PHYSICAL REVIEW B **71**, 094109 (2005)

Diffusion of point defects in shocked molecular crystals

Yu. Skryl[1] and Maija M. Kuklja[2,*]
[1]*Institute of Mathematics and Computer Science, University of Latvia, Rīga LV-1459, Latvia*
[2]*Division of Materials Research, National Science Foundation, Arlington, Virginia 22230, USA*

(Received 7 May 2004; revised manuscript received 11 October 2004; published 30 March 2005)

The dynamic response of a molecular crystal containing defects to shock wave loading is modeled and the resulting diffusion of point defects is simulated. It is shown that diffusion proceeds not only via the stress assisted diffusion, which is point defect diffusion in a stress field, also known as the Gorsky effect, but also through defect diffusion in the field of inertial forces. The method for modeling diffusion of point defects in shocked solids is developed. It is shown that diffusion in the inertial field significantly exceeds the stress diffusion in organic molecular crystals. Interplay between stress-assisted and inertial diffusion leads to the separation of light particles from heavy particles due to the shock wave front excitation, e.g., heavy and light molecules diffuse to different directions from the wave front. The diffusion mechanisms and the separation effect are discussed in great detail for organic molecular crystals under shock wave excitation.

DOI: 10.1103/PhysRevB.71.094109 PACS number(s): 61.72.Ji, 66.30.−h, 62.50.+p, 61.66.Hq

I. INTRODUCTION

Throughout the last half of the century, significant advances have been achieved in the field of shock wave physics. The energy of the shock wave is dissipated within the material as it travels through it[1,2] leading to polymorph phase transitions,[3] chemical decomposition,[4,5] chemical synthesis,[6] polymerization of monomers,[7] and defect formation.[8,9] Intensive studies on dynamic effects in shock waves[10,11] recently appeared ranging from a very general description based on nonequilibrium thermodynamics[12] to large-scale molecular dynamics[7,13] to *ab initio* calculations.[14,15] Despite the significant progress in the field, not much is known about defects in materials and their behavior under shock loading.[2,16,17]

This article is an attempt to simulate the dynamic behavior of a molecular crystal containing point defects under the action of a shock wave progressing through the crystal. The effect of the strong dynamic compression of the material on defect diffusion is considered and compared to the stress-assisted diffusion.[18] It is shown that a shock wave progressing across a solid with a high molecular mass creates a field of inertial forces, which affects point defect movements much more drastically than strain stresses. This purely dynamic effect will be referred to hereafter as inertial diffusion. This effect leads to the vacancy movement away from the compressed region unlike in the Gorsky effect, where vacancies are forced to drift towards the compressed part of the material. The redistribution of defects in this manner results in the formation of a “vacancy super saturation zone,” a narrow zone with high vacancy concentration that moves along with the shock front. On the other hand, diffusively mobile molecules will be moving in the opposite direction, towards the compressed material. This will result in a rapid increase in the concentration of diffusing molecules on the surface of the crystal at the moment the impact wave enters the crystal, which will be referred to as a molecular super saturation zone. In some cases, for example, in the presence of impurities, this can lead to a new phase formation.

The intensity of inertial diffusion is greatly dependent on molecular mass. This is especially well manifested for the organic molecular crystals studied here. When the masses of the molecules are small, the inertial forces are also small, and therefore the diffusion in the shock wave proceeds via the Gorsky effect. Should the diffusion system have both light and heavy molecules, the shock wave front should move them apart. The heavy molecules will inertially move against wave movement whereas the light molecules, in accordance with stress-assisted diffusion, will move along with the shock wave. We will refer to this selective behavior of the shock wave front as a separation effect. The inertial diffusion, stress-assisted diffusion, the separation effect, and their consequences will be described here in detail. We also discuss a possible experiment to test our theory and some experimental evidence available from literature, which lends an additional support to our theoretical predictions.

II. BASIC THEORY OF DIFFUSION IN SHOCKED SOLIDS

Once a shock wave enters a crystal it creates a strong stress in the material. Assuming the crystal has preexisting vacancies and no other defects, one of the effects of the shock wave on the crystal will be the diffusion of vacancies in the non-uniform stress field in the wave front region. In the classical case of material stress, or stress-assisted diffusion,[18] atoms or molecules that increase the lattice parameters tend to move to the expanded regions of the crystal, while atoms that decrease the lattice parameters tend to move to the compressed regions.[19] Therefore, according to Gorsky,[18] vacancies must move along the density gradient created by the shock wave. The shock wave, while progressing across the crystal, gathers vacancies, transferring them from the uncompressed part of the crystal to the compressed part.

However, in addition to stress diffusion, there is another mechanism of vacancy redistribution in shock waves that we will refer to as point defect diffusion in the field of inertial forces, or simply “inertial diffusion.” Viewed from the frame of reference in which the shock is stationary, inertia drives molecules from the undisturbed region to the compressed region of the crystal. Vacancies, on the contrary, are driven in the opposite direction, to the uncompressed part. Hence, inertial diffusion is associated with motion opposite to that of stress diffusion. The net vacancy flow is a result of the two competitive processes.

The diffusion model is described here in terms of a one-dimensional random walk. Here, x_1 and x_2 are neighboring sites of a crystalline lattice with the parameter a. Assume for simplicity that the shock wave travels from right to left and that the gradient of both elastic E_c and kinetic E_k energies is negative: $E_\mathrm{c}(x_1) > E_\mathrm{c}(x_2)$ and $E_\mathrm{k}(x_1) > E_\mathrm{k}(x_2)$. Then, the resulting probability flux between sites x_1 and x_2 can be written as

$$j(x) = j_-(x_1 \to x_2) - j_+(x_2 \to x_1), \tag{1}$$

where

$$j_\pm = aW_\pm p\left(x \mp \frac{a}{2}\right)\left[1 - p\left(x \pm \frac{a}{2}\right)\right].$$

Here $p(x \pm a/2)$ is the probability of a molecule occupying a site. W_+ is the frequency of jumps from the site x_1 to the site x_2 in the forward direction and W_- is the frequency in the reverse direction. They are represented as

$$W_+(x_1 \to x_2) = W_0 \exp\left(\frac{E_c^- - \Delta E_k/2}{k_B T}\right) \tag{2}$$

and

$$W_-(x_1 \leftarrow x_2) = W_0 \exp\left(\frac{E_c^+ + \Delta E_k/2}{k_B T}\right),$$

where W_0 is frequency of jumps in the absence of variation in energy of the system; $E_c^\pm = E_c(x \pm a/2)$ is the material stress energy at the corresponding sites $(x \pm a/2)$ and ΔE_k is the difference in kinetic energy between the neighboring sites. Both types of energy are calculated per single molecule. Equations (1) and (2) satisfy the local balance condition

$$\frac{W_+(x_1 \to x_2)}{W_-(x_1 \leftarrow x_2)} = W_0 \exp\left(\frac{\Delta E_c + \Delta E_k}{k_B T}\right). \tag{3}$$

Here, the frequencies of jumps are proportional to the elastic energy E_c and to the difference of the kinetic energies between sites ΔE_k. A sign in front of the difference is chosen with the assumption that the probability of a molecule jump towards the crystalline lattice motion is higher than one in the opposite direction.

Stress diffusion occurs when the frequency depends upon the material stress energy only. Then the probability of particle jumps from the region of higher stress to the region of lower stress is much greater than the probability of jumps in opposite direction. Vacancies, in contrast, move in the direction of higher stress. If the jump frequency depends upon the kinetic energy difference only, molecular drift in the field of inertial forces occurs. The molecules move against the acceleration of the lattice, i.e., in our case, to the left-hand side. This results in the activation energy for lattice molecule jumps against the crystalline lattice motion (to the more compressed region in our case) being lower. The substance becomes more condensed and vacancies tend to move out of the compressed part of the material. Further, expanding the probability $p(x \pm a/2)$, the final energy $E(x \pm a/2)$, and the frequencies $W_\pm$ in a Taylor series in x, and taking into account only linear terms, one gets an equation for probability flux in the form

$$j(x) = -a^2 W_0 \exp\left(\frac{E_c}{k_B T}\right)\left[\frac{\partial p(x)}{\partial x} + \frac{1}{k_B T} p(x) \frac{\partial E}{\partial x}\right], \tag{4}$$

where $E = E_c - E_k$. This can be easily transformed into an equation based on concentrations if one recalls that only half of the current concentration can move to the neighbor site at each elementary process, i.e., $p(x) \to C(x)/2$. Then one obtains the equation for the particle and vacancy flux

$$J(x) = -D\left[\frac{\partial C(x)}{\partial x} \pm \frac{1}{k_B T} C(x) \frac{\partial E}{\partial x}\right], \tag{5}$$

where a + sign corresponds to diffusion of molecules, a − sign corresponds to diffusion of vacancies, and the D is the corresponding diffusion coefficient.

Note that the molecular diffusion coefficient is $D = D_0 \exp[-(E_0 - E_c)/k_B T]$, where E_0 is the activation energy and D_0 is the pre-exponential factor for the uncompressed material, while the vacancy diffusion coefficient can be represented as $D = D_0 \exp(-E_0/k_B T)$. In fact, unlike the molecular diffusion coefficient, the vacancy diffusion coefficient should not depend on pressure. This is because the activation energy E_0 for vacancy diffusion can be represented[20] as a sum the vacancy migration energy E_M, which decreases under pressure [see Eq. (2)], and the vacancy formation energy E_V, which increases under pressure.[21] Hence these two contributions nearly compensate each other. It would be reasonable to suggest that the diffusion coefficient for impurity atoms diffusing via a vacancy mechanism also does not depend on static stress or this dependence is rather weak.

It can be seen from Eq. (5) that, when $E = E_c$, the molecular flow is positive ($F_c = -\mathrm{grad}E_c > 0$, where F_c is an elastic force) and directed away from the shock wave front, i.e., towards the uncompressed part of the material (Gorsky effect). On the other hand, when $E = -E_k$, then the molecular flow is negative [$F_k = -\mathrm{grad}(-E_k) < 0$, where F_k is an inertial force] and directed towards the shock wave front, i.e., towards the compressed part of the material. The net molecular flow is a strong function of the interplay between these two energies (two forces). As is seen from these equations, the direction of the flow of vacancies is opposite that of the flow of the molecules and, therefore, in the case of dominating inertial diffusion, the vacancies will be diffusively forced out of the crystal.

It should be noted here that the diffusion equations for both the vacancy and molecular flows can be also obtained by using the Fokker-Planck equation, describing the diffusion in the external field.[22] The model proposed here is more exhaustive since it suggests a description for the action of inertial and stress fields on an activation energy for the diffusion of point defects. More so, the model also yields dependence of the diffusion coefficients on the pressure [see Eq. (4)], which is impossible to obtain from the formal use of

TABLE I. The structure of the shock wave. p_1 is the impact wave amplitude, ρ_1 is density of the material, v_1 is the mass velocity, D is the shock wave velocity, H is the width of the shock wave front, E_c and E_k are the elastic and kinetic energy per molecule, respectively.

N	p_1 (GPa)	T_1 (K)	ρ_1 (g cm^{-3})	v_1 (km s^{-1})	D	H (μm)	E_c (eV)	E_k *HMX* (eV)	E_k CH$_2$
1	16	1252	2.67	1.56	5.41	34.5	1.02	3.26	0.18
2	18	1414	2.72	1.69	5.62	32.5	1.15	3.82	0.21
3	20	1580	2.76	1.81	5.82	20.9	1.27	4.38	0.24

the Fokker-Planck equation. The correlation with the classical theory supplies some confidence in a consistency of the original suppositions that our model was based on.

III. RESULTS OF NUMERICAL MODELING

From a knowledge of the material stress distribution, one can determine the effect of the shock wave on the redistribution of point defects by numerical solution of the diffusion equation (5) with the zero diffusion flux on the crystal boundaries. The exponential difference method has been used here for the 1D case.[23] This method allows us to obtain a rather good solution on relatively rough grids in cases of large gradients. In calculations a typical molecular crystals such as *HMX* ($C_4H_8N_8O_8$) was used. The initial vacancy distribution was assumed to be uniform with concentration $C_0=10^{16}$ cm^{-3} (see the monograph of Silinsh[24]). We chose the molecular diffusion constants $E_0=1.85$ eV and $D_0=7\times10^{10}$ cm^2 s^{-1}, for anthracene, which is a typical organic crystal.[24] Because this work is only qualitative, this diffusion coefficient will be used in calculations of distribution functions for both vacancies and molecules. In fact, only the self-diffusion coefficient is considered here for simplicity of the description. Impurity atoms can move several times faster as well as several times slower than self-diffusion proceeds. We are not aware of data for the diffusion coefficients of specific impurity diffusion in anthracene or *HMX* crystals. Therefore, only estimates are used here.

The amplitude of the shock wave was chosen in the range from 16 to 20 GPa. The shock wave structure in solid *HMX* was calculated analytically by using the hydrodynamic approximation and the method developed earlier.[25] The accurate value of the molecular elastic energy, which is not a trivial problem, has been obtained from first-principles quantum-mechanical calculations of the total energies for the *HMX* unit cell for a range of different compressions.[26] The parameters of the shock wave, such as density of the material, mass and shock wave velocities, temperature at the shock front, and the front's width at several different impact pressures are listed in Table I, they agree well with the published data for a typical explosive materials.[27,28] The consensus observed provides assuring evidence of the quality of the developed calculation scheme for shock wave structure modeling.

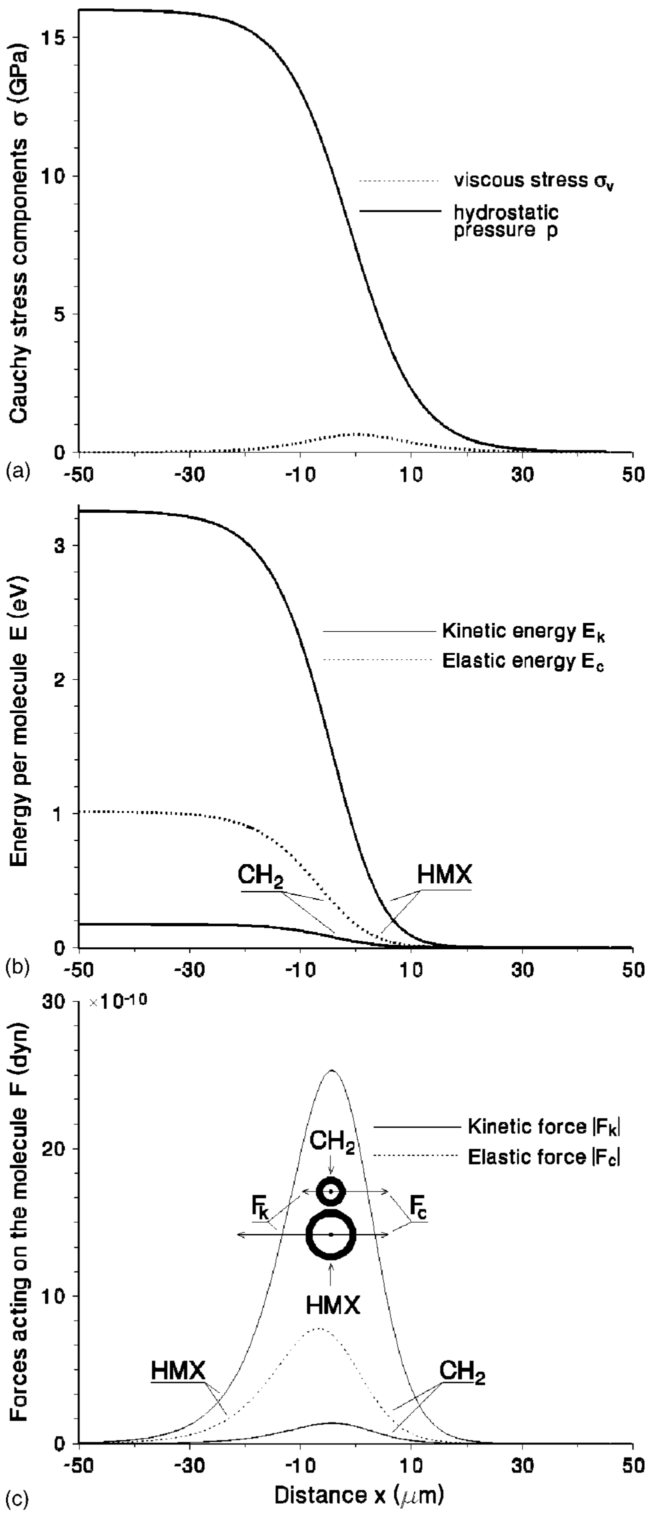

FIG. 1. Distribution functions of (a) Cauchy stress components, (b) the energy per molecule, (c) forces acting on each molecule within the shock wave front at $p_1=16$ GPa in solid *HMX*.

A. Supersaturation zone and separation effect

The distribution of the stress components in the shock wave front along with the elastic and kinetic energy per *HMX* molecules and corresponding forces is shown in Fig. 1. The pressure p and viscous stress σ_v distributions obtained

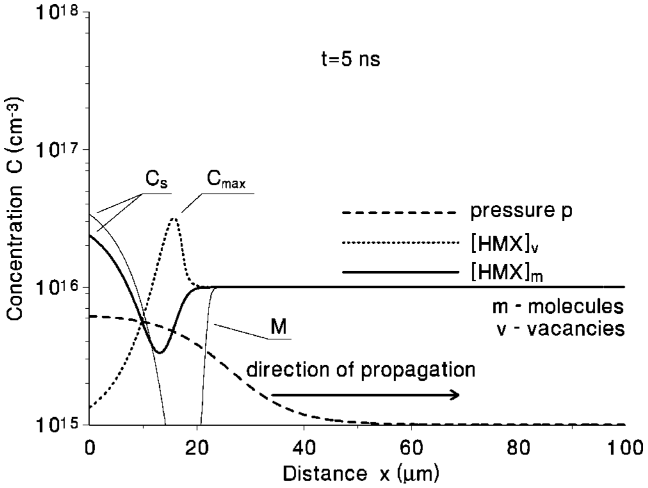

FIG. 2. The response of the molecular and vacancy distributions to a shock wave progressing across the solid *HMX* is shown. The shock wave with the amplitude of 16 GPa is scaled to show in the same figure (dashed line). An effect of the increased diffusion coefficient of *HMX* molecules (interstitial mechanism) under pressure is shown with the marker *M* (fine solid line).

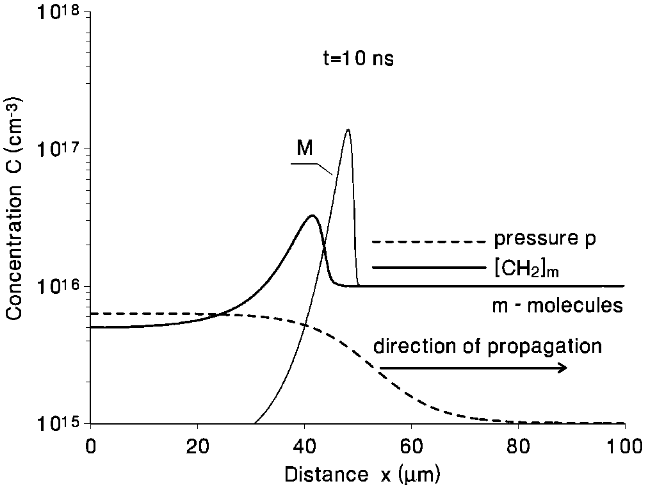

FIG. 3. The response of the CH_2 impurity distributions to a shock wave progressing across the solid *HMX* is shown. An effect of the increased diffusion coefficient of CH_2 molecules (interstitial mechanism) under pressure is shown with the marker *M* (fine solid line).

are shown in Fig. 1(a). The shock wave amplitude was taken as $p_1=16$ GPa. As is seen from Figs. 1(b) and 1(c), a portion of the kinetic energy corresponding to one *HMX* molecule and the force attributed to it significantly exceeds the potential energy and the corresponding to it elastic force responsible for the Gorsky effect. This is valid only for relatively heavy molecules such as *HMX*. For light molecules such as CH_2, for example, the opposite is true. The inertial force will be insignificant and the Gorsky effect will dominate. It was assumed that the elastic energies per *HMX* and CH_2 molecules are the same. This approximation is fairly weak because molecular elastic energy depends strongly on the crystalline lattice and elastic properties of the material. It is even more problematical to estimate the elastic energy per impurity molecule than per host molecule. Therefore, a value equal to the *HMX* molecular energy was used here, which is a slightly overestimated one. In fact, the corresponding energy for CH_2 in the *HMX* matrix should be smaller. This assumption, however, will not skew our results.

The response of the molecular distribution to a shock wave progressing across the solid is shown in Fig. 2 (the inertial diffusion effect) and Fig. 3 (the stress diffusion effect). The zero of time is at the moment when the wave front has entered the crystal up to its half pressure point. The pressure may or may not have an influence on the diffusion coefficient for migrating molecules [Eq. (5)]. Specifically, this depends on the diffusion mechanism; the drift of molecules via the interstitial mechanism is strongly dependent on pressure while the flow of molecules via the vacancy mechanism is not. The difference is clearly displayed in the figures.

The result of diffusion redistribution of *HMX* molecules $C=[HMX]_m$, in the crystal due to the shock wave traveling across the material is shown in the figures by the solid line. The direction of the diffusion flux is opposite to the direction of the shock wave due to the dominating inertial forces, as was expected. The *HMX* molecule concentration increases at the crystal surface, namely, at the surface where the shock wave originally hit the material. Molecules are forced towards the surface. The effect is especially pronounced at the early stage of the wave entering the crystal. Right after the wave enters the crystal, a narrow zone of mobile molecules is formed with the concentration maximum C_s at the surface of the crystal. This zone can also be referred to as a surface supersaturation zone and is relatively short lived. If the molecules do not participate in any reactions on the surface, this zone dissipates gradually as the wave travels further into the crystal.

Similarly one can consider diffusion of heavy metal impurities and fragments of large organic molecules present in the crystal. An inertial drift of those molecules will always be rather strong, exceeding the Gorsky effect. On the other side, the situation will be completely opposite for the light molecules such as CH_2. The corresponding solution of Eq. (5) for $C=[CH_2]_m$ is displayed in Fig. 3. In this case, the inertial force is insignificant and the CH_2 molecules are forced out of the compressed region of the material. The shock wave drives them further towards the bulk crystal creating a zone with a high concentration of molecules with the maximum C_{max}, the bulk supersaturation zone. Unlike the surface supersaturation zone, the bulk supersaturation zone moves along with the shock wave. If no phase transition and chemistry occur in the bulk supersaturation zone while the shock wave is moving, all of the excess molecules are going to the surface supersaturation zone. Only after that, if no precipitations form on the surface (we do not consider any precipitations here) excess of CH_2 molecules will redistribute back over the entire material when the shock wave front leaves the crystal. In the described example, the characteristic time for the diffusion system to relax back to the initial concentration value C_0 is fairly short, about 30 ns.

We will refer to the observed phenomena as a separation effect of the shock wave. The shock wave front “recognizes” light and heavy molecules and forces them to move towards opposite directions. In the case of activated segregation, this will lead to the growth of new phases of different molecular constitutes on the opposite surfaces of the crystal.

Figures 2 and 3 show how the pressure has an effect on the diffusion coefficient for atoms/molecules that diffuse via interstitial mechanism. As is seen, the increase of the diffusion coefficient results in a $C_{\max}$ increase for the CH_2 molecule (Fig. 3). The surface concentration C_s of the *HMX* molecule only slightly increases, although, the well of the concentration minimum becomes deeper (Fig. 2). It is worthwhile to note that the diffusion coefficient is increased under pressure by three orders of magnitude, which is consistent with the experimental results reported on pressure dependent impurity diffusivity in silicon.[29]

Just out of curiosity, let us consider what inertial forces do to the vacancies that are always present in crystals under equilibrium conditions. The diffusion distribution functions $C=[HMX]_v$ calculated from Eq. (5) for *HMX* crystals are plotted in Fig. 2 by the dotted line. As for light molecules, the bulk supersaturation zone, which is moving along with the shock front, is formed. However, instead of the molecular supersaturation we are dealing with the vacancy supersaturation here. This worthy of note outcome also appears due to inertial forces.

B. Defect aggregation

In an earlier study, it was demonstrated by quantum-chemical calculations that vacancies interact attractively in *R*D*X* ($C_3H_6N_6O_6$) crystals.[30] It was also found that the presence of defects reduces the activation barrier for decomposition of *R*D*X* molecules[31] and *F*O*X*-7 ($C_2H_4N_4O_4$) molecules[17] in the solid phase. Formation and/or growth of voids is known to happen due to crystal growth, rapid expansion in metals,[32] hydrostatic tensile loading,[33,34] axisymmetric stress,[35] thermal softening and adiabatic shear bands,[36] thermal diffusion,[37] and other reasons. From the results obtained in this study, it appears that, under shock wave loading, preexisting vacancies in the crystal tend to form a special zone with a super high concentration moving along with the shock wave front. Hence, the question arises as to whether it is possible for vacancies to aggregate under shock compression conditions creating large vacancy clusters or voids.

The vacancy concentration is strongly dependent not only upon the shock wave amplitude but also on the distance traveled by the wave in the crystal. The concentration maximum $C_{\max}$ in the saturation zone as a function of the distance traveled by the shock wave in the crystal is shown in Fig. 4. As is seen, the vacancy supersaturation $C_{\max}/C_0$ at 18 and 20 GPa, can reach high magnitudes, greater than 10^3. For such large supersaturation levels it is possible for vacancies to aggregate into pores even against compression forces. Based on thermodynamic considerations,[38] a necessary condition for vacancy aggregation is that the energy of vacancy supersaturation should be greater than the energy of the elastically compressed material $k_BT\ln(C_{\max}/C_0)>E_c$. Figure 4 shows the critical concentrations of vacancies $C_{\max}=C_{\text{crit}}$ with the horizontal lines indicating the point where the energy of the vacancy solution is equal to the elastic energy of the compressed crystal. It is seen from Fig. 4 that vacancy aggregation can start when supersaturation reaches the critical value. A wave with much lower amplitude is not able to create supersaturations causing void formation because the maximum vacancy concentration in the stationary regime is lower than the necessary critical concentration of vacancies. For example, a wave with amplitude of 16 GPa produces a maximum vacancy concentration of an order of magnitude lower than the critical concentration (Fig. 4).

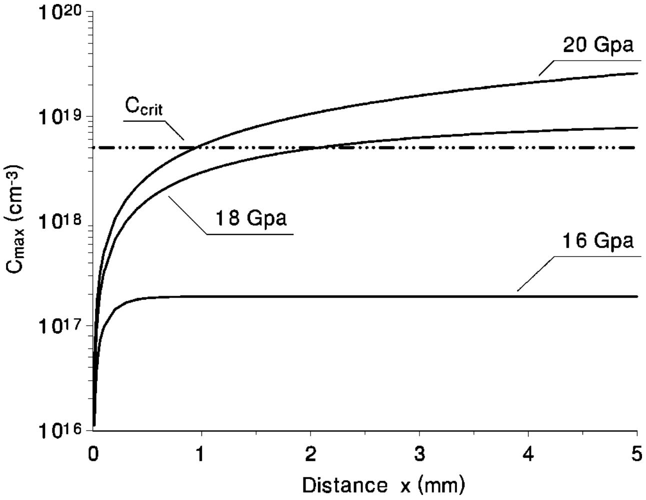

FIG. 4. Maximum of the vacancy concentration in the bulk supersaturation zone as a function of the distance the shock wave front traveled in the crystal at different shock wave amplitudes. When the vacancy concentration is higher than C_{crit}, vacancy aggregation and formation of voids occur.

It should be brought up here that defect aggregation takes place not only for vacancies but also for other defects as the shock wave activates all types of molecular movements in the material including its own atoms, molecules, and impurities. The molecules and atoms move towards the surface or bulk of the crystal forming regions with rather high atomic/molecular concentration. In these regions, atomic clusters and impurity aggregates can be created under certain conditions. Although the concentration saturations for molecules are not as high as for vacancies, the formation of an impurity aggregate is more probable than void formation, because the stresses of the compressed material will stimulate not only the diffusion processes but also the impurity aggregate growth and segregation.

IV. EXPERIMENTAL EVIDENCE AND DISCUSSION

Obviously, the formation of the supersaturation zone as well as the effect of the concentration separation is essentially a nonequilibrium phenomenon. One might think that these effects manifest themselves only in dynamics, and if there are no phase or chemical transformations in the diffusion system there is no chance to reveal any traces of

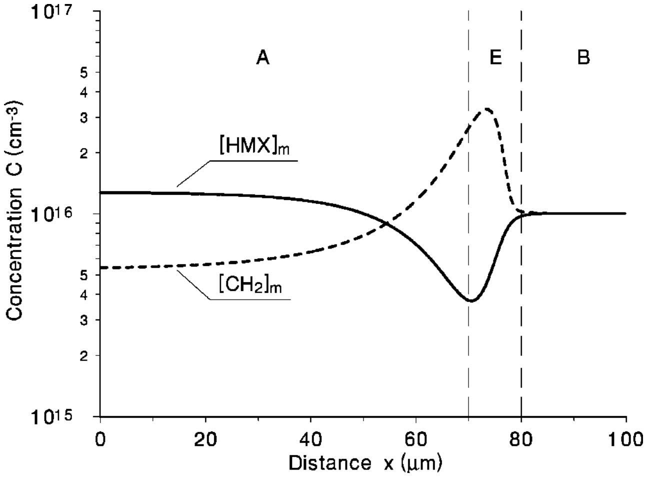

FIG. 5. The concentration distributions (vacancy mechanism) for *HMX* and CH_2 molecules after the divergent shock wave with the rapidly dropping amplitude traversed across the *HMX* crystal. The initial amplitude of the shock wave is 20 GPa, it is dropping with the speed of 0.5 GPa/ns. The crystal consists of the excited region *A* with a steady trend of increasing or decreasing concentration, pristine region *B* with the equilibrium concentration C_0, and the intermediate region *E*.

redistribution of point defects in the crystal. Let us consider how (if at all possible) to obtain immobile concentration distributions in the crystal that underwent shock wave excitation. In other words, we would like to find conditions that possess the same characteristic pattern of defect distributions after the shock is gone and the crystal is back under normal conditions. In doing so, we simulate what happened with the concentration distributions in the crystal when the divergent shock wave with rapidly dropping amplitude traversed across the crystal. Figure 5 shows concentration functions for *HMX* and CH_2 molecules after the shock wave with the initial amplitude of 20 GPa traveled in the *HMX* crystal, assuming that the initial excitation amplitude is rapidly dropping with the speed of 0.5 GPa/ns. In this picture, the crystal consists of the excited region *A* with a steady trend of increasing or decreasing concentration, pristine region *B* with the equilibrium concentration C_0, and the intermediate region *E*, which is, most likely, very difficult to determine experimentally because its linear size is of the order of one half of the shock wave front width. The redistributions obtained are very similar to experimentally measured distributions of some chemical elements in rudimentary rocks artificially or naturally treated by the spherical shock waves.[39,40]

For now, there is no experimental proof or demonstration of our theoretical predictions because the inertial diffusion of point defects has not been investigated experimentally yet. A few data is found in literature that point to the selectivity of the shock wave, which can be related to a diffusion process.[41] Measurements of polarization semiconductors[42] and metals[43] observed change of polarity of the shock front in polar dielectrics[44,45] and ultrafast diffusion that make possible the realization of shock-induced synthesis and shock-induced densification[46,47] can serve as illustrative examples. Thus, polarization of liquid electrolytes[48] can be interpreted in terms of inertial and stress diffusion as a diffusive separation of ions due to the existence of two opposite forces at the front, stress force and inertial force, induced by the shock wave. Polarization of polar dielectrics[44,45] can be similarly interpreted as a rotation of massive nonuniformly charged molecules in the filed of two forces. It is well established experimentally that the molecule in the shock front tends to turn in such a way that the lighter part of the molecule aligns along the shock wave movement,[45] which also follows from our conclusions. Existence of a single force in the shock front would preclude this alignment and the change of polarity[45] would be impossible to register.

A study on diffusion in shock waves will provide much more quantitative information regarding the forces and the phenomena than polarization measurements. Therefore, comparison with experimental literature and our results presented in Fig. 5 lead us to suggest the possible experiments for studying an inertial diffusion and a separation effect in the shock waves. We suggest that a metallic sample, i.e., iron, doped with a heavy impurity, i.e., gold or lead, be exposed to spherically diverging shock waves. Several techniques currently exist for producing these sorts of shock waves.[40,49,50] Judging from the diffusion coefficient of Au in Fe, redistribution due to diffusion should take place starting from 100 GPa. Ideally, while the shock wave is in a diverging regime, one of the concentration distributions shown in Fig. 5 should be obtained for impurities in the studied sample. Another series of experiments can be set up with both heavy (Au or Pb) and light (Al) impurities in the Fe sample under the one-dimensional shock wave loading. After the shock wave is gone, Au should be mostly segregated on one surface of the sample while Al should be on the opposite surface. Intensity of the separation effect would be reflected in the surface concentration of segregated elements.

V. SUMMARY AND CONCLUSIONS

This work aimed at showing that dynamic processes of defect diffusion might play an important role in enhancing aggregation of defects in organic crystals under shock loading. The structure of shock waves in molecular crystals is described analytically using the conservation laws with a Mie-Gruneinsen equation of state. Molecular and vacancy diffusion is simulated by deriving a point defect diffusion equation and integrating it with the exponential form of the finite difference approximation. It is found that diffusion of point defects in organic molecular crystals under shock loading is due to inertial forces appearing under compression, not due to elastic forces, and therefore, inertial diffusion might have a stronger effect than diffusion in the stress field. The shock wave, while moving across the crystal, creates a very narrow, of the wave front width order of magnitude, chemically active zone with a superhigh vacancy or impurity concentration. In these zones, aggregations of point defects in the form of voids or molecular clusters can occur under favorable conditions.

Inertial forces will always dominate in crystals with large molecular mass and polyatomic molecules. If the molecular crystal contains light impurity atoms or molecules, the inertial force is insignificant, and redistribution of impurities proceeds via stress-assisted mechanisms. If the crystal contains both heavy and light particles, they tend to be separated by the shock front (the separation effect of the shock front). We also suggest an idea for experimental observation of the inertial diffusion and the separation effect in shock waves. The results obtained demonstrate that point defect diffusion may be significant in molecular solids under shock loading and may have important effects on various physical and chemical phenomena in shock waves.

ACKNOWLEDGMENTS

This work has been supported in part by the Division of Materials Research of the U.S. National Science Foundation. Any appearance of findings, conclusions, or recommendations expressed in this article are those of the authors and do not necessarily reflect views of the National Science Foundation. The authors are very grateful to F. J. Zerilli and A. A. Belak for their valuable comments on the manuscript and numerous stimulating discussions.

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*Author to whom correspondence should be addressed.

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