to an "intermolecular metastable trigger" reaction mechanism, which occurs at the atomic/molecular scale and has been proposed and investigated since 1995 [13,23]. The "intermolecular metastable trigger" reaction mechanism can occur by the formation of an "initiation site" where two adjacent molecules approach each other to trigger a concerted decomposition reaction. Specific crystallographic directions are facilitated in these regards. The reaction mechanism is in agreement with both the "hot spot" theory and the results of Von Kallman, Muraour, and Garner as well as explaining those energetic phenomena inexplicable by the "hot spot" theory alone [13]. It thus appears to extend the "hot spot" theory to a form that can be a basis for a mesoscopic approach to energetic material or explosive sensitivity, as outlined in this paper.

Observations and Results

The Formation of "Hot Spots" on Energetic Crystals

The formation of "hot spots" on single crystals of RDX, which were laser irradiated at a wavelength of 1060 nm, was recorded under high magnification with a high-speed framing camera. A non-Q-switched Nd/glass laser was utilized [26], with a pulse width at half-maximum of 300 μs and an energy variable between 1.5 and 10.0 J. The laser beam could be focused down to a spot size of 1 mm diameter, achieving laser energy densities of the order of 1270 J/cm^2. The Nd/glass laser beam radiation was blocked from entering the high-speed camera by placing a 1060 nm filter in front of the objective. All RDX crystals were irradiated on the (210) crystal facet, and the high-magnification photography was achieved by mounting a microscope objective of ×35 onto a high-speed camera.

‘‘Hot spots’’ were observed to form at localized sites where microscopic flashes of light or inflammation were observable and found to be located primarily at the crystal edges and corners, irrespective of the size and positioning of the focused laser beam on the crystal surface. The ‘‘hot spot’’ dimensions varied from 10 to 100 μm in diameter. The reaction was observed to propagate from the ‘‘hot spot’’ sites, at a typical rate of 75 ms^{-1}. That the observed and recorded microscopic flashes could be attributed to ‘‘hot spots’’ was confirmed by following the propagation of the deflagration reaction (by high-speed photography), by post-irradiation analysis or examination of the ‘‘hot spot’’ areas for those crystals recuperated after irradiation, and by recording the formation of sites remotely from the focused laser beam spot [26,27]. Figure 3 shows a typical series of high-speed framing photographs for the earliest sequence, where the ‘‘hot spots’’ can be seen to form on the corners and edges of the crystal facets and at the center of the focused laser beam spot. The interframe time is 20 μs.

RDX slices next were obtained by sectioning large crystals of RDX 2–3 cm in dimension using a solvent saw. The resulting slices were polished on a soft, solvent-soaked cloth and were lightly etched to remove any preparation-induced surface damage. The solvents utilized for the slicing and polishing were dimethyl formamide and cyclohexanone, respectively. High-speed photography of the laser irradiation of the (001) slice plane was performed. The formation of the ‘‘hot spots’’ was recorded. It was found that the first ‘‘hot spots’’ were located

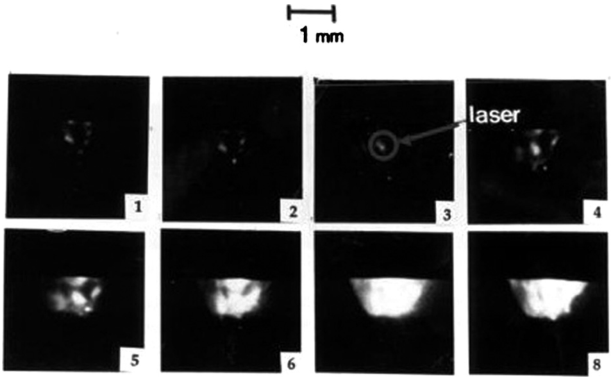


Figure 3. Formation of "hot spots" in single crystals of RDX. High-speed photography of a single crystal of RDX ($2 \times 4 \times 2$ mm) in darkness, irradiated by a focussed Nd/glass laser beam (non-Q switched). Interframe time 20 µs. Ramaswamy Ph.D. Thesis, 1993. Numerous HSPs show "hot spots" $\sim 10^{-2}$–10^{-3} cm (10–100 µm) formed on crystal edges and corners (irrespective of size of laser beam), which expand ~ 75 m/s.

on the slice edge, remote from the laser beam and at times at a distance of about 2 cm [27] from the focused beam. The energy input by the laser was too low in intensity to have created the ignition site on the slice edge thermally by heat conduction, and internal laser reflections did not appear, from the geometry of the system, to have conveyed the laser radiation to the slice edge, which was checked. The energy to trigger the ignition thus appears to have traveled from the focused laser beam spot to the crystal slice edge mechanically or in the form of phonons. In the site or slice corner where ignition took place, focusing of the phonon waves appears to have concentrated or focused to a point source, to form a "hot spot." The observation of the latter phenomenon explains why the "hot spots" recorded on the RDX crystals preferentially tend to occur on the crystal corners and edges, irrespective of the location of the focused laser beam spot.

Finally, for all RDX crystals where "hot spots" were recorded, a limited amount of surface cracking always was found to form and be associated with the crystal at the ''hot spot'' sites (the crystals were recuperated after the laser irradiation at threshold levels for the start of a deflagration). However, when considerable fragmentation of the crystal was observed, no ''hot spots'' were recorded. This demonstrates that the mechanisms that produce cracking and crystal fragmentation in RDX are not responsible for ignition, but that when ignition takes place, a limited amount of surface cracking always is associated with the decomposition. This is depicted in Figure 4.

Furthermore it was found that the detonation of the laser-irradiated crystals of RDX could be achieved only with confinement [27]. This differs from the primary explosives, where onfinement is less critical. It was shown that the effect of the confinement is to trap the decomposition gases, which are themselves generating heat, as detected by placing heat-sensitive paper at various locations in the deflagration gases [27]. The results demonstrate that in the case of secondary explosives, for the ''hot spot'' to lead to a full detonation of a crystal, confinement is necessary to trap the decomposition gases, which are themselves generating heat as well as producing surface pressure, necessary to assist in triggering the initiation reactions.

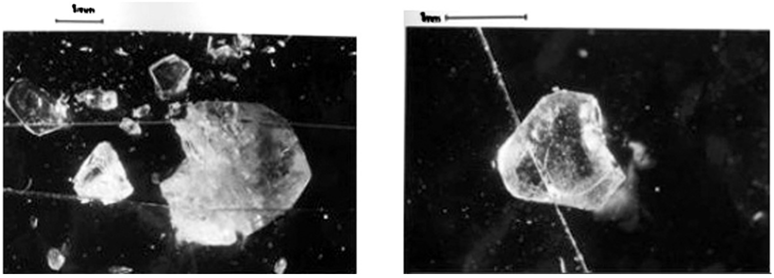


Figure 4. Formation of ''hot spots'' in single crystals of RDX. Considerable cracking and fragmentation of RDX crystal could take place with no initiation. However when initiation took place a small amount of cracking was limited to the ''hot spot'' sites.

The Formation of "Reaction Sites" on Energetic Crystals

Different microscopy techniques were used to analyze the RDX crystal sites or areas where the "hot spots" were observed to have formed [27]. This could be performed for those RDX crystals where the ignition was subthreshold such that the "hot spots," recorded by high-speed photography, first were found to form and to quench immediately. The sites were examined initially by optical microscopy, and micrographs of the limited amount of surface cracking, associated with the sites, obtained. Figure 5 is an example of one such optical micrograph. The surface topography was measured using a He-Ne laser interference microscope, which further evidenced the cracks. Figure 5 shows an example of the He-Ne laser interference micrograph. Finally, various higher magnification images of the "hot spot" areas were obtained by scanning electron microscopy, as shown in Figure 5. They revealed many "volcano"-like structures, identified as "reaction sites." Surface material or volume is missing or forming a "crater" in the "reaction sites" and appears to have been lost or released in the form of decomposition gases.

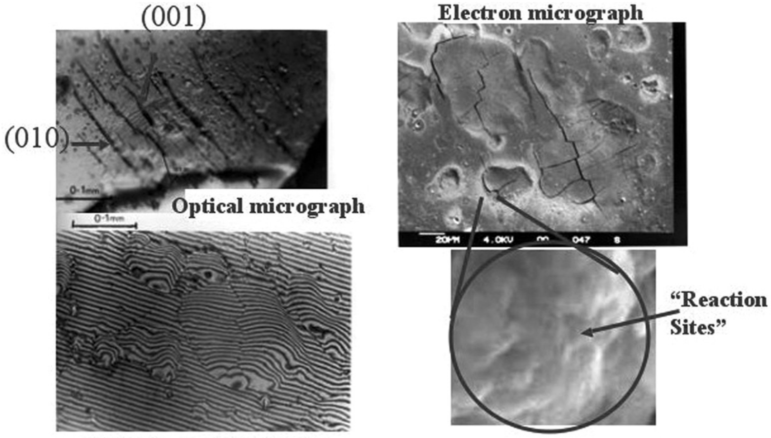
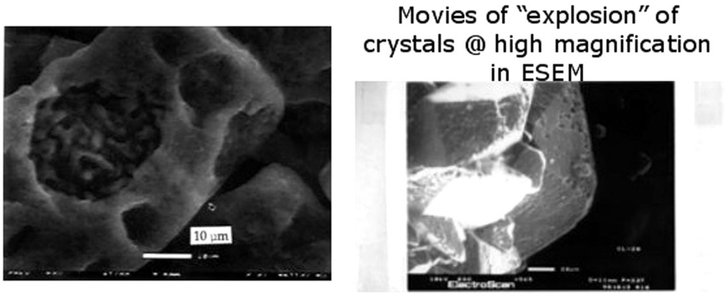


Figure 5. Formation of "hot spots" in single crystals of RDX.

The ‘‘reaction sites’’ were examined at higher resolution in an environmental scanning electron microscope, and their formation and propagation filmed within the same microscope. The environmental scanning electron microscope has the advantage over standard scanning electron microscopes that no conductive sample coating is necessary for the imaging. The transformations in the microscope thus can be followed in real time on a videocamera connected to the microscope, and a movie recorded. Furthermore it has the advantage that different chemical atmospheres can be introduced within the sample chamber to interact with the latter, and the decomposition products can be collected and analyzed.

A large number of different energetic crystals were ignited thermally inside the ESEM either by focusing the electron beam or by means of a ‘‘hot plate,’’ and movies of the ignitions made. The energetic crystals examined include RDX, HMX, AP, ADN, Cl-20, NTO, TNAZ, and AN [23–25]. Figure 6 provides example images of the ‘‘reaction sites’’ recorded during their formation on different energetic crystals. The movies recorded the first formation of the ‘‘reaction sites,’’ expansion, and coalescence of the same up to complete ignition of the crystals. The phenomenology of the observed reactions differed greatly among the various



ADN **CL-20**

Figure 6. Formation of ‘‘reaction sites’’ in single crystals of energetics. Studies on single crystals- AP, HMX, RDX, ADN, CL-20, NTO, TNAZ with ESEM reveal formation of ‘‘initiation/reaction sites’’ $<10^{-5}$ cm (1 μm) during initiation.

energetic materials, but energetic materials of a similar class or structure appear to behave similarly. Thus oxidizers tend to react in a similar fashion, though with different rates according to the chemical structure, and the same goes for explosives, of the primary or secondary form. In the ESEM, RDX reacts very much like HMX, though the rate in RDX is far slower, and the ''reactions'' appear less ''dramatic'' or energetic; the same goes for other explosives with chemical structures of the same family. The collected residues from the decomposition products confirmed that decomposition had taken place [23].

The chamber pressures are very low, around 2.4 torr, and appear to allow the reactions to occur at a slower rate than at atmospheric pressure, permitting the reactions to be followed or filmed in real time. In fact, the speed of the reactions or formation of the ''reaction sites'' also was found to be a function of the chamber pressure and increased with the same [24]. The formation of the ''reaction sites'' can be described as a surface ''hiccup'' with a determined average frequency, which varied with the energetic material and with the chemical nature or gaseous species in the environmental chamber. For example, water vapor was found to increase drastically the reactivity of the energetic materials.

It was observed that the shape of the ''reaction sites'' varied between the different energetic materials and showed a morphological resemblance with the crystal habits on which they formed, indicating that the crystal structure plays an important role in the formation of the ''reaction sites.'' The rate of expansion of the ''reaction sites'' differs along different crystallographic directions. However, the shape of the sites, although resembling the crystal habit, often has a reverse relation to the morphology, that is, a faster rate of decomposition along directions of slower crystal growth and vice versa. This is seen clearly in the micrographs of ADN of Figure 7.

The Formation of ''Initiation Sites'' on Energetic Crystals

By probing or examining the ''reaction sites'' at still higher magnifications using the atomic force microscope, one finds

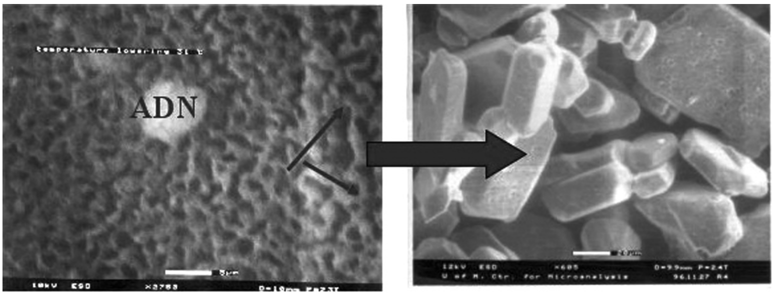


Figure 7. Formation of "reaction sites." Shape of "reaction sites" can be linked with morphology and crystal structure of energetic material.

that the "reaction sites" are smaller and smaller in dimension, tending toward the molecular to atomic scales. A single crystal of ammonium perchlorate was laser irradiated with focused laser pulses of nanosecond duration [28]. The nanosecond laser pulses had a duration of 8 ns at FWHM and an energy per pulse of 0.25 J. The beam was focused onto the (001) crystal habit of an AP crystal with a spot size of 1.68 mm. The power in the nanosecond laser beam was 31 MW, and the power density was 14 MWmm^{-2}. Figure 8 is an optical micrograph of the surface of the AP crystal after nanosecond laser pulse irradiation, with the crystal orientations well identified and labeled on the micrograph. The latter had been identified by Laue back-reflection X-ray diffraction. As can be seen, two sets of cracks can be observed to have superposed, arising from both the orthorhombic and cubic crystal phases of AP. In fact, AP undergoes a reversible phase transformation from the orthorhombic form to the cubic rock-salt crystal form at 240°C. Decomposition in AP commences at around 200°C and extends to 530°C. The cracks evidenced in Figure 8 demonstrate that the laser irradiation raised the temperature of the crystal surface above 240°C. It also shows that decomposition of AP was triggered. The environmental scanning electron microscope was used to search for evidence of surface decomposition. Indeed, "initiation/reaction sites" were observed to have

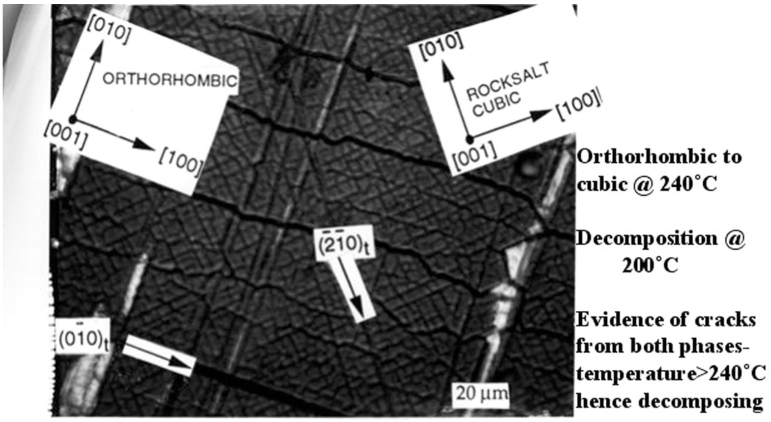


Figure 8. Cracking of AP crystal. AP irradiated with nanosecond laser pulse shows cracking from orthorhombic and cubic phases.

formed amid the finer cracks. With the atomic force microscope the sites were examined at still higher magnifications [24]. Figure 9 shows an example of such a site, which was found to

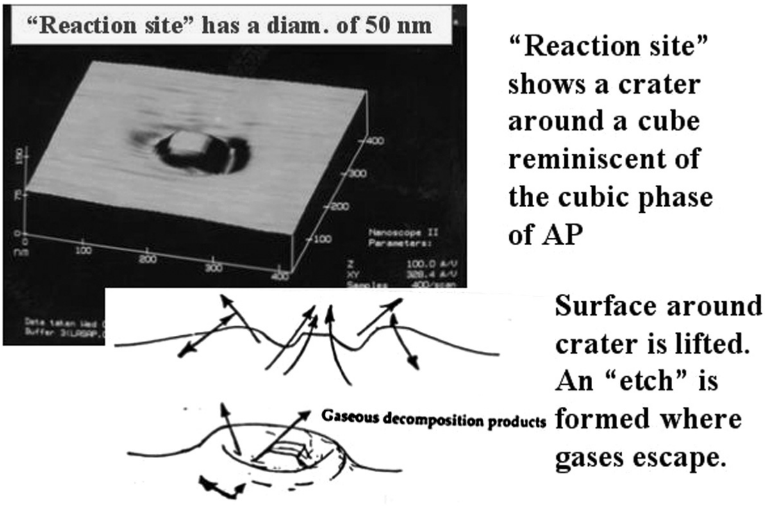


Figure 9. Formation of a "reaction site."

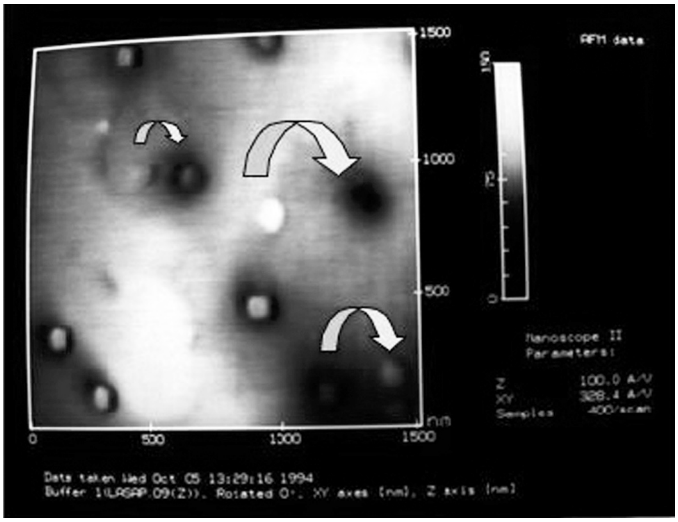
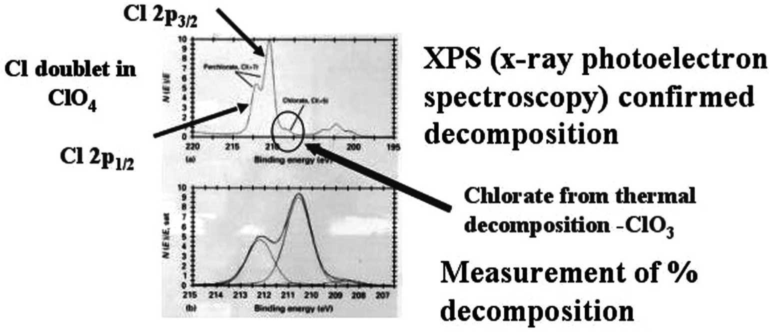


Figure 10. Atomic force micrograph of AP ns laser-irradiated surface showing ‘‘initiation sites.’’ 2.5 Million ‘‘Reaction sites’’ in 1 mm Laser beam diameter. All cubes lie along crystallographic cubic directions as identified from cracks. Some cubes ‘‘pop’’ off from craters.

be about 50 nm in diameter, consisting of a crater with a cube inside reminiscent of the cubic crystal structure of AP. Figure 10 shows how the ‘‘reaction site’’ was formed.

In a focused laser beam spot about 2.5 million sites were found in 1 mm laser beam diameter! Figure 10 shows a typical atomic force micrograph where all cubes can be seen to lie along the crystallographic cubic direction, as identified from the crack directions. Many cubes can be seen to have ‘‘popped’’ out of the craters and lie next to them. This is further indication of the gaseous decomposition products being emitted from the craters.

That decomposition had occurred effectively at the crater sites was verified by X-ray photoelectron spectroscopy [28]. Figure 11 shows a typical spectrum in the region of the Cl, 2p orbital level for the irradiated sample. The visible doublet



XPS (x-ray photoelectron spectroscopy) confirmed decomposition

Chlorate from thermal decomposition -ClO_3

Measurement of % decomposition from area overlap

ClO_2 hypochlorite Cl peaks generally observed for mechanical impact

Figure 11. X-ray photoelectron spectroscopy results. "Initiation/ reaction sites" probed at higher resolution with AFM (atomic force microscope).

arises from the $2p_{3/2}$ and $2p_{1/2}$ lines of chlorine. A small shoulder on the right-hand side of the $2p_{3/2}$ line at a separation of about 1.7 eV is observable and indicative of a small amount of decomposition. Curve fitting of the spectra is shown, and an estimated overall 3% decomposition detected. This is in agreement with the small dimension of the sites and the total surface sampled area, which they cover. The decomposition product is ammonium chlorate, NH_4ClO_3. This product is seen mostly in thermal decomposition studies as compared with mechanically impacted samples that generally show the formation of ammonium hypochlorite, NH_4ClO_2, and other lower oxy-acids.

Examination of the flat unreacted surface of ammonium perchlorate evidences the individual molecules as verified by a computer simulation of the position and size of the molecules, shown in Figure 12. What is particularly interesting is that a detailed analysis of the pixel intensities in the molecules actually reveals the individual atoms as shown in Figure 12. This demonstrates that single atoms in energetic materials potentially can be "observed" directly by atomic force microscopy. Such an analysis was performed for areas inside the crater,

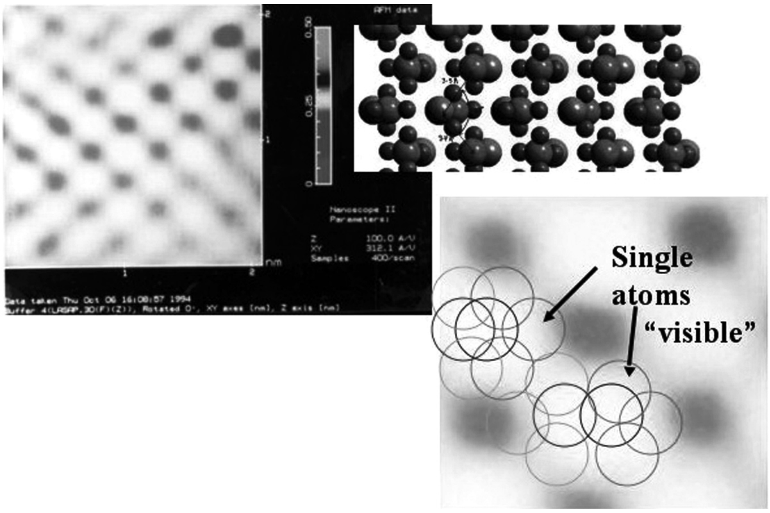


Figure 12. Detection of atoms in AP by atomic force microscopy. Individual molecules of AP evidenced by AFM and in good agreement with simulation.

which shows a large reorientation of the atomic positions at the surfaces. Since smaller and smaller sites can be located tending toward the atomic/molecular dimensions, it is evidence for the fact that initiation has occurred at such a level or at an ''initiation site,'' which expands to form the visible submicron sites known as ''reaction sites.''

Discussion

Bowden et al. [1–6] demonstrated how liquid and solid explosives fundamentally behave in a similar fashion where initiation takes place through a thermal mechanism, the input energy in any form being degraded and concentrated into localized regions of heat or ''hot spots.'' The time dependency of the initiation reactions was introduced through Rideal and Robertson's [8] formulation, which set a minimum critical size for the ''hot spot'' to trigger an explosion. However, a number of energetic phenomena including the velocity of detonations could not be explained or understood in terms of the ‘‘hot spot’’ theory alone. Thus some underlying phenomenon/a of the initiation process appeared to be missing. Von Kallman [14], Muraour [15], and Garner [16,17], on the other hand, were of the view that the simultaneous decomposition of a few adjacent molecules would be sufficient to set off an explosion. This was a first attempt to generate a molecular/atomistic understanding of the initiation, which seemed to shed some light on the observed detonation velocities, but which was at first sight in contradiction with the ‘‘hot spot’’ theory and with some of the early experimental results.

More recent experiments of the laser irradiation and high-speed photography of single crystals of RDX have captured and recorded the formation of the ‘‘hot spots’’ in the crystal. The latter tend to form prevalently on the crystal edges and corners, and a phonon-focusing mechanism has been identified as the source for these ‘‘hot spots.’’ The localization of the reactions or inhomogeneity of the initiation phenomenon is evident where reaction first appears to start at point sources. When the crystals are subjected to gaseous pressure and confinement, they tend to explode, which evidences that the external pressure and heat facilitate the reactions at these points.

In fact, high-magnification examination shows that the micron-scale ‘‘hot spot’’ sites have great structure and are filled with even smaller submicron localized areas of reaction. An analysis of the filming and formation of a number of ‘‘reaction sites’’ in different explosives in an electron microscope shows that they have distinct crystallographic features, with a reverse relation to the crystal growth characteristics or morphology of the energetic crystals. By increasing the chamber pressure in the electron microscope, the speed of formation of the ‘‘reaction sites’’ increases. The introduction of gaseous species such as water also affects the rate or speed of the reactions. This further proves that pressure, heat, and gaseous species can facilitate the formation of these point sources. By analyzing the ‘‘reaction sites’’ with the atomic force microscope, one finds that the very first sites to form are smaller and smaller in dimension, tending toward atomic/molecular scales. If the simultaneous decomposition of adjacent molecules is necessary for the formation of a point source, the smallest point or localization that can be achieved can come when two adjacent molecules meet or approach at a single point.

In fact, evidence has been provided for a ‘‘metastable intermolecular trigger’’ reaction mechanism [13], where neighboring molecules in the crystal lattice of an energetic material can come close enough at a single point to start a concerted reaction through an intermolecular oxidation-reduction reaction, which can trigger the breaking of the first bond in an explosive molecule. In an intermolecular oxidation-reduction reaction, the atomic environment around a given molecule can be seen to have atomic positions and separations already located or positioned to form or favor the formation of reaction products. Thus pressure and heat facilitate the approach and reaction of the neighboring molecules. The ‘‘metastable intermolecular trigger’’ reaction mechanism is depicted for RDX in Figure 13. It is an atomistic physiochemical view of the initiation and is a mechanism that can trigger the simultaneous decomposition of two adjacent molecules.

If the reaction products are released as soon as they form, this further facilitates the initiation and explains why the decomposition in solid explosives mainly occurs on or near the surface and progresses into the bulk of the crystal along an interface with specific crystallographic directions. In the case of liquids, initiation also is facilitated at a bubble surface, since the release of gaseous reaction products can occur readily within the bubble. Furthermore the liquid-to-gaseous interface of the bubble surface permits the reorientation of molecules to occur with greater ease, thus creating a higher probability for ‘‘initiation site’’ formation.

The scanning electron micrographs obtained by Walker, Gane, and Bowden [18], show that in the case of thallium azide the direction of the decomposition is parallel to the (001) planes, forming a surface structure of bipyramids depicted in Figure 14, where the common base is in the (001) plane and the pyramidal faces correspond to the (112) planes. The fine structure of the ‘‘reaction sites’’ and steps on the bipyramidal

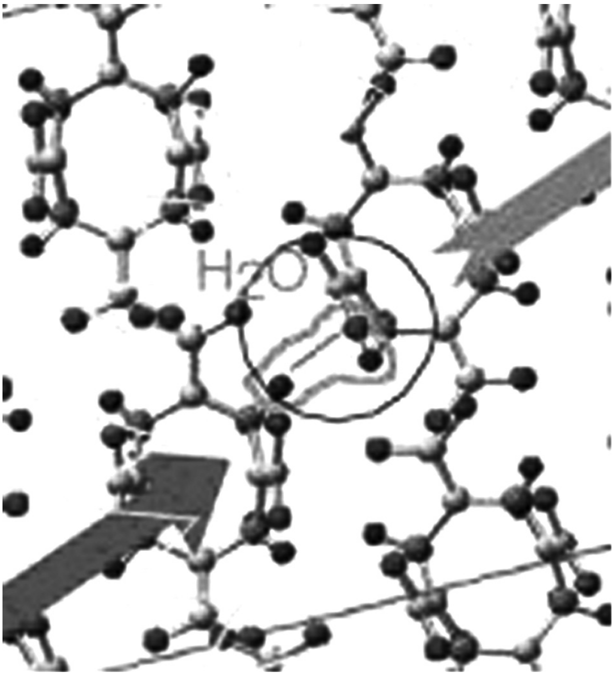


Figure 13. ‘‘Intermolecular metastable trigger’’ reaction in RDX.

faces reveal that the decomposition is usually in the (112) orientation. In a similar way for sodium azide, it is shown that the decomposition occurs along the (111) orientation.

Figure 15 shows the crystal lattice structure and unit cell of thallium azide, and Figure 16 is the thallium azide lattice with the thallium ions and nitrogen atoms inserted as spheres with the nominal ionic radius for Tl^+ of 1.5 Å and the covalent radii for the nitrogen atoms of 0.74 Å in the $N^-{-}N^+{-}N^-$ structure of the azide ion. The (112) plane is drawn on the thallium azide structure in Figure 16, where the [001] direction can be seen to be parallel to the labeled *z*-axis. On analysis of the ‘‘interionic’’ separation among all ions and atoms in the crystal structure, it is noted that the (112) plane cuts along a crystal orientation where the N^+ and N^- ions of two neighboring azide

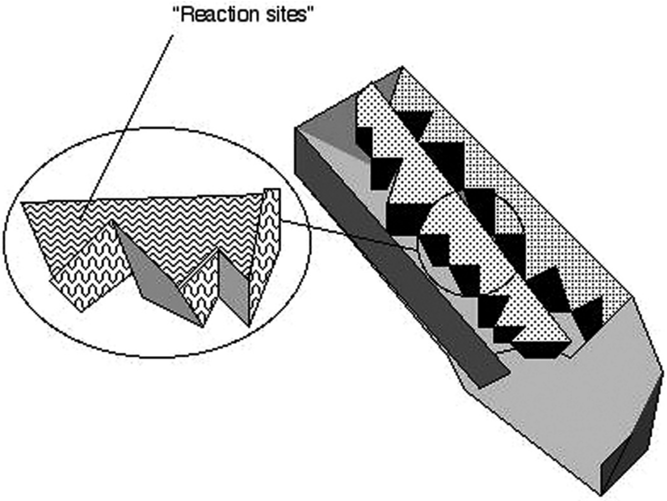


Figure 14. ‘‘Reaction sites’’ in thallous azide.

ions are the closest, and the same goes for the other faces of the bipyramid. Thus the ‘‘interionic’’ separation of the N^+ and N^- ions is 1.75 Å and of the Tl^+ in this orientation is 1.39 Å. This shows that decomposition occurs where the atoms are closest to form the reaction product N_2 (and Tl metal), which is in agreement with the ‘‘metastable intermolecular trigger’’ reaction mechanism, where the closest atoms in neighboring molecules are positioned to form reaction products, and are thus the trigger for the first initiation. The reaction in thallium azide also progresses along the [001] direction from one molecular layer to the next because this is the direction in which the closest Tl^+ ions are found with a separation of 0.678 Å. The nearest ‘‘interionic’’ separations are depicted in Figure 17.

Figures 18 and 19 show the crystal lattice structure of sodium azide with the (111) crystal plane included. Again, as for thallium azide the (111) plane is located along a crystalline orientation where the $N^{(+/-)}$ ions are the closest as well as for the Na^+ ions. The closest separation for the N^- ions is 0.059 Å, and for the Na^+ ions it is 1.738 Å. The Na^+ nominal radius has been taken as 0.95 Å. The shape of the ‘‘reaction sites’’ thus can

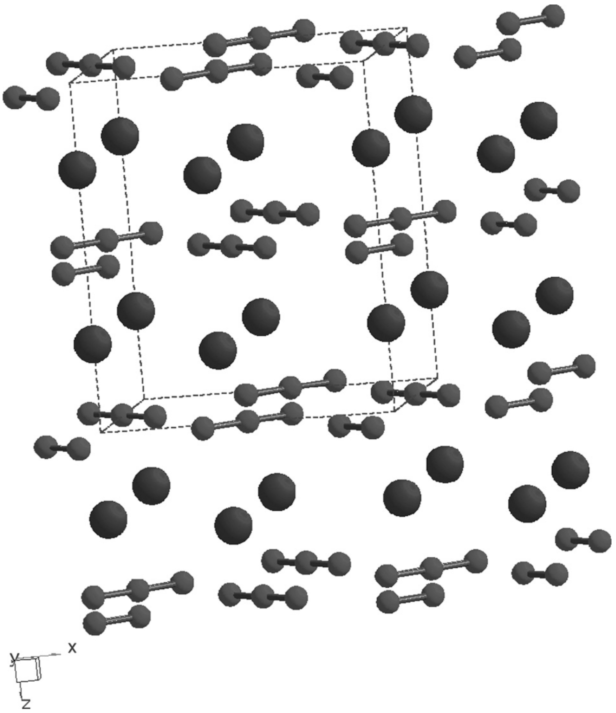


Figure 15. Crystal lattice structure of thallium azide showing the unit cell.

be readily explained in terms of an “intermolecular trigger mechanism.”

However, it is to be noted that the shape of the “reaction sites” also tends to have a reverse relation to the crystal morphology or crystal growth characteristics. The reason for this is that the direction where crystal growth is fastest generally produces smaller crystal facets and vice versa. The fastest crystal growth occurs where the surface intermolecular forces are largest and thus the most closely packed orientations. These are also the directions where the intermolecular trigger reaction mechanisms are most likely to start owing to the closer atomic separations. A larger proportion of energetic material is thus etched away in these orientations, giving a reverse relation to

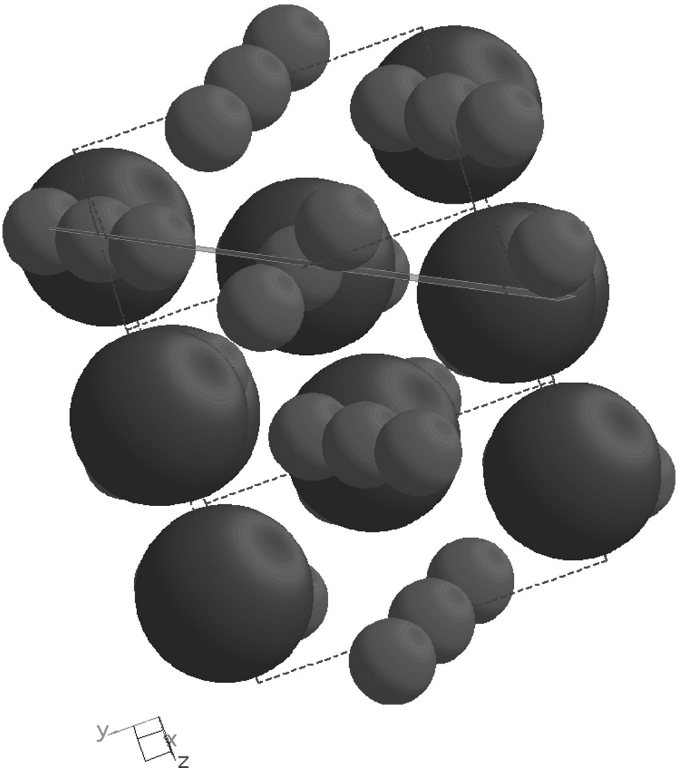


Figure 16. Thallium azide unit cell with (112) plane included.

the crystal habit, as depicted in Figure 20, taking ADN as an example. It also explains why the minor morphological facets in sodium azide were observed by Evans and Yoffe [20] to be more sensitive to photochemical decomposition than the major ones.

Von Kallman, Garner, and Muraour held the view that the simultaneous decomposition of a few adjacent molecules was sufficient to trigger an explosion, a principle that appeared to be in conflict with the ''hot spot'' theory. Von Kallman [14] demonstrated it experimentally by bombarding explosives with ionic projectiles and showed that explosion took place [14]. The cross section and density of the projectiles was such that it

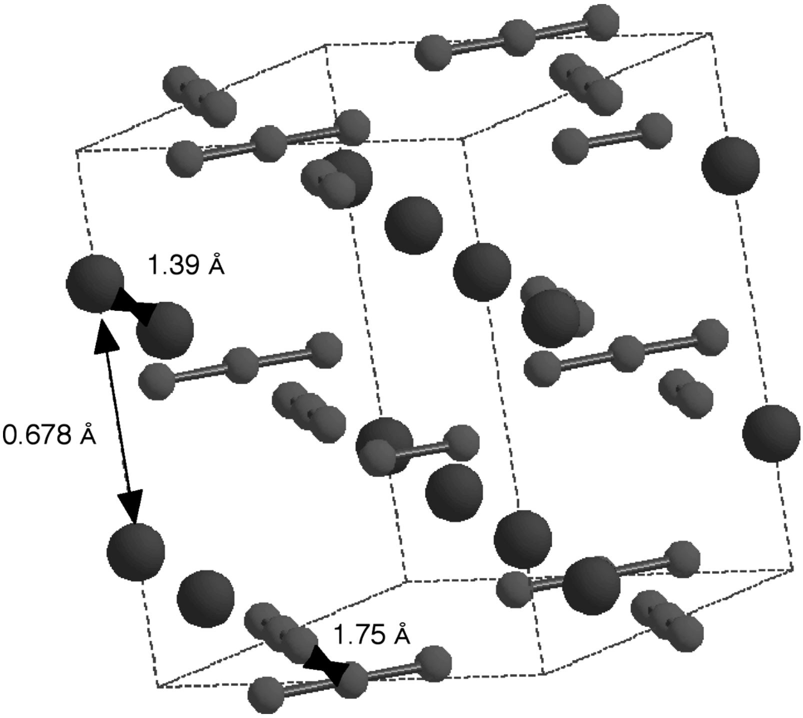


Figure 17. "Interionic" distances between nearest neighbor ions.

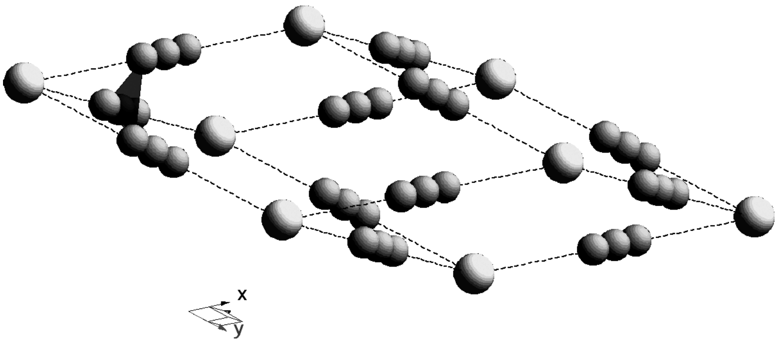


Figure 18. Crystal structure of sodium azide showing the unit cell and (111) plane located at nearest neighbor N^- ions.

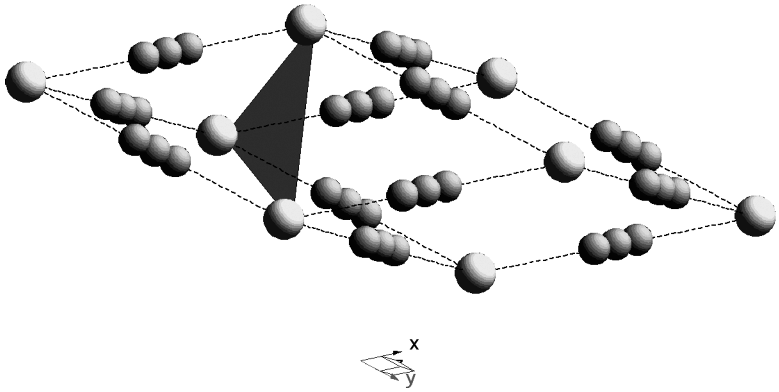


Figure 19. Unit cell of sodium azide with (111) plane located at nearest neighbor Na^+ ions.

could excite only a few neighboring molecules. Garner [29] instead argued that the velocity of detonation exceeds that of sound and traverses each molecular layer of an explosive in

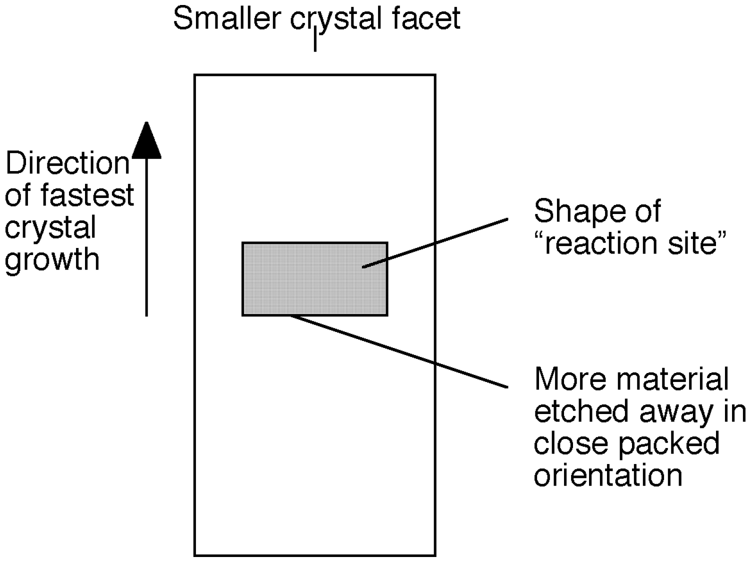


Figure 20. Formation of "reaction site" on ADN.

$\sim 10^{-13}$ s. Since the molecular reaction time for unimolecular processes is 10^{-11} to 10^{-12} s, the wave of chemical reaction was considered to have a thickness of about 10, [16] that is, a few energetic molecules up to 100 molecules. Furthermore Garner studied the probability of explosion of lead azide near its decomposition temperature and found that the very small and unpredictable variations in temperature and time that separate a detonation from a no-detonation can be explained in terms of the formation of detonation nuclei containing a few energetic molecules. In fact, Muraour [15] extended this statistical argument to all explosives, arriving at the generalized conclusion that the probabilistic nature of energetic material initiation must be due to the fact that the initiation reaction commences or starts at single points where the simultaneous decomposition of several adjacent molecules is needed. With these views in mind, one may understand why Bowden and Singh's [6] experiments bombarding explosives with fission products did not result in explosions but only local transformations in the crystals. Thus the velocity, density, and cross section of the projectiles were insufficient to excite neighboring nuclei of decomposition or "initiation sites" in a time commensurate with the development of an explosion reaction.

The "metastable intermolecular trigger" reaction mechanism is a physiochemical atomistic view of the mechanics or mechanism, which can trigger the simultaneous decomposition of adjacent molecules. Such a mechanism readily can explain the detonation velocities in energetic materials as well as a number of energetic phenomena inexplicable by the classical "hot spot" theory alone, such as the explosion of ozone during its cooling or liquefaction to form oxygen, the spontaneous detonation of crystals of lead azide as they grow in solution, and the application of gas pressure to 300 atm on nitrogen iodide, which causes its spontaneous detonation [13].

Finally, the sensitivity to initiation of different polymorphic forms of the same energetic material is known to differ, as can be seen for α, β, δ, and γ HMX. Similarly single crystals of energetic materials such as PETN and nitromethane show a shock initiation sensitivity anisotropy. Again these phenomena have

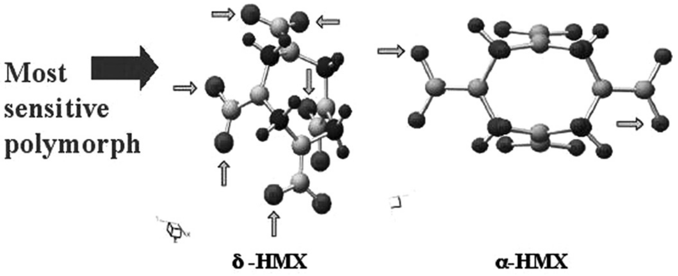


Figure 21. Difference in impact sensitivity between δ and α HMX due to "intermolecular trigger" reaction. 6 out of 8, O atoms in molecule are already ideally configured to form H_2O molecules.

been explained in terms of the "metastable intermolecular trigger" reaction mechanism [13]. When the polymorphs of HMX are studied in detail, one finds that the most sensitive polymorph or the δ form has six out of eight of its oxygen atoms in the HMX molecule already configured with respect to the surrounding hydrogen atoms in positions and angular relations to form water molecules, which is depicted in Figure 21 [13]. In fact, water is one of the main reaction products of the decomposition of HMX and other organic energetic materials. When one compares this with α HMX, which has a similar density to the δ form, one finds that only two out of eight of its oxygen atoms are configured to form water molecules. Such an analysis and understanding thus can form a foundation to a mesoscopic approach to energetic material sensitivity, which may render possible in the near future tailoring of the energetic materials in a way that the "trigger reactions" are hindered until a higher threshold is achieved. Thus while maintaining the required performance properties, an increase in the insensitivity and safety of the energetic materials may be achieved.

Acknowledgments

Many thanks to ONR for former support of this work. Special thanks and gratitude to Dr. Richard Miller, retired ONR.

Thanks go to Dr. Jagdish Sharma for his atomic force microscopy and many years of close collaboration. Finally, many thanks to the Cavendish Laboratory, University of Cambridge.

References

[1] Bowden, F. P., M. F. R. Mulcahy, R. G. Vines, and A. Yoffe. 1947. *Proc. Roy. Soc., A*, 188: 291.

[2] Bowden, F. P., M. F. R. Mulcahy, R. G. Vines, and A. Yoffe. 1947. *Proc. Roy. Soc., A*, 188: 311.

[3] Bowden, F. P., M. A. Stone, and G. K. Tudor. 1947. *Proc. Roy. Soc., A*, 188: 329.

[4] Bowden, F. P. and O. A. Gurton. 1949. *Proc. Roy. Soc., A*, 198: 30.

[5] Bowden, F. P. and K. E. W. Ridler. 1936. *Proc. Roy. Soc., A*, 154: 640.

[6] Bowden, F. P. and K. Singh. 1954. *Proc. Roy. Soc., A*, 227: 22.

[7] Field, J. E. 1992. *Acc. Chem. Res.*, 25: 489.

[8] Rideal, E. K. and A. J. B. Robertson. 1948. *Proc. Roy. Soc., A*, 195: 135.

[9] van't Hoff, J. H. 1884. Etudes de Dynamique Chimique published by Lepizig: Geast & Portig, 1985 for book series "Ostwalds Klassiker der exaten Wissenschaften."

[10] Frank-Kamenestki, D. A. 1939. *Acta Phys.-Chim.*, Russia, 10: 365.

[11] Rice, O. K. 1940. *J. Chem. Phys.*, 8: 727.

[12] Dainton, F. S. 1942. *Trans. Faraday Soc.*, 38: 227.

[13] Ramaswamy, A. L. 2001. *J. Energ. Mat.*, 19: 195.

[14] Von Kallman, H. and W. Shrankler. 1933. *Die Naturwissenschaften*, 21/23: 379.

[15] Muraour, H. 1933. *Chimie et Industrie*, 30: 39.

[16] Garner, W. E. and A. S. Gomm. 1931. *J. Chem. Soc. Aug.*, 2123.

[17] Garner, W. E. and C. H. Moon. 1933. *J. Chem. Soc.*, 1398.

[18] Walker, R. F., N. Gane, and F. P. Bowden. 1966. *Proc. Roy. Soc., A*, 294: 417.

[19] Bowden, F. P. and H. T. Williams. 1951. *Proc. Roy. Soc., A*, 208: 176.

[20] Evans, B. L. and A. D. Yoffe. 1959. *Nature*, 183: 1241.

[21] Boggs, T. L. and K. J. Kraeutle. 1969. *Comb. Sci. & Tech.*, 1: 75.

[22] Herley, P. J., P. W. M. Jacobs, and P. W. Levy. 1970. *Proc. Roy. Soc., A*, 318: 197.

[23] Ramaswamy, A. L. 1998. *Proc. 11th Int. Det. Symp.*, Colorado, Aug., p. 412.

[24] Ramaswamy, A. L. 2001. In L. DeLuca and K. Kuo (eds.), *Combustion of Energetic Materials*, Begell House Inc., New York (2002).

[25] Ramaswamy, A. L. 2000. *J. Ener. Mat.*, 18: 39.

[26] Ramaswamy, A. L. and J. E. Field. 1996. *J. Appl. Phys.*, 79: 3842.

[27] Ramaswamy, A. L. 1993. Ph.D. Thesis, Cambridge University.

[28] Ramaswamy, A. L., H. Shin, R. W. Armstrong, C. H. Lee, and J. Sharma. 1996. *J. Mat. Sci.*, 31: 6035.

[29] Garner, W. E. 1938. *Trans. Faraday Soc.*, 34: 985, 1008.