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

On the Difference in Impact Sensitivity of Beta and Delta HMX

Blaine W. Asay; Bryan F. Henson; Laura B. Smilowitz; P. M. Dickson

Online publication date: 18 June 2010

To cite this Article Asay, Blaine W. , Henson, Bryan F. , Smilowitz, Laura B. and Dickson, P. M.(2003) 'On the Difference in Impact Sensitivity of Beta and Delta HMX', Journal of Energetic Materials, 21: 4, 223 — 235
To link to this Article: DOI: 10.1080/713770434
URL: http://dx.doi.org/10.1080/713770434

Energetic Materials, 21: 223–235, 2003

ISSN: 0737-0652 print
DOI: 10.1080/07370650390274548

Taylor & Francis
Taylor & Francis Group

On the Difference in Impact Sensitivity of Beta and Delta HMX

BLAINE W. ASAY
BRYAN F. HENSON
LAURA B. SMILOWITZ
P. M. DICKSON

Los Alamos National Laboratory,
Los Alamos, NM, USA

The beta-to-delta phase transition in HMX has been implicated as the primary reason behind the increased sensitivity of the explosive as it is heated. Both physical and chemical changes accompany the transition, but no study has conclusively shown which specific change, or set of changes, is responsible. We present evidence that shows that the mechanical differences, in and of themselves, do not result in increased sensitivity to shock compression of HMX.

Keywords: HMX, polymorphs, impact sensitivity, phase transition

Introduction

The organic nitramine molecule octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) is an energetic material used as a crystalline high explosive that has been studied for many years. It exists in three distinct crystalline polymorphs and one hydrate; alpha, beta, delta, and gamma. Each form is characterized by different physical and chemical behavior. The beta and delta forms are of particular interest because the former is the polymorph that is used in typical formulations, and delta is the form that is observed to result upon heating of beta. Along with a large difference in density (∼7%), differences in

Address correspondence to B. W. Asay, Los Alamos National Laboratory, Los Alamos, NM 87545, USA. E-mail: bwa@lanl.gov

impact sensitivity between the two polymorphs have also been reported. This has potential implications for safety when dealing with material that has been heated or damaged in some way. Both the physical and chemical differences between the polymorphs have been invoked as explanations for the differences in response. We report on experiments and analysis that help to elucidate the answer to this question.

Background

Phase Change

When beta HMX is heated at rates from 0.05 to 10 °C/s the conversion to delta is obtained at temperatures from 158 to 190 °C. Beta and delta are the only stable forms in the regimes that we will be discussing in this report. The crystal structure of these materials has received a great deal of study (see, e.g., [1,2]), and the kinetics of the transition have been extensively examined (see, e.g., [3–6]). The precise temperature at which conversion occurs is dependent on both the heating rate and the environment. For example, in the presence of plasticizer commonly used in plastic bonded formulations, conversion occurs at lower temperatures than if the HMX is in its pristine state [6]. The environment also determines whether or not the explosive will remain in the converted state upon cooling or if it will revert to beta.

Upon heating of beta HMX, anisotropic volumetric thermal expansion occurs (0.0131%/K). Upon the transition from beta to delta, additional expansion occurs as the density changes from 1.90 to 1.79 g/cc. This large volumetric expansion creates crystalline damage in the form of voids and cracks, providing inclusions and surfaces for the formation of hot spots, shear planes, and other structures that promote shock initiation.

The polymorphic phase transition also induces molecular and lattice changes. Beta HMX is in the chair form, while delta is in the boat form. The delta lattice has a more open morphology than the beta form [8]. The different configurations possess different thermochemical properties as well as different morphologies. To cite two examples, the heat of solution in nitromethane for beta HMX is 4.4 kcal/mole, while for the delta form it is 1.5 kcal/mole [9], and the melting point of beta HMX is 245.5 °C, while that for delta is 280.5 °C [10]. Sublimation and vaporization quantities have been calculated and compared as well (cf. [11]). All of these behaviors ultimately derive from the free energy change that results on going from beta to delta.

The enthalpy of the phase transition is 30 J/g. This endotherm can have a pronounced effect on the thermal history of the surrounding material. For example, during a slow ramp, once the transition begins, the temperature can fall by 10 ℃, affecting subsequent heat transfer.

These changes are not only of academic interest. The physical and chemical differences can have a profound influence on the material behavior and reactivity during heating because explosive response is a function of both the chemical and physical state of the explosive, as will be shown.

Drop-Weight Impact Test

Sensitivity, as used to gauge the reactivity of explosive in a given situation, is a very ill-defined term, but its use is ubiquitous because of the need to handle and use reactive materials properly. There are literally hundreds of tests that are performed to gauge HE behavior, and none of them are all-inclusive or produce data that are totally predictive. One (incomplete) measure of explosive sensitivity is the drop-weight impact test [12]. This test has formed the basis for many safety-related judgments and is nearly universally used as a qualitative measure of sensitivity. It consists of a large weight that falls and strikes a small sample of explosive. The weight is dropped from a range of heights, and, using the Bruceton up-and-down method, a height is determined (the "50% height") at which, statistically, 50% of the time the example reacts violently and 50% of the time it does not. The impactor can either be smooth ("Type 12B") or be coated with grit ("Type 12A"). The choice of impactor can have a significant effect on both the absolute magnitude of the drop height as well as the relative ordering of sensitivity between explosives.

The precise mechanism of ignition during these tests is not well understood and depends on many equipment-dependent factors. While sensitivity rankings on a single machine are typically reproducible, data gathered on one machine usually do not match or correspond exactly to those acquired on other machines. However, it has been a useful device for placing explosives in rank order of their sensitivity to this particular type of ignition. And in general it produces an ordering that makes sense (e.g., PETN>HMX>TNT).

Impact Sensitivity of Beta and Delta HMX

The different polymorphs of HMX received their first detailed study in the early 1940s as it was discovered that HMX was a major impurity

in the manufacture of RDX. The difference in sensitivity of the polymorphs was investigated as the cause of differences in sensitivity between various batches of RDX being produced [9]. Much of this early work was difficult to conduct because of the lack of understanding of how to produce pure forms of each polymorph and an incomplete knowledge of their respective stability. Cady and Smith [13] compiled and analyzed the earlier studies, resolving some of the contradictions, and they also completed further studies of their own. They found that in every sample tested the delta HMX was more sensitive; in some cases by a considerable margin. Compared to the work of others that they compiled and reviewed, they state that their findings were in agreement with the earlier studies, and that the sensitivity of delta HMX is independent of the crystal size and the method by which it was prepared. They found that the delta form was more sensitive when tested without grit on the drop weight (i.e., in the Type 12B machine). Increases in sensitivity of from ∼30–60% (as measured by reduced drop height) were recorded depending on the impactor and the material purity. The 50% height for the delta form was the same order as that found for PETN, the most sensitive of the commercial secondary explosives.

Cady [10] later reported that although some data, particularly in the United Kingdom, had been interpreted to mean that delta HMX was nearly as dangerous as lead azide, they concluded that this was not the case. The erroneous results could be properly understood once the differences in testing methods and equipment were taken into account. In further work Cady suggests that because of the differences in melting point (245.5 and 280.5 °C for beta and delta, respectively), in samples with mixed polymorphic content, the delta acts as a higher melting grit and thus sensitizes the sample to impact.

Herrmann et al. [7] report experiments that showed changes in sensitivity of up to 80% (as measured by impact energy). Further they state that the delta sensitivity reaches that of primary explosives. They also report that the friction sensitivity is only slightly greater for delta than for beta. Combustion rate measurements were conducted and showed that delta HMX burns approximately twice as fast as does the beta form.

We recently conducted a study in which HMX crystals were converted to the delta form and then tested on the 12A impact machine. A reduction in drop height of 22% was measured, with the delta HMX having a drop height comparable to PETN [14].

In summary, it has been well established by numerous investigators over the years that the sensitivity of HMX to drop-weight impact increases upon phase conversion. The absolute magnitude of this change is in some doubt, but our experience is consistent with assertions that the conversion leaves the material in a state of sensitivity comparable to PETN, a secondary explosive. This does not mean, however, that the change is of no interest. Quite the contrary, there are many reasons why a more complete understanding of this behavior is desired. Primary among these is the fact that it is believed that the endothermicity of this phase transition plays a major role in its combustion and detonation behavior.

Experiments Conducted to Suggest the Origin of the Difference in Sensitivity

Mechanical vs. Chemical Effects

A difference in behavior upon impact between beta and delta HMX has been reported. To this point no conclusive answer has been given as to why this difference exists. The reason for the change can be either physical (mechanical) or chemical in nature. It is well known that materials with voids are more easily ignited by shocks than more homogeneous materials (e.g., see [15]). Weeks et al. [16] invoke this reason for the increased sensitivity because a great deal of mechanical damage is done to the crystals during heating and phase transition. Kohno et al. [17] performed *ab initio* calculations to demonstrate that the differences in behavior are the result of differences in strain energy and the $N-NO_2$ bonds. However, Kohno's conclusion is problematic without further study because of the large change in the molecular structure and the changed chemical reactivity that also occurs.

It has been found that the transition from beta to delta can be reversed under the proper conditions. However, the physical damage that occurs during conversion remains during reversion. Thus, one can separately investigate the effects of mechanical damage and chemical change in the following way. Samples of PBX 9501 (95% by volume HMX in a bimodal distribution of $\sim$120 and 30 μm diameter particles formulated with Estane and a 50/50 eutectic mixture of bis(2,2-dinitropropyl) acetal and bis(2,2-dinitropropyl) formal) may be heated until the HMX is converted to the delta phase. Such a sample may also be reverted back to the beta phase. There are now

three possible states: the first is pristine PBX 9501, the second is damaged PBX 9501 (heated and then quickly cooled) with the HMX in the delta phase, and the third is damaged PBX 9501 with the HMX in the beta phase (heated and then slowly cooled). One can compare the impact response of the first and third samples where mechanical damage is the only variable. One can also compare the response of the second and third samples where the crystal morphology is the only variable. The two effects (physical and chemical) are thus isolated. We present experimental results on such samples to determine their relative importance in one particular impact regime. Rather than conducting this experiment on the drop–weight impact machine, we opted to use a gas gun with optical access to visualize the results and perhaps better understand the mechanism.

Experiments

The experiments performed consisted of observing the impact of the samples described above, in the shape of a thin right circular cylinder, onto a sapphire surface. The details of the flow and ignition mechanism subsequent to impact were observed directly by fast optical imagery and IR radiometry.

A disk of explosive (5 mm × 1 mm) was glued onto the front of a small polyethylene projectile (10 × 10 mm, right circular cylinder). This assembly was then fired down the barrel of a gas gun. In experiments reported here the gun barrel was not evacuated, and a compression heating of gases in the barrel was observed. The visible light emission from this compression was observed to precede impact and persist for approximately 2 μs in some cases.

Tests were conducted at velocities from 150 to 350 m/s and yielded a wealth of response phenomenology, which will be the topic of further publications. The results described here were observed for impact velocities between 230 and 260 m/s. We restrict ourselves to that particular velocity range for this article to be able to compare the different material responses arising from the same impact mechanism. The broader range of velocities studied result in several different ignition mechanism regimes to be described elsewhere.

Unconfined samples of PBX 9501 were heated to 172 °C at 5 °C/min and held at temperature for 1 hour, thus converting the HMX to the delta phase. The conversion to delta was directly verified by both the observed change in second harmonic generation (SHG) efficiency [18] and by Raman spectroscopy. The sample was then

reverted to beta HMX by the application of a carefully prescribed cooling curve cool at 3 °C/min to 123 °C and hold until reversion is complete [6]. The reversion to beta was again directly verified both by SHG and Raman spectroscopy.

Three representative examples, each demonstrating behavior characteristic of the material being tested, are shown. Figure 1 shows the image sequence obtained when pristine PBX 9501 containing beta HMX was impacted at 234 m/s. Note that the initiation of reaction begins first in a ring around the outside of the disk and proceeds toward the center. Figure 2 shows images after impacting PBX 9501 that had been converted to delta. The impact velocity was 254 m/s. While the initial ignition shown in frame 2 appears similar to that observed in the pure beta material in Figure 1, the remaining frames demonstrate ignition that is typified by a more global reaction that occurred throughout the volume of the sample. The reaction in the unheated sample spreads radially inward, while reaction in the heat-treated sample exhibits an ignition that appears simultaneously throughout. This may be an indication of a transition from shear ignition to shock ignition, but further study will be required to be certain. Figure 3 shows images after impact of material that had been converted to delta, and then reconverted to the beta phase. The impact velocity was 257 m/s. This ignition sequence clearly has the character of the original pristine material that was entirely beta phase. The reaction front velocities were measured for two representative tests using the pristine and reverted HMX and then fitted to a line. The precise location of the front was difficult to identify, and thus there is some scatter in the measurement. The velocity for the pristine material was 187 m/s ± 25, and for the reverted material it was 130 m/s ± 29. When these velocities are considered with the standard deviations, they are very similar.

A total of 14 experiments were conducted. Of these, 11 showed precisely the behavior explained above. The other three, although showing evidence of the trend, were not incontrovertible: that is, elements of the behavior were uncharacteristic of the explosive being tested. Differences in sample mounting and impact velocity are being investigated as a possible explanation of the differences.

Discussion

The reader is referred to Duffy and Mellor [19] for a review of drop-weight impact machines. Much has been written on the mechanisms

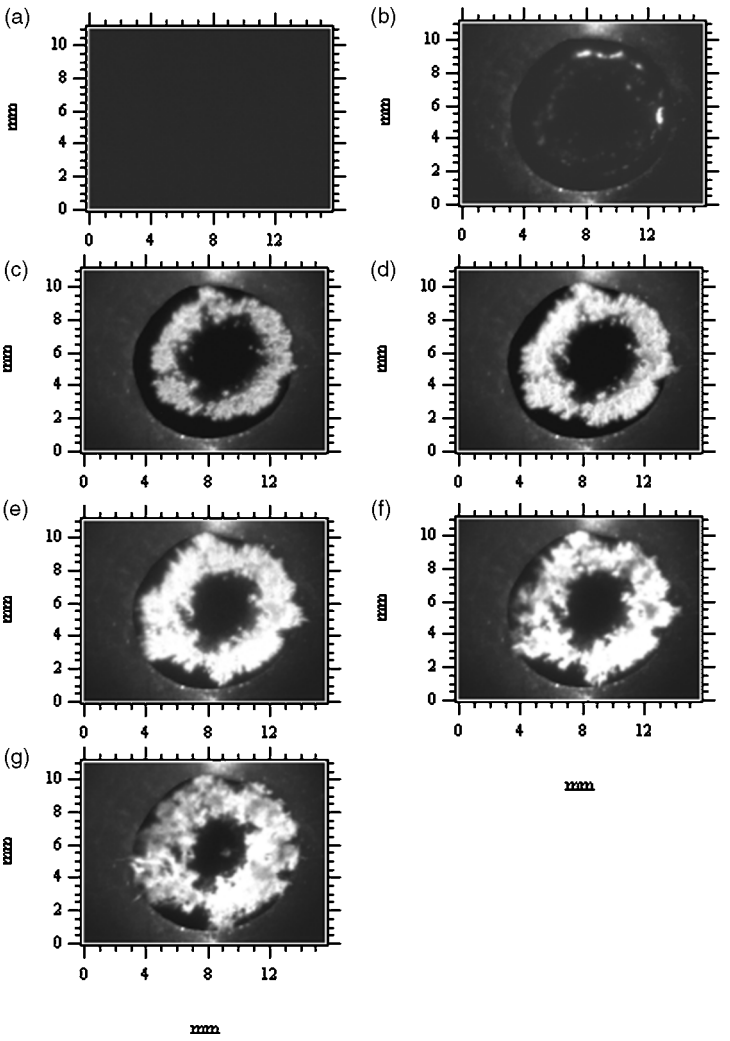

Figure 1. Image sequence obtained when pristine beta PBX 9501 was impacted at 234 m/s. Framing times were (a) 0.2, (b) 2, (c) 4, (d) 6, (e) 8, (f) 10, and (g) 12 μs.

of initiation by hot spots [15,20]. Many of these studies have used the drop-weight impact machine. They have found that major initiation mechanisms include adiabatic collapse of trapped gases, friction,

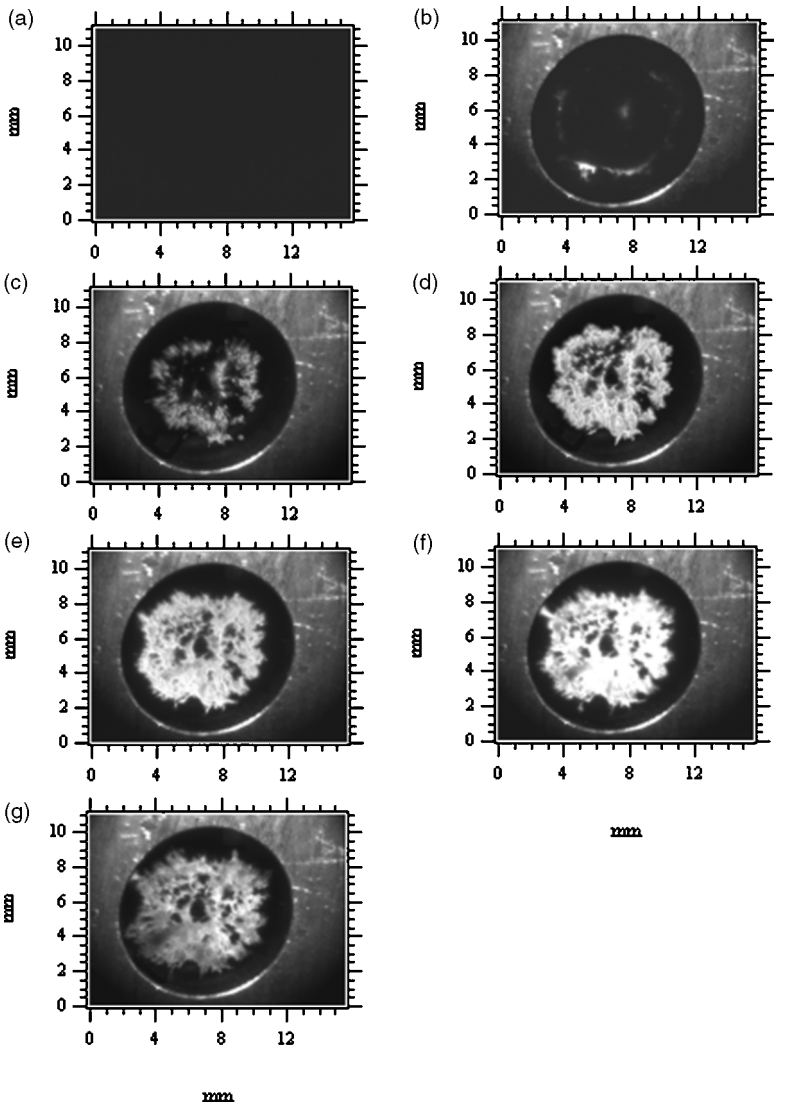

Figure 2. Image sequence obtained after impacting PBX 9501 that has been converted to delta. Impact velocity was 254 m/s. Framing times were (a) 0.2, (b) 2, (c) 4, (d) 6, (e) 8, (f) 10, and (g) 12 μs.

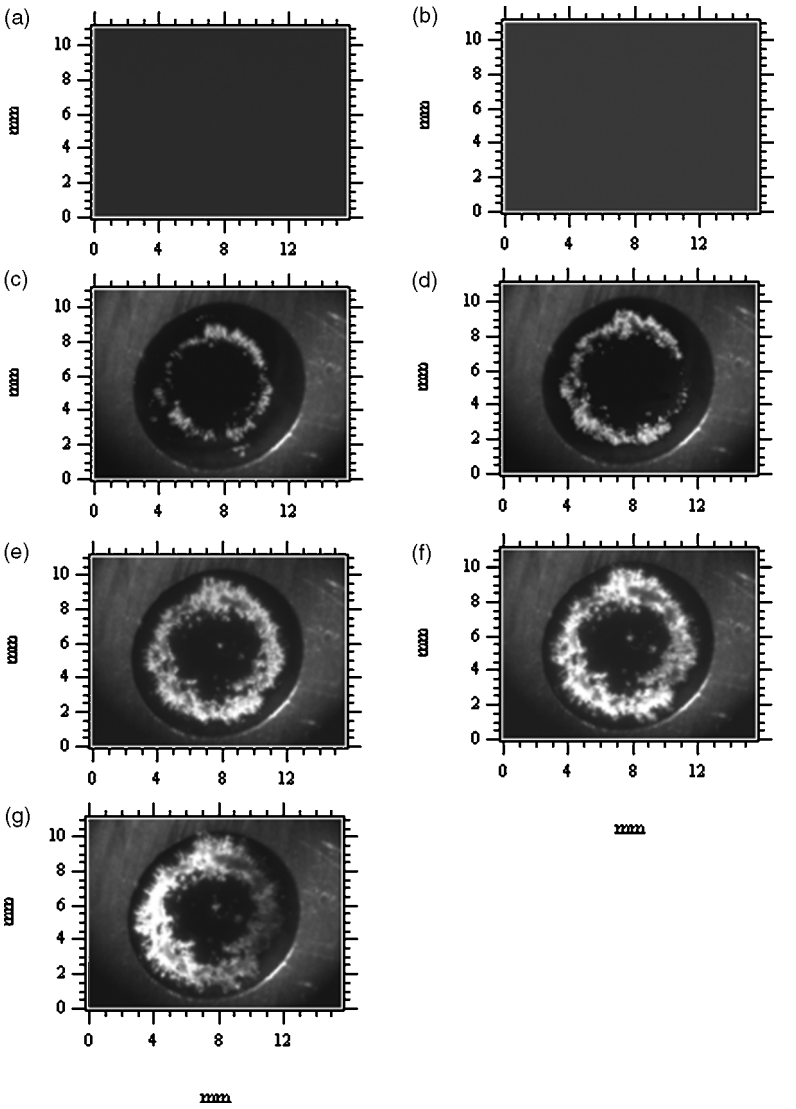

Figure 3. Image sequence obtained after impact of material that had been converted to delta, and then reconverted to the beta phase. Impact velocity was 257 m/s. Framing times were (a) 0.2, (b) 2, (c) 4, (d) 6, (e) 8, (f) 10, and (g) 12 μs.

adiabatic shear, viscous heating, and heating at crack tips, among others. Each of these mechanisms undoubtedly operates under specific conditions, and often several will be important in a given environment. It is known that the region of highest strain rate occurs at the edges of a specimen being compressed [21,22]. It appears from the data presented here that the explosives containing beta HMX always ignite in this region of high shear. The delta HMX appears to ignite spontaneously, at least within the temporal resolution of our measurements. While no absolute time after impact is available (cameras were triggered upon first light), the delta HMX appears to have ignited more quickly as well. This is consistent with a shock-induced ignition, or it may indicate that the delta HMX ignites at lower levels of shear. This is certainly in harmony with the previously cited findings of increased sensitivity of delta HMX compared to beta.

Because the observed ignition behavior of pristine and reverted beta HMX are the same, we conclude that the physical differences between samples containing beta and delta HMX are not the important factor in the increased sensitivity of the delta phase to planar impact. Both the ignition and propagation of reaction of delta occur much more rapidly than either of the other two sample types, while the physical damage of the reverted sample is the same as that for the delta sample.

Much more study is needed to quantify fully the differences in sensitivity. For example, studies subjecting the samples to pure shock or shear would help delineate the reasons for the differences in behavior. We are designing several experiments that will address such questions. The data presented in this report provide a firm basis on which to construct further work.

Acknowledgments

We wish to acknowledge numerous discussions with H. H. Cady, who has helped to illuminate the problem and has made significant suggestions. This work was supported by the high explosives science and surety programs at Los Alamos National Laboratory.

References

[1] Choi, C., and H. Boutin. 1970. A study of the crystal structure of beta-cyclotetramethylene tetranitramine by neutron diffraction. *Acta Cryst.* B26: 1235–1240.

[2] Cobbledick, R. E., and R. W. H. Small. 1974. The crystal structure of the delta form of HMX. *Acta Cryst.* B30: 1918–1922.
[3] Brill, T. B., and R. J. Karpowicz. 1982. Solid phase transition kinetics: the role of intermolecular forces in the condensed-phase decomposition of HMX. *Journal of Physical Chemistry* 86: 4260–4265.
[4] Karpowicz, R. J., and T. B. Brill. 1983. Kinetic data for solid phase transitions by Fourier transform infrared spectroscopy. *Applied Spectroscopy* 37: 79–81.
[5] Henson, B. F. et al. 2002. The beta-delta phase transition in the energetic nitramine HMX: thermodynamics. *Journal of Chemical Physics* 117: 3780–3788.
[6] Smilowitz, L. et al. 2002. The beta-delta phase transition in the energetic nitramine HMX: kinetics. *Journal of Chemical Physics* 117: 3789–3798.
[7] Herrmann, M. et al. 1992. Thermal expansion, transitions, sensitivities and burning rates of HMX. *Propellants, Explosives, Pyrotechnics* 17: 190–195.
[8] Brill, T. B., and C. O. Reese. 1980. Analysis of intra- and intermolecular interactions relating to the thermophysical behavior of alpha, beta, and delta HMX. *Journal of Physical Chemistry* 84: 1376–1380.
[9] Blomquist, A. T. 1943. The polymorphism of HMX. Office of Scientific Research and Development, 1–70.
[10] Cady, H. H. 1986. Sensitivity and Handling hazards of delta HMX Obtained by Heating PBX 9404. *17th International Annual Conference of ICT*, Karlsruhe, Germany.
[11] Lyman, J. L. et al. 2002. Thermochemical functions for gas-phase, 1,3,5, 7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), its condensed phases, and its larger reaction products. *Combustion and Flame* 130: 185–203.
[12] Gibbs, T. R., and A. Popalato. 1980. *LASL Explosive Property Data*. Berkeley: University of California Press.
[13] Cady, H. H., and L. C. Smith. 1962. Studies on the polymorphs of HMX. Los Alamos, Los Alamos National Laboratory, 1–50.
[14] Scott, P. D. 1998. Impact sensitivity testing. Los Alamos National Laboratory, Los Alamos, NM.
[15] Field, J. E. 1992. Hot spot ignition mechanisms for explosives. *Acc. Chem. Res.* 25: 489–496.
[16] Weeks, B. L. et al. 2002. Monitoring high-temperature solid-solid phase transition of HMX with atom microscope. *Ultramicroscopy* 93: 19–23.
[17] Kohno, Y. et al. 1994. A relationship between the impact sensitivity and the electronic structures for the unique N−N bond in the HMX polymorphs. *Combustion and Flame* 96: 343–350.
[18] Henson, B. F. et al. 1999. Dynamic measurement of the HMX b-d phase transition by second harmonic generation. *Phys. Rev. Lett.* 82: 1213–1216.

[19] Duffy, K. P., and A. M. Mellor. 1994. *Journal of Propulsion and Power* 9: 337–344.
[20] Field, J. E. et al. 1992. Hot-spot ignition mechanisms for explosives and propellants. *Phil. Trans. R. Soc. Lond. A* 339: 269–283.
[21] Field, J. E. et al. 1985. Mechanical properties of PBX's and their behavior during drop-weight impact. *Proceedings of the 8th Symposium (International) on Detonation*, Albuquerque, NM.
[22] Metzner, A. P., and C. S. Coffey. 1993. *Hot spot initiation of plastic-bonded explosives during the rapid flow phase of the drop weight impact test. 10th International Detonation Symposium*. Boston, MA.