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# **Time Resolved Phase Transitions via Dynamic Transmission Electron Microscopy**

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### **Auspices Statement**

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**FY06 LDRD Final Report**  
**Time Resolved Phase Transitions via Dynamic**  
**Transmission Electron Microscopy (DTEM)**  
**LDRD Project Tracking Code: 06-ERD-007**  
**Bryan W. Reed, Principal Investigator**

**Abstract**

The Dynamic Transmission Electron Microscope (DTEM) project is developing an *in situ* electron microscope with nanometer- and nanosecond-scale resolution for the study of rapid laser-driven processes in materials. We report on the results obtained in a year-long LDRD-supported effort to develop DTEM techniques and results for phase transitions in molecular crystals, reactive multilayer foils, and melting and resolidification of bismuth. We report the first *in situ* TEM observation of the HMX  $\beta$ - $\delta$  phase transformation in sub- $\mu\text{m}$  crystals, computational results suggesting the importance of voids and free surfaces in the HMX transformation kinetics, and the first electron diffraction patterns of intermediate states in fast multilayer foil reactions. This project developed techniques which are applicable to many materials systems and will continue to be employed within the larger DTEM effort.

**Introduction/Background**

Phase transitions are essential and ubiquitous in physics and materials science, but often the phenomena are on time and length scales that are difficult to access experimentally. While pulsed X-ray and femtosecond laser techniques can obtain spectroscopic and diffraction information, in comparison to electron microscopy they are very limited in their spatial resolution and in their ability to form real-space images.<sup>1</sup> *In situ* experiments in the transmission electron microscope (TEM) can obtain very high-resolution real-space images in addition to spectroscopic and diffraction information, but the time resolution in conventional TEM (of order 30 ms) is orders of magnitude too slow to capture most of the interesting processes associated with phase transitions in materials. To investigate these processes on their own scales and to connect directly to atomic-scale simulations, it would be ideal to have an instrument that can simultaneously obtain nanometer-scale spatial and nanosecond-scale temporal resolution.

In response to this need, Lawrence Livermore National Laboratory (LLNL) launched an effort to build a Dynamic Transmission Electron Microscope (DTEM) (Figure 1) on the model of work done since the 1980's in Professor Oleg Bostanjoglo's group at the Technical University of Berlin.<sup>2</sup> The LLNL effort (which began with a collaboration with Professor Bostanjoglo) applied the insights and developments from the Berlin efforts and incorporated more modern technology in electron optics, lasers, and detectors. This effort has been a success, yielding an instrument capable of obtaining electron diffraction patterns and images in single 10 ns to 30 ns long pulses containing millions of electrons.<sup>3,4</sup>

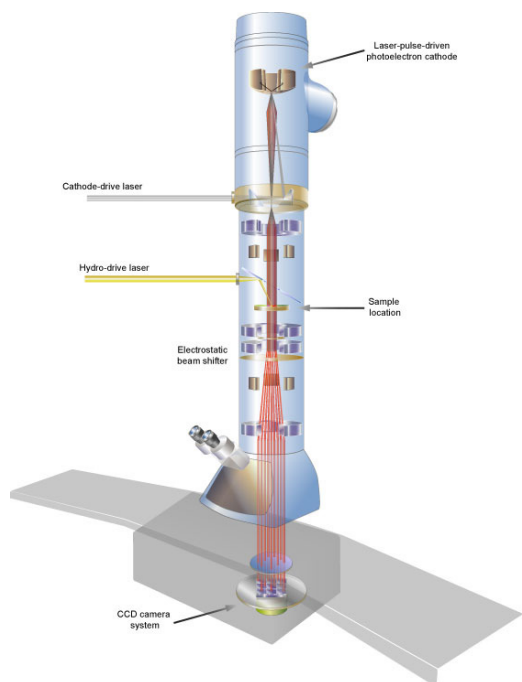


Figure 1. The DTEM adds two lasers to a standard TEM to turn it into a nanosecond pump-probe instrument for *in situ* experiments.

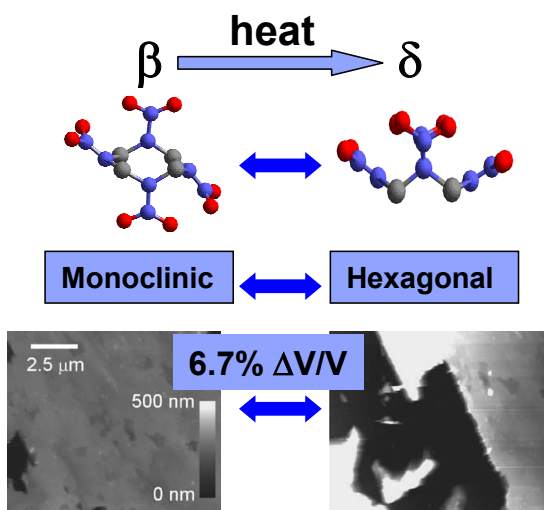


Figure 2. The  $\beta$ - $\delta$  crystalline transformation in HMX involves a change in molecular conformation, crystal symmetry, and microstructure.

Scientific research has been performed in parallel with the instrument development in order to produce the preliminary results and techniques required to continually push the DTEM project to the next level. This report describes the subset of this research that was performed over a 12-month period with the support of the Laboratory Directed Research and Development (LDRD) program.

## Research Activities

The LDRD-supported work was in three areas: The  $\beta$ - $\delta$  crystalline phase transformation in the molecular high explosive HMX, propagating reaction fronts in reactive multilayer foils (RMLF), and melting and resolidification in bismuth.

HMX is a crystalline, molecular high explosive of significant programmatic interest, whose  $\beta$ - $\delta$  phase transition changes the crystal lattice, the molecular conformation, and the microstructure (via a 7% volumetric change), with complex and poorly understood nucleation and growth kinetics and mechanistic paths<sup>5-9</sup> (Figure 2). It is therefore inherently interesting from the standpoint of fundamental physics (the role of multiple length scales in phase transitions being a hot topic that has proven difficult to experimentally access). Such kinetically-controlled transitions are ubiquitous and fundamental in chemistry and biochemistry, with related materials ranging from photoactive ferroelectrics to highly coordinated biomolecules. The goals of the LDRD-supported research were to unravel the complicated behavior of this material through DTEM experiments and

simulations, and also to develop broadly-applicable techniques for using the DTEM to study complex processes in many kinds of radiation-sensitive organic materials.

The RMLFs are materials, composed of alternating thin layers of metal, which can sustain a rapidly-propagating, highly exothermic, diffusion-controlled reaction (Figure 3). DTEM investigations enable us to examine the reaction zone *in situ*,

providing information about the structure and morphology of metastable intermediate phases and the melting of reactants and/or products. This information is essential for modeling foil reactions and designing foils for specific applications such as joining and ignition.

The third component was to be an investigation of laser-driven rapid melting and resolidification in bismuth, using both temperature and pressure to drive the transformations. It was decided that this work was to be deferred until the second and third years of the project, apart from some preliminary proof-of-principle experiments for the driving of lateral shock waves in bismuth thin films using short-pulse lasers, in the manner demonstrated by our close collaborator Steven Yalisove (unpublished work). The experiments were performed, demonstrating microstructural modification in the vicinity of the laser spot but not yet conclusively showing the presence of a shock wave. We regard the development of a laser shock drive in the DTEM as being of high importance, and we are planning to resume such tests when opportunities arise.

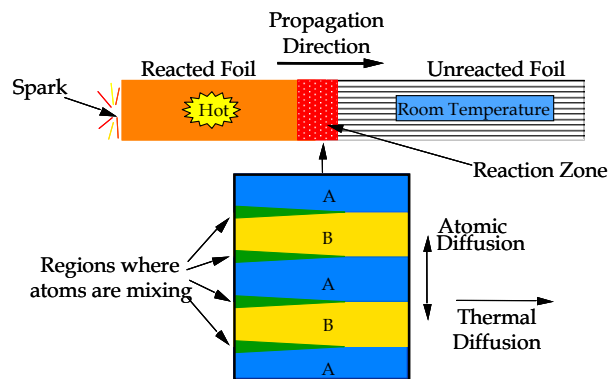


Figure 3. The reactive multilayer foils consist of alternating layers (a few tens of nm thick) of metal which, when sparked, will rapidly interdiffuse. This releases heat which drives further interdiffusion in a front that propagates at a few m/s.

## Results/Technical Outcome

The project (which was funded for one year) was initially scoped and paced to be a three-year effort, with the first year to be spent developing techniques, laying groundwork, and generating preliminary results concurrently with the evolution of the DTEM hardware itself.

We achieved the ability to drive the desired transformation in HMX, overcoming numerous obstacles and allowing us to contradict a literature claim<sup>10</sup> that the  $\beta$ - $\delta$  transformation cannot be driven in vacuum. This result was presented at the 2006 International Microscopy Conference in Sapporo, Japan. The essential problem is that this material is complex and unstable, so that numerous undesired processes can compete with the desired transformation. These processes include photochemistry, sublimation, radiation damage, and amorphization.

We minimized photochemistry by choosing the appropriate sample drive laser wavelength. The difficulty is that HMX is largely transparent to visible light, while the ultraviolet light which it strongly absorbs will tend to break bonds. This would complicate the experiment, since we are primarily interested in the temperature-driven phase transformations of intact HMX molecules. Through a combination of measurements and computations of the  $\beta$ -HMX optical absorption spectrum, we determined that the optimum drive wavelength was  $\sim 350$  nm, which is in the low-energy tails of an ultraviolet resonant absorption peak. Thus the sample could absorb significant amounts of laser energy at this wavelength without undergoing excessive photochemistry. The DTEM drive laser is a Nd:YAG type operating at a wavelength of 1064 nm. The optimal HMX drive was produced by frequency-tripling this to 355 nm.

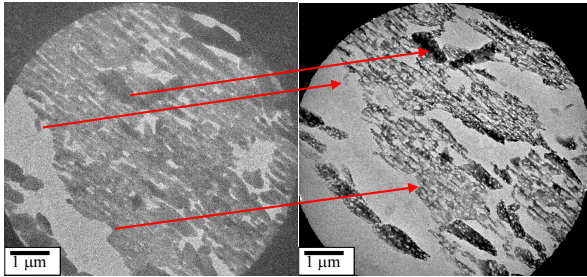


Figure 4. Low-dose images of HMX acquired with conventional *in situ* TEM. (Left) Image of undamaged  $\beta$ -HMX. (Right) Image of HMX after heating and modest electron radiation dose. Arrows show corresponding features on the sample, which moved during the process.

temperature range where the desired transformation is rapid. The material visibly broke apart, developed pock marks on grains of initially uniform appearance, and gradually vanished, leaving an amorphous residue. This behavior was highly repeatable. At no point in the conventional *in situ* experiments did a diffraction pattern appear other than those consistent with a mix of  $\beta$ -HMX and amorphous material. It is possible that similar phenomena account for previous reported failures to drive the transformation in vacuum.

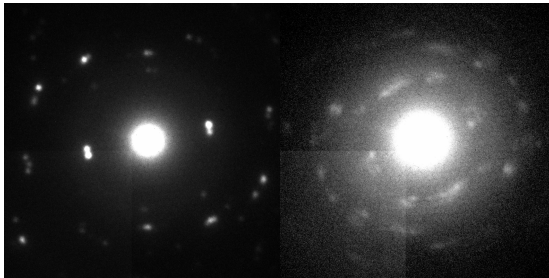


Figure 5. Diffraction patterns showing the successful driving of the  $\beta$ - $\delta$  HMX transformation in the DTEM. Left: Coarse-grained  $\beta$ -HMX before application of a laser pulse. Right: Fine-grained  $\delta$ -HMX after the laser pulse (increased digital contrast settings).

Second, by preheating the entire material, diffusive heat loss from the treated region was slowed, allowing us to control the amount of time the sample stayed above the transformation temperature. It was the combination of all of these things—the presence of the fast laser heating, at an optimized frequency, combined with a conventional heating holder—that allowed us to perform the first successful driving of this transformation in a TEM sample.

The crystallites of the product  $\delta$ -HMX phase were much smaller than the sub- $\mu\text{m}$   $\beta$ -HMX crystals from which they grew. The two diffraction patterns in Figure 5 were taken under identical electron optical conditions, but the contrast in the  $\delta$ -HMX pattern had to be digitally increased in order to clearly show the pattern. The  $\beta$ -HMX pattern shows only a few very bright, sharp spots, indicating that only a few crystal orientations are present in the area selected for diffraction. The  $\delta$ -HMX pattern shows spots that are much weaker and far more numerous. This shows that the

We determined that it was extremely difficult, if not impossible, to observe the  $\beta$ - $\delta$  transformation using conventional *in situ* TEM techniques (Figure 4). This is because conventional heating is performed with a resistive heater that operates on a time scale of seconds to minutes, and on this time scale the sub- $\mu\text{m}$  HMX particles were observed to sublime and possibly decompose and amorphize (probably with some assistance from the electron beam, which even in low-dose conditions still causes significant radiation damage) before they could reach the

In contrast, efforts to drive the transformation in the DTEM were successful (Figure 5). The sample temperature history was controlled with a combination of slow preheating using a conventional heating stage and rapid heating to a point significantly above the transformation temperature using the DTEM's 10 ns pulsed drive laser. The preheat accomplished two things. First, it let us minimize the amount of heating performed by the sample drive laser, thus keeping any photochemistry to a minimum.

resulting  $\delta$ -HMX is nanocrystalline, and also that each  $\beta$ -HMX crystal can nucleate multiple  $\delta$ -HMX crystals. Under the conditions of the experiment, then, the process appears to be growth-limited rather than nucleation-limited. This also tells us that considerably more signal is required to identify  $\delta$ -HMX than  $\beta$ -HMX in the TEM.

In order to investigate the nucleation and growth of  $\delta$ -HMX from an initial  $\beta$ -phase, we performed extensive classical molecular dynamics (MD) simulations using an accurate force field<sup>11</sup> specifically developed to reproduce the cohesive energies and densities for both the  $\beta$ - and  $\delta$ -phases of HMX. We found that even at temperatures

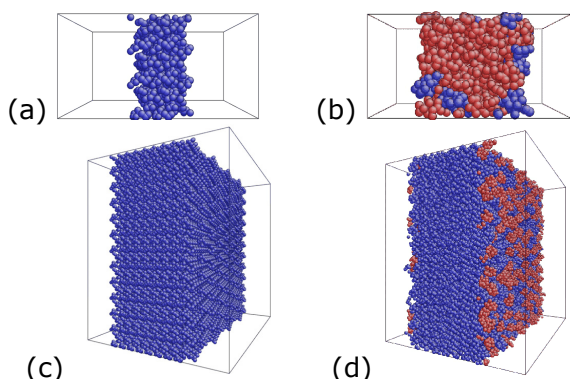


Figure 6. Molecular Dynamics simulations at 550K on initially  $\beta$ -HMX slabs with exposed (001) surface. A thinner slab (a) readily converts into amorphous  $\delta$ -HMX (b) within 0.6 ns, while a thicker slab (c) remains stable even after 2.4 ns with only a few surface molecules dynamically transforming between chair and boat conformations (d).

as high as 550K the  $\beta \rightarrow \delta$  conversion occurs only in the presence of significant defect-density involving surfaces, vacancies, voids, pre-existing  $\delta$ -nuclei, etc., which act as nucleating centers. Although such simulations provide useful atomic-level insights, one needs to be aware that the conversion of  $\beta \rightarrow \delta$  in reality occurs on a time-scale much longer than would be possible to simulate with standard MD. Even so, the simulation results (Figure 6) have helped us to construct a more complete picture of what is probably happening in the experiment. Most likely, the surface molecules in our sub- $\mu\text{m}$  crystals are constantly fluctuating between the  $\beta$  and  $\delta$  conformations while the interior

molecules are far less active. Occasionally, on a time scale of some nanoseconds that probably varies with the local thickness of material, one of these fluctuations will take hold, forming a critical nucleus of  $\delta$  material that eventually grows into a nanocrystal. The results suggest that this process can happen independently in many different sites on the  $\beta$ -HMX crystal's surface.

A second aspect we analyzed computationally was the rate of sublimation of  $\beta$ -HMX as a function of temperature. For such estimates, a common approximation employed for monatomic systems is that a surface atom (at a kink site) desorbs with a frequency  $\nu \cdot \exp(-\Delta E/k_B T)$ , where  $\Delta E$  is the activation barrier for an atom at a kink site to desorb, and  $\nu$  is an effective vibrational frequency, typically chosen around  $10^{12} \text{ sec}^{-1}$ . We found that the above approximation completely breaks down for molecular systems like HMX, unless one assumes a large  $\nu$  in the neighborhood of  $10^{14} \text{ sec}^{-1}$ . A proper treatment involves a full partition function of the molecule in the gas phase as well as in the crystal, including full rotational and vibrational contributions. This is found to reproduce the equilibrium vapor pressure over a wide range of temperature. It can also reproduce the measured rates of sublimation, provided further experimental details like particle morphology, the presence of a boundary layer, or the flow field of a carrier gas are taken into account. A journal article describing this correction is in review. We also plan to submit a combined theoretical/experimental journal paper on the competition between sublimation and transformation.

We also demonstrated the ability to perform time-resolved diffraction measurements on the HMX crystals, consisting of diffraction patterns taken before, during, and after the laser-induced heat pulse (Figure 7). The low signal levels and inherent complexity of the HMX diffraction patterns has made quantitative analysis difficult, and we also found that the repeatability of the sample drive was somewhat low. We saw that in many cases the diffraction pattern practically disappeared in the "during" shot. Considering the relative signal levels in the diffraction patterns in Figure 5, and the low signal levels available in the DTEM's time-resolved operating mode at the time the experiments were done, the apparent disappearance of the diffraction pattern is consistent with the formation of the  $\delta$  phase; however it is also consistent with the simple destruction of the sample, which we must take as the default hypothesis. To observe the  $\delta$  phase in a time resolved experiment, we will have to increase our signal levels. Further, more work will be required to understand how to drive the  $\beta$ - $\delta$  transformation with high repeatability.

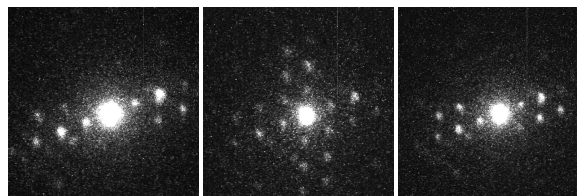


Figure 7. Pulsed diffraction patterns obtained on HMX in the DTEM. (Left) Before, (Middle) during (1  $\mu$ s after the laser hit), and (Right) after the laser-induced heat pulse. On this particular shot, the sample region rotated slightly upon heating but remained a single crystal of  $\beta$ -HMX throughout.

The current pace of DTEM development is such that the feasibility of this experiment will be much greater in the near future. Since the close of this LDRD project, the work of Thomas LaGrange and others within the larger DTEM development effort has substantially improved the achievable signal-to-noise levels by (1) Acquiring a more sensitive camera, (2) Stabilizing and improving the beam quality of the cathode laser, and (3) Better optimizing the configuration of the electron optical column. Ongoing work on the laser systems and the electron optical design is expected to improve the signal levels still further.

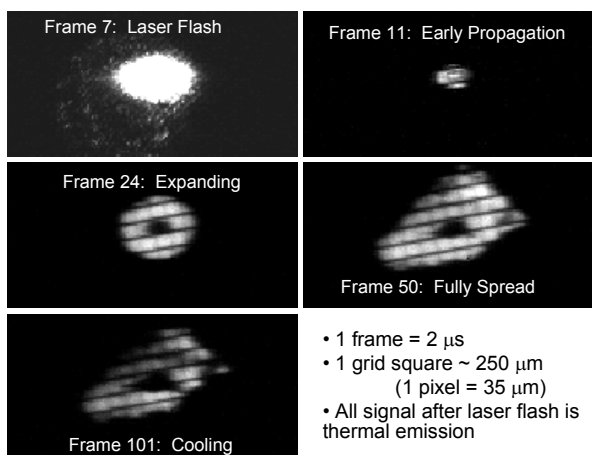


Figure 8. A series of images from the fast optical camera showing the evolution of the RMLF front. The visible mesh lines are from the standard copper TEM grid. The irregularly-shaped glowing region in frame 50 is the complete piece of foil that was ignited in this experiment.

were necessarily quite thin (less than 200 nm thick), there was concern that surface effects would modify (and possibly halt) the propagation of the reaction front. For

We now turn to the second component of the project, namely the reactive multilayer foils. The graduate student who performed the bulk of the work, Judy Kim, was (and continues to be) fully supported under a SEGRF fellowship, and the work continues with funding by the Department of Energy, Office of Basic Energy Sciences and via a collaboration with the University of California at Davis. The present report will therefore describe the research progress for the period (FY06) during which the work received LDRD support.

Preliminary experiments were required to determine the conditions necessary to ignite the foils in a DTEM experiment. Since the TEM samples



example, radiant heat loss to the surfaces should be more significant as the RMLF thickness decreases. Since the samples reach white-hot temperatures, this was potentially a cause for concern. Also, the effect of the zero-pressure boundary condition on the surfaces might have been significant (as the material will tend to rapidly expand as it heats), as it might impact the ability of the layers to hold together as they react. Further, the ability to ignite the foil in air did not necessarily imply that success would be had in vacuum, since for the thin foils reaction with atmospheric oxygen could play a significant role. Finally, it was not a priori obvious what the optimum laser intensity, wavelength, and pulse duration would be to initiate a self-perpetuating reaction front.

Therefore a series of experiments was performed in which various free-standing foils were struck by a laser beam in a vacuum chamber, with a high-frame-rate optical camera (on loan from LLNL's B Program) watching the thermal radiation from the sample. These experiments successfully determined conditions under which a thin RMLF consisting of Al and Ni/V layers could be driven by the infrared DTEM drive laser, in vacuum. The high-speed camera results were particularly helpful (Figure 8). They showed the reaction front propagation rate to be 14 m/s under these conditions, that the front takes many tens of  $\mu\text{m}$  before it stabilizes into a relatively steady wave, and that the thermal rise time of this wave is of order  $10 \mu\text{s}$  while the decay is more than 10 times slower. These results were invaluable in determining where and when to look to see a particular point in the reaction front during the actual DTEM experiments.

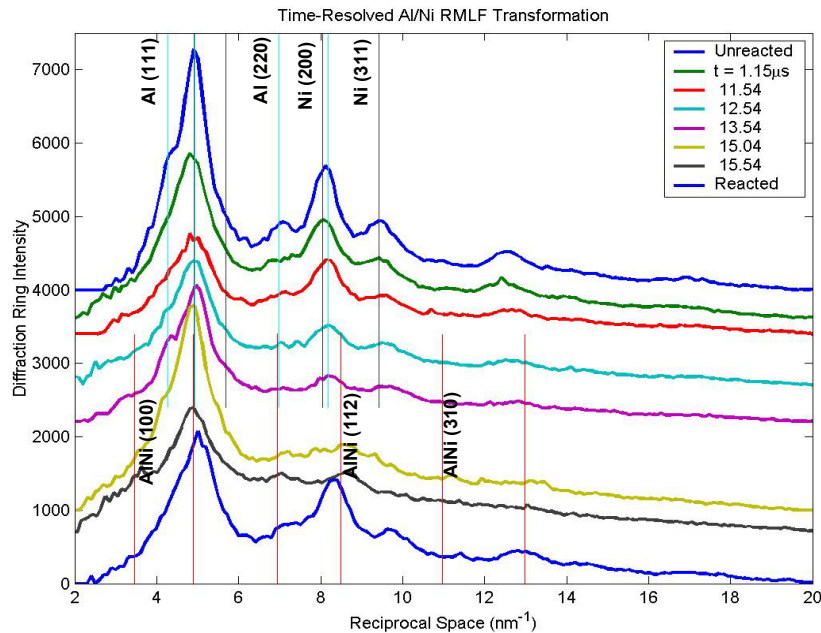


Figure 9. Example DTEM diffraction patterns showing the evolution of material phases in the RMLFs.

Having determined these parameters, the DTEM experiments consisted primarily of selected-area electron diffraction patterns collected from points roughly  $400 \mu\text{m}$  from the reaction initiation site, with time delays ranging from  $\sim 20 \mu\text{s}$  to  $\sim 40 \mu\text{s}$  allowing clear identification of various stages in the reaction front. At the end of the LDRD project, these time-resolved diffraction measurements showed a well-defined transition between the initial fcc Al and Ni/V structures to what has been tentatively

identified as a mixture of liquid Al and an intermetallic solid phase, occurring in a <2  $\mu\text{s}$  span of time some 10  $\mu\text{s}$  after the initial arrival of the reaction front (Figure 9). Further measurements since this time have helped to clarify the sequence of events. Results were presented at the 2006 International Microscopy Conference in Sapporo, Japan and are being prepared for submission to a refereed journal.

### **Exit Plan**

The reported work occurred within the context of the greater DTEM project, which is ongoing. As the DTEM is a very new instrument (and the only one in its class), any development of techniques, and any demonstration of measurements that are impossible on any other platform, will have significant leverage toward the future development of the LLNL DTEM project in particular and the field of time-resolved electron microscopy in general. This LDRD project provided the context and the support for such work at a critical stage in the development of the DTEM, just as the instrument was making the transition from basic proof-of-principle demonstrations to quantitative experimental results. It is unlikely that the results such as those in Figures 5, 7, and 9 could have been generated on any other current experimental platform. Results are in preparation for publication.

The DTEM project as a whole is generating numerous publications<sup>1,3,4,12-15</sup> and significant attention at major microscopy conferences (with invited talks at the 2005 and 2006 Microscopy and Microanalysis conferences and at the 2006 International Microscopy Conference, for example). The DTEM team, through workshops and frequent contact with university collaborators and the Office of Basic Energy Science (BES) at the Department of Energy, is constantly in the process of identifying areas where the DTEM's current and near-future capabilities would yield ground-breaking results. Ongoing scientific work on the DTEM is supported by BES, SEGRF, and university collaborations, and DTEM work is featured in three proposals to BES and one proposal to LDRD. In the longer term, efforts are underway to connect DTEM's capabilities to programmatic needs, taking advantage of the fact that DTEM experiments occur on the same time and length scales (nanometers and nanoseconds) as large-scale atomistic simulations. The DTEM has the potential to directly see the processes that govern the evolution of material strength under extreme conditions. Every step we take in terms of technique and instrument development takes us closer to this goal.

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