Kinetics of the γ–δ phase transition in energetic nitramine-octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine

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Abstract
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ABSTRACT

The solid, secondary explosive nitramine-octahydro-1,3,5,7-tetranitro-1,3,5,7 or HMX has four different stable polymorphs which have different molecular conformations, crystalline structures, and densities, making structural phase transitions between these nontrivial. Previous studies of the kinetics of the $\beta$–$\delta$ HMX structural transition found this to happen by a nucleation and growth mechanism, where growth was governed by the heat of fusion, or melting, even though the phase transition temperature is more than 100 K below the melting point. A theory known as virtual melting could easily justify this since the large volume difference in the two phases creates a strain at their interface that can lower the melting point to the phase transition temperature through a relaxation of the elastic energy. To learn more about structural phase transitions in organic crystalline solids and virtual melting, here we use time-resolved X-ray diffraction to study another structural phase transition in HMX, $\gamma$–$\delta$. Again, second order kinetics are observed which fit to the same nucleation and growth model associated with growth by melting even though the volume change in this transition is too small to lower the melting point by interfacial strain. To account for this, we present a more general model illustrating that melting over a very thin layer at the interface between the two phases reduces the total interfacial energy and is therefore thermodynamically favorable and can drive the structural phase transition in the absence of large volume changes. Our work supports the idea that virtual melting may be a more generally applicable mechanism for structural phase transitions in organic crystalline solids.

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I. INTRODUCTION

The solid secondary explosive nitramine-octahydro-1,3,5,7-tetranitro-1,3,5,7 or HMX is a molecular crystal with four different stable polymorphs known as $\alpha$, $\beta$, $\delta$, and $\gamma$. The molecular conformations, crystalline structures, and densities are dramatically different between these four polymorphs, making their structural phase transitions and kinetics unique and fundamentally interesting. Past work measuring the $\beta$–$\delta$ transition time using optical second harmonic generation found the kinetics to follow a nucleation and growth model, where growth was governed by the heat of fusion. Subsequent work explained that the lowest energy pathway between these two structures was through an intermediate melted state, followed by recrystallization in the higher temperature phase, a theory known as virtual melting. A detailed understanding of the phase diagram and conditions under which the different HMX polymorphs are stable is also important since different polymorphs have different reactivities and explosive sensitivities. A possible phase diagram for HMX is shown in Fig. 1, compiling different values from the literature. However, there are still discrepancies and very different phase transition temperatures have been

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reported in different studies (compare Ref. 7 to Ref. 3). While there have been a few studies on the kinetics of the \(\beta\rightarrow\gamma\) phase transition, much less is known about the other structural phase transitions in HMX. Knowing whether or not the nucleation and growth model, and the virtual melting mechanism apply to the other phase transitions in HMX could further validate this theory. According to previous work,\(^5\) virtual melting can occur when there is enough lattice strain at interfaces between the two different phases to lower the melting point (276° in \(\delta\)-HMX) to \(\alpha\) or below the phase transition temperature. This strain comes about from a volume per unit cell mismatch between the two phases, which is largest between the \(\beta\) and \(\delta\) phases.\(^9\) In particular, it was predicted that interfacial lattice strain would not be sufficient to induce virtual melting in the \(\gamma\rightarrow\delta\) HMX phase transition\(^5\) since in this case, the volume change is only half (\(-3.3\%)\) of that in the \(\beta\rightarrow\delta\) transition (6.7%).\(^9\) This leads to the question of whether or not virtual melting still happens in this case, and if there can be other mechanisms of inducing the intermediate melted state in the absence of a large volume mismatch between the two phases.

Here we investigate the phase transition kinetics of \(\gamma\)-HMX using powder X-ray diffraction (XRD). \(\gamma\)-HMX, which may under some conditions be a hydrate rather than a true polymorph,\(^9,11\) is often the structure found in nanocrystals or nanocomposites formed either by vapor deposition or by abrupt precipitation out of solution.\(^12,13\) \(\gamma\)-phase sub-\(\mu\)m HMX has a lower explosive sensitivity than other forms of HMX yet is still an effective explosive,\(^12,13\) making it useful for designing insensitive explosives.

Using time resolved X-ray diffraction, we measured the phase transition time for the \(\gamma\rightarrow\delta\) phase transition versus temperature in the 155°–176° temperature range. We found these kinetics to be second order and in good agreement with the same nucleation and growth model used for the \(\beta\rightarrow\delta\) transition by simply changing to the thermodynamic constants to those for \(\gamma\)-HMX. The growth mechanism governed by the heat of fusion points to a virtual melting mechanism for the \(\gamma\rightarrow\delta\) phase transition in HMX even though the volumetric change is not enough to lower the melting point to the phase transition temperature in this case.\(^9\)

II. EXPERIMENTAL METHODS

To study the phase transition kinetics of the \(\gamma\rightarrow\delta\) transition in HMX, we used a commercial Bede X-ray diffractometer based on copper K-\(\alpha\) radiation (photon energy 8 keV). With this instrument, which collects a powder diffraction pattern by using a scanning photomultiplier tube coupled to a scintillator across the ring pattern, we could measure an XRD pattern in the range of 2\(\theta\) \(-10°\) as fast as a few seconds. To measure the phase transition kinetics, we quickly (at \(-20°\ C/min\)) ramped the sample to some final temperature \(T_f\) in the range of 155°–176°. The sample temperature was then held constant until the XRD pattern stopped changing (i.e., the structural phase transition was complete), while continually measuring the powder diffraction pattern. The \(\gamma\)-HMX used in this study was prepared by abruptly precipitating HMX from the solution which produced a high purity powder (expected to be >99%) with a sub-\(\mu\)m grain size, as described here.\(^12\) 5–7 mg of the powder was placed in a 3 mm \(\times\) 7 mm and 0.1 mm deep cavity in the copper sample mount. A heater was attached to the back of the sample mount, and several thermocouples were attached to its surface (where the sample cavity is) for setting and monitoring the sample temperature. A commercial Raman spectrometer with a 785 nm laser was also used to confirm the phase of the samples before and after the XRD experiments. A detailed description of our experimental apparatus can be found in Ref. 14.

III. RESULTS

A. X-ray diffraction measurements

Figure 2 shows time resolved powder XRD measurements corresponding to the \(\gamma\rightarrow\delta\) phase transition in HMX at 168°. The sample temperature versus time is shown in Fig. 2(a), and 2(b) shows an image of the powder diffraction pattern versus time and diffraction angle 2\(\theta\). The one-dimensional cuts of this image in Fig. 2(c) show the initial pattern of the \(\gamma\) phase, how this transforms over about 40 min, and then the final \(\delta\) phase X-ray diffraction pattern.

To see how the phase transition time varied with temperature, the measurements shown in Fig. 2 were repeated at different sample temperatures between 155° and 176°. To analyze the kinetics, we selected the \(\delta\)-HMX peak at 2\(\theta\) = 15.4° since this peak does not overlap with any diffraction peaks from any of the other HMX polymorphs. Then, integrating over this peak, we get the one-dimensional curves shown in Fig. 3.
for several different temperatures. Because we measured the phase transition from before it started until completion, these one dimensional curves represent the δ-phase mole fraction versus time x(t), which goes from 0 to 1. It is also helpful to plot the kinetics in terms of the half time t_{1/2} or time that it takes the δ mole fraction to reach 50%, as shown in the inset of Fig. 3.

B. Nucleation and growth model

From the data in Fig. 3, since x versus time and t_{1/2} versus temperature are not linear on a log scale, it can be immediately seen that the γ−δ phase transition is not governed by linear kinetics, or a simple exponential and a single rate constant. Similar kinetics were also observed using SHG measurements to time resolve the β−δ HMX phase transition. The β−δ phase transition kinetics were explained using a nucleation and growth model which we also apply here to the γ−δ transition.

The nucleation and growth model is explained in detail in Ref. 2, and here we adopt it to the γ−δ phase transition. This model is based on the following 3 processes:

\[ γ−HMX \xrightarrow{k_1} δ−HMX, \] (1)

\[ γ−HMX + δ−HMX \xrightarrow{k_2} δ−HMX, \] (2a)

\[ γ−HMX + δ−HMX \rightarrow γ−HMX. \] (2b)

k_1 and k_2 are the rate constants for nucleation of a δ or a γ phase, respectively, while k_3 and k_4 represent the growth of either the new δ or γ phase.

Using the rate laws in Eqs. (1) and (2), the following differential equation describes the time dependence of the δ mole fraction x in terms of the four rate constants:

\[ \frac{dx}{dt} = k_1 + (γ_0(k_2 - k_3) - (k_1 - k_4))x + γ_0(k_4 - k_2)x^2. \] (3)

γ_0 is the initial concentration of the γ phase. As described in Eq. (3), when only one of the two phases is present, the growth terms go to 0 since there must first be some nucleation of the new phase, before it can grow. This is qualitatively consistent with the measurements in Fig. 3 for the δ mole fraction x versus time. Initially, when x is small and nucleation is the dominant process, the conversion is slower. As x increases, growth takes over and the conversion to the δ phase speeds up. Once x approaches one, growing domains begin to overlap and the conversion slows down again.

To quantitatively fit this model to our data in Fig. 3, we use the solution to Eq. (3) for x(t), or the half time, t_{1/2}, from Ref. 2 given by the following 2 equations:

\[ x(t) = \frac{1}{2γ_0(k_2 - k_3) - (k_1 - k_4)} \left( k_1 + k_4 + γ_0(k_2 - k_3) \right) \]

\[ - \sqrt{B} \tan \left( \frac{k_1 + k_4 + γ_0(k_2 - k_3)}{\sqrt{B}} + \frac{1}{2} t_{1/2} \right). \] (4)

\[ t_{1/2} = \left( \frac{2(\tan(\frac{k_1 + k_4 + γ_0(k_2 - k_3)}{\sqrt{B}}) - \tan(\frac{k_1 + k_4}{\sqrt{B}}))}{\sqrt{B}} \right)^{-1}. \] (5)

The constant B is defined as

\[ B = -k_4^2 - 2k_4(k_1 + γ_0(k_2 - k_3)) - (k_1 + γ_0(k_2 - k_3))^2. \] (6)

The positive sign in Eqs. (4) and (5) corresponds to the γ−δ transition, while the negative process is reversion of δ back to γ-phase.

Writing the four rate constants as Arrhenius equations, Eqs. (4) and (5) can be expressed in terms of thermodynamic constants, most of which are known for HMX.
To determine the relevant thermodynamic constants for the \( \gamma-\delta \) phase transition, we followed the same procedure used in Ref. 2. While we do not know the exact microscopic nucleation mechanism, previous measurements on the \( \gamma-\delta \) phase transition managed to isolate and measure first order kinetics said to be from nucleation from which they determined the enthalpy of nucleation \( \Delta H_{\text{nuc}} \) and the phase transition \( \Delta H_{\text{phase}} \) enthalpy.\(^{15}\) Table I and Eq. (7) show how \( k_1 \) and \( k_{-1} \), the nucleation rate constants, are defined in terms of the nucleation and phase transition enthalpies and entropies.

For the \( \beta-\delta \) phase transition, it was hypothesized, and fit well to the kinetics measured with SHG, that the relevant enthalpy and entropy for the growth rate constants are \( \Delta S_{\text{fusion}} \) and \( \Delta H_{\text{fusion}} \), both of which are known for HMX.\(^{16}\) Later, the theory of virtual melting justified this by explaining that volumetric strain at a \( \beta-\delta \) phase boundary can lower the melting temperature from 276 °C, what it normally is at ambient pressure for \( \delta \)-HMX, to the phase transition temperature.\(^{6,5}\)

To describe the \( \gamma-\delta \) phase transition here, we also used the heat of fusion in the growth rate constants \( k_2 \) and \( k_{-2} \), as shown in Table I.

Using known thermodynamic constants to determine the four rate constants in Table I and using the empirically determined prefactors \( Q \) from Ref. 2 leave only 2 unknowns in Eqs. (4) and (5), the phase transition entropy \( \Delta S_{\text{phase}} \) and the nucleation entropy \( \Delta S_{\text{nuc}} \). Using Eqs. (4) and (5), we fit the model to the measurements shown in Fig. 3, making the two unknown entropies free parameters. The results of the best curve fit to our full data set are shown in Fig. 3 and in Fig. 4. The numerical values used for the thermodynamic constants are given in Table II. Figure 4 also shows, for comparison, the \( \beta-\delta \) half times measured from SHG in Ref. 3, and the nucleation-only \( \gamma-\delta \) data from Ref. 15 using Raman spectroscopy.

### IV. DISCUSSION

The close fit of the model to the data suggests that a nucleation and growth model, where growth is governed by melting, is applicable to the \( \gamma-\delta \) phase transition. The temperature where the asymptote occurs, the point where \( T = \Delta H_{\text{phase}}/\Delta S_{\text{phase}} \), fixes both of the free parameters and also gives a precise definition to the phase transition temperature \( T_{\gamma-\delta} = 150.4 \)°C which should be independent of sample details and apply to any \( \gamma \)-HMX sample. One reason for small discrepancies between the data and fits to the model could be because \( x \) is a macroscopic quantity averaged over many nucleation sites, while the experiment may not be completely insensitive to microscopic effects. As shown in Ref. 3, the onset of nucleation will happen at different times for different grains depending on the local sample details (impurities, exact size of a grain, etc.).

#### A. Comparison to Brill’s data

As noted in the introduction, several studies of phase transitions of different HMX polymorphs were performed in the 1980s\(^{7,15}\) using Raman spectroscopy. Contrary to our results, linear kinetics governed only by nucleation were observed. These are the data shown in Fig. 4 from Brill et al., from which \( \Delta H_{\text{nuc}} \) and \( \Delta H_{\text{phase}} \) were taken for our model (see Table II). As seen in Fig. 4, having only nucleation makes the kinetics much slower since growth speeds up the conversion. Similarly, Brill and co-workers’ kinetics

---

**TABLE I. Thermodynamic parameters used in the nucleation and growth model.**

<table>
<thead>
<tr>
<th>( Q (\text{cm}^3/\text{mol}) )</th>
<th>( \Delta S (J/\text{mol K}) )</th>
<th>( \Delta H (\text{kJ/mol}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 )</td>
<td>1</td>
<td>( \Delta S_{\text{nuc}} + \Delta S_{\text{ph}} )</td>
</tr>
<tr>
<td>( k_{-1} )</td>
<td>1</td>
<td>( \Delta S_{\text{nuc}} + \Delta S_{\text{ph}} )</td>
</tr>
<tr>
<td>( k_2 )</td>
<td>3 \times 10^{-10}</td>
<td>( \Delta S_{\text{fus}} + \Delta S_{\text{ph}} )</td>
</tr>
<tr>
<td>( k_{-2} )</td>
<td>3 \times 10^{-10}</td>
<td>( \Delta S_{\text{fus}} )</td>
</tr>
</tbody>
</table>

**TABLE II. Numerical values for thermodynamic parameters used for the fits in Figs. 3 and 4.**

<table>
<thead>
<tr>
<th>( \Delta H_{\text{phase}} )</th>
<th>( \Delta S_{\text{phase}} )</th>
<th>( \Delta H_{\text{nuc}} )</th>
<th>( \Delta S_{\text{nuc}} )</th>
<th>( \Delta H_{\text{growth}} )</th>
<th>( \Delta S_{\text{growth}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 kJ/mol</td>
<td>150.4°C</td>
<td>219 kJ/mol</td>
<td>142.1/kmol</td>
<td>69.9 kJ/mol</td>
<td>127.1/kmol</td>
</tr>
</tbody>
</table>

**Fig. 4.** The measured half times (\( t_{1/2} \)) versus temperature (the same data as in the inset in Fig. 3) and a fit to the nucleation and growth model using the values for the thermodynamic constants shown in Table II (blue). Data from Smilowitz et al. on the \( \beta-\delta \) kinetics measured with SHG\(^3\) and a fit to the same model using the parameters given in Ref. 2 (dark orange). The \( \gamma-\delta \) kinetics measured with Raman spectroscopy from Brill and Karpowicz\(^{16}\) and their first order kinetics fit (purple). The vertical dashed lines show the phase transition temperatures for \( \beta-\delta \) and \( \gamma-\delta \) defined as \( \Delta H_{\text{phase}}/\Delta S_{\text{phase}} \), or the point where the asymptote in the model curves occurs. The solid lines are the fits, and the dots are the data.
measurements also showed only nucleation for the $\beta$–$\delta$ phase transition. In both cases, we do not completely understand how they managed to avoid growth, which could either have to do with how their samples were prepared, or the Raman spectroscopy probe that they used. We note that compared to XRD or SHG, the difference in the Raman spectra of the different HMX polymorphs is more subtle, especially for the higher frequency peaks which come from function groups rather than the crystal lattice. However, Brill et al. observed the kinetics through changes in Raman peaks corresponding to intermolecular forces which should also be a probe of long-range crystalline structure, just as with XRD or SHG.

B. Virtual melting for $\gamma$–$\delta$

The mechanism of virtual melting discussed in Ref. 5, where the melting point is lowered at a $\beta$–$\delta$ interface (following some nucleation) due to a large lattice volume mismatch and relaxation of the elastic energy, cannot alone account for a melt-mediated phase transition in the case of $\gamma$–$\delta$. This is because the volume change going from $\gamma$–$\delta$ is only half of that of the $\beta$–$\delta$ transition and even more elastic energy would be required to melt the stressed HMX in this case since the $\gamma$–$\delta$ phase transition is 10 °C lower in temperature than $\beta$–$\delta$ (see Fig. 4).

Instead we present a more general argument in which a melt intermediate state can still be accessed and is the energetically favorable route from the $\gamma$ to the $\delta$ phase. This is based on the idea that the interfacial energy between melted HMX and the two solid phases is lower than that between the two crystalline phases. The energy reduction at the $\gamma$–$\delta$ interface, $E_{\text{int}}$, containing a melted layer of the width $l_m$ is given by

$$E_{\text{int}} = \gamma_{\text{int}} + y_{\text{ym}} + (\Delta G_{m - \delta} - g_e)l_m - \Delta y \exp(-l_m/l_{\text{int}}),$$

(8)

where $\gamma_{\text{int}}, \gamma_{\text{ym}}$, and $y_{\text{ym}}$ are the energies of the $\gamma$–$\delta$–melt, and $\gamma$–melt interfaces. $\Delta y = \gamma_{\text{ym}} + y_{\text{ym}} - y_{\text{int}}$ is the change in the energy when the $\gamma$–$\delta$ interface is replaced by $\delta$–melt and $\gamma$–melt interfaces. $l_{\text{int}}$ is the characteristic length scale parameter proportional to the interface width. $\Delta G_{m - \delta}$ is the difference in the bulk Gibbs energy of the melted and $\gamma$ phases, and $g_e > 0$ is the elastic energy due to strain from the lattice mismatch at the $\gamma$–$\delta$ interface (i.e., what was considered in Ref. 5). Equation (8) takes two things into account: (1) short-range interactions between two solid–melt interfaces due to a non-uniform crystalline structure at the interface17–19 and (2) the complete relaxation of the lattice mismatch induced by the interfacial elastic stresses during melting ($g_e$). One can use a more complete model for the long-range forces between the interface,19,20 which should give the same order of magnitude that we calculate with the simpler model presented here. Similar to Refs. 4 and 5, for simplicity, we assume that only the $\delta$ phase melts, but only minor changes would be needed to take into account that in reality, both phases can melt to some extent.

Now we solve for the thermodynamic equilibrium width of the melted layer, $l_m$, by minimizing the energy in Eq. (8) with respect to the thickness of the melted layer, $l_m$,

$$l_m^* = l_{\text{int}} \ln \left( \frac{\Delta y}{\Delta G_{\text{int}}} \right); \quad \Delta G = \Delta G_{m - \delta} - g_e.$$

(9)

Next we analyze the thermodynamic conditions under which the intermediate melted state can occur within the solid–solid interface. Since the phase transition temperature is far below the melting temperature, $\Delta G_{m - \delta} > 0$. In contrast to the $\beta$–$\delta$ phase transformation for which $\Delta G_{m - \delta} \leq g_e$ due to a large volumetric transformational strain ($\varepsilon_0$), for the $\gamma$–$\delta$ phase transformation $\Delta G_{m - \delta} > g_e$, since the volumetric transformation strain and consequently the elastic energy are much smaller.\textsuperscript{5,4} Since the natural log is only defined for positive arguments, the condition for existence of the interfacial melt layer is

$$-\Delta y > \Delta G_{\text{int}}.$$

(10)

To estimate $\Delta G$, we take the volumetric transformational phase transition for the $\beta$–$\delta$ and $\gamma$–$\delta$ phase transitions to be 0.08 and 0.033, respectively.\textsuperscript{5} To first approximation, the elastic energy is proportional to $\varepsilon_0^2$ and $\Delta G_{\gamma - \delta}$ is taken to be 0.033/0.08\textsuperscript{2} is 1.522 kJ/mol, where $g_e = 8.947$ kJ/mol (see Ref. 5).

Next we set $\Delta G_{m - \delta} = \Delta h_{m - \delta} - T\Delta s_{m - \delta}$, where any pressurization is neglected. We consider that $T = T_{\gamma - \delta} = 423.4$ K, the lowest temperature at which the $\gamma$ to $\delta$ transition was observed (See Fig. 4). The equilibrium thermodynamic conditions under which the $\gamma$–$\delta$ phase transition is observed are given in Table II, but to be consistent with Ref. 5, we use the values extrapolated to low temperatures, which are $\Delta s_{m - \delta} = 132.70$ J/mol K, $\Delta h_{m - \delta} = 66 272.3$ J/mol. From these values, we obtain $\Delta G = 8565$ J/mol. Multiplying this value by the molecular volume $V_m = 1.8 \times 10^{-4}$ m\textsuperscript{-3}, we obtain $\Delta G = 4.758 \times 10^{-7}$ J/m\textsuperscript{3}.

Substituting in typical values $l_{\text{int}} = 1$ nm, from Eq. (10), we get that $-\Delta y > 0.048$ J/m\textsuperscript{2}. Assuming that $\Delta y = -0.1$ J/m\textsuperscript{2}, we obtain from Eq. (10) that the thickness of the melted layer is 0.74 nm, a reasonable number for interfacial melting. The melted layer corresponds to the minimum energy, i.e., it is at thermodynamic equilibrium. Thermal fluctuations are not required since there is no energy barrier in Eq. (8) versus $l_m$.

The value $-\Delta y > 0.1$ J/m\textsuperscript{2} has been reported for surface melting for a number of materials, like Si, Ru, W, and Re; see Ref. 21. The energy of the $\gamma$–$\delta$ interface, which is an interface between two very different molecular structures, is expected to be much higher than the energy of two solid–melt interfaces. Due to the dramatic difference in the crystalline structures of the two polymorphs, this interface cannot be a coherent interface. Transformation to a semicoherent interface by nucleation of dislocations is probably not energetically favorable either, because of the complex crystal structure and the small chance of nucleation by dislocation in a thin stressed interfacial layer. Therefore, the appearance of the melted layer at thermodynamic equilibrium plays three major roles in the $\gamma$–$\delta$ phase transition: (1) It provides a mechanism for a reconstructive phase transition between two crystal structures through disordering. (2) It provides a...
mechanism for the loss of coherence at the $\gamma$–$\delta$ interface. (3) It removes the athermal interfacial friction caused by the interaction of the interface with the long-range stress field of different lattice defects such as dislocations, point defects, and grain boundaries. A liquid as the hydrostatic medium does not interact with the stress field of crystal defects, and consequently, athermal resistance to the interface propagation does not occur. This is why the interface can propagate at temperatures slightly above the phase equilibrium temperature $T_{\gamma-\delta}$.

While the intermediate melted layer exists at thermodynamic equilibrium within the moving interface, at points in space through which the moving interface passes, the melt begins in the $\gamma$ phase which then recrystallizes in the $\delta$ phase, i.e., it represents a virtual melt like intermediate phase along the $\gamma$–$\delta$ transformation path.

One possibility to keep in mind is that $\gamma$–HMX may under some conditions be a hydrate where some number of water molecules are part of its unit cell structure. If this is the case, the volumetric change upon transition from $\gamma$–$\delta$ may be larger than expected, making an additional driving force, $g_e$, for virtual melting. Also, no direct evidence was seen in the X-ray diffraction measurements of melting (characterized by very broad peaks), consistent with the fact that the disordered layer is very thin (sub-nm) and makes up a small fraction of the total material probed by the centimeter-wide X-ray beam.

C. Reversion

As discussed above, the kinetics model also predicts a $\delta$–$\gamma$ phase transition or that conversion back the $\gamma$ phase will happen at temperatures lower than $T_{\gamma-\delta}$. So far, having tried a number of experiments after conversion to the $\delta$ phase holding the sample temperature constant at different points between 130° and 150°, no reversion to $\gamma$ or any other phase has been observed. As shown in Ref. 3, it could be that a very specific temperature ramp is needed to achieve this. Even though we have shown here that the melt intermediate state is easier to access than previously thought, other factors can prevent certain phase transitions. For example, the increased reactivity of the liquid can lead to a partial or full decomposition of the solid rather than structural phase transitions. This may play a role in making the reversion back to a low temperature phase difficult to achieve.

D. A broader view of the virtual melting phenomena

While the concept of virtual melting was first applied to solid, organic explosives 15 years ago and explained as a relaxation of the elastic energy, since then there have been various realizations of this in a wide range of materials. Here, we name a few of these: (1) For geological materials like ice, or cosite, there is both theoretical and experimental evidence that the mechanisms of certain crystal-crystal and crystal-amorphous phase transitions at extreme pressures occur by virtual melting. The same is true for certain electronic materials like Si and Ge. In the theory used in this work, similar to what was performed here for $\gamma$–$\delta$ HMX, a reduction in surface energy was taken to be a driving force for virtual melting. (2) Virtual melting was also detected as an intermediate step in a crystal–to–amorphous phase transition in an anti-diabetic pharmaceutical Avandia. (3) Crystal-crystal phase transitions via an intermediate, surface–induced pre-melting (similar to the mechanism described here for $\beta$–$\delta$ HMX) were experimentally and theoretically confirmed for the metastable pre-perovskite to cubic perovskite transition in PbTiO$_3$ nanofibers, an important ferroelectric material. In this case, the observation of a nanometer-thick amorphous layer between two solid phases following quenching was taken to be evidence of virtual melting. (4) The phase transition between square and triangular lattices of colloidal films of microspheres was also found experimentally to occur by virtual melting. In this case, the thickness of the melted layer was on the order of the radius of the spheres, or $\mu$m, making it directly observable with light field microscopy. A more complete theory of virtual melting in these systems can be found here. In aluminum and copper, plastic deformation and stress relaxation under high strain rates have also been predicted thermodynamically and by MD simulations to occur by virtual melting. In this case, melting occurred at 4000 K below the thermodynamic equilibrium temperature at equilibrium pressure and was caused by the relation of deviatoric stresses during melting. The importance of virtual melting for phase transitions and plastic flow in different materials was reviewed in Ref. 28.

Recently, a much more detailed phase field theory of virtual melting has been developed and simulations were performed for crystal-crystal phase transitions. This more sophisticated model takes into account both the reduction in the interfacial energy and mechanics. Numerous nontrivial scale and kinetic effects have been revealed through this work. In particular, melting depends not only on changes in interfacial energy but also on the ratio of the width of crystal-crystal to crystal-melt interfaces. For some of these ratios, following melt nucleation, metastable melts remain even when the melt/solid interface energy is higher than the energy of the solid/solid interface and hysteresis has been exhibited from the melting–solidification process. Incomplete melting and critical melting nuclei were found within the crystal-crystal interfaces. Therefore, in light of the many recent examples of melting far below the melting temperature and the role that this plays in a range of structural phase transitions, we do not find it surprising that melting plays a role in other structural phase transitions in solid organic explosives, even when the volume change due to the transition is relatively small.

V. CONCLUSIONS

We presented kinetics measurements of the $\gamma$–$\delta$ structural phase transition in HMX using powder X-ray diffraction, finding phase transition times between 7 and 103 min in the 153°–176° temperature range. These results are consistent with a nucleation and growth model, where growth of $\delta$ nucleation sites is governed by melting, just as was
found for the $\beta-\delta$ HMX phase transition. However, virtual melting was previously not expected for the $\gamma-\delta$ transition since it is not accompanied by a large enough volume expansion to create enough strain to lower the melting point to the phase transition temperature, as in the model used to describe the $\beta-\delta$ transition. Here we presented a more general mechanism of virtual melting showing that interfacial melting is still thermodynamically favorable since a melt-solid interface has a lower energy than the solid-solid interface between delta and $\gamma$-HMX. This sub-nanometer interfacial melted layer then drives the growth of the new $\delta$ phase.

This work provides more insight into structural phase transitions in organic solids and more examples of melting far below the melting point and the role that it plays in phase transitions.

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