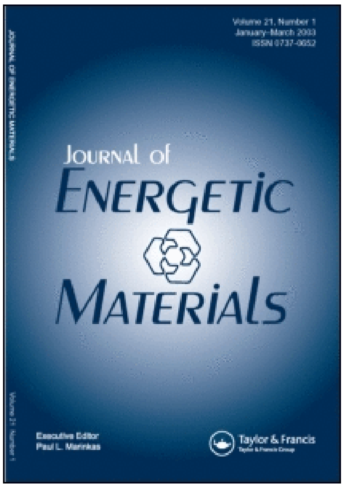

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Molecular Dynamics Simulation of Shock Wave Propagation through RDX Crystal Lattice

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This article provides the results of molecular dynamics (MD) simulation for the process of nonreactive shock wave propagation through hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) crystal lattice. Special attention is paid to the calculation of processes related to redistribution of the kinetic energy of molecular ordered motion behind the shock wave front into the intermolecular and intramolecular vibrations.

Keywords: computer molecular dynamics, detonation, equation of state, modeling

One method for studying the response of energetic materials to intensive external effects is the method of molecular dynamics (MD) simulation. This article provides the results of MD simulation for the process of nonreactive shock wave propagation through hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) crystal lattice. Special attention is paid to the

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calculation of processes related to redistribution of the kinetic energy of molecular ordered motion behind the shock wave (SW) front into the intermolecular and intramolecular vibrations.

To describe interatomic interaction in an RDX crystal, the interatomic force field developed in Smith and Bharadwaj [1] has been used. To perform MD simulation of shock wave propagation through an RDX crystallite, the MD cell shape was a rectangular box having the size 1,344 Å in the direction of shock wave propagation and 71 and 66 Å in the transverse directions. The RDX crystallite was a rectangular box having the size 80 unit cells in the direction of shock wave propagation and 6 unit cells in the transverse directions, parameters of the unit cell are $a = 12.75$ Å, $b = 11.8$ Å, $c = 11.02$ Å. The number of molecules in the crystallite is 23,040, and the number of atoms is 483,840. A shock wave in a crystallite was generated by piston motion on the left crystallite boundary in the (100) crystallographic direction, on the right boundary the free surface was fixed, and periodic boundary conditions were set in the directions transverse to the shock wave propagation direction. To calculate shock wave parameters in the crystallite of interest, cross-sectional layers transverse to the shock wave propagation were specified. The thickness of every layer was 5 Å; thus, every layer held about 90 molecules. We performed these MD simulations using the LAMMPS [2] code.

The temperature of the molecular translation motion (temperature of intermolecular vibrations) and the temperature of atomic vibrations have been calculated in correspondence with the following procedure.

We analyzed each cross-sectional volume in a crystallite, containing N molecules of a similar type, each containing F atoms. Hereinafter the following symbols are accepted: $j = 1, 2, \ldots, N$ are the molecule numbers and $i = 1, 2, \ldots, F$ are the atom numbers in the molecule. A molecule was considered as a classical particle having three translational degrees of motion freedom. The molecular mass is determined by the obvious relationship $\mathrm{M}_\Sigma = \sum_{\mathrm{i}=1}^{\mathrm{F}} \mathrm{m}_\mathrm{i}$, where m_i is an atomic mass with the number i.

Components of center-of-mass velocity of each molecule are determined by the following relationship:

$$
\begin{aligned}
V_{jx} &= \frac{1}{M_\Sigma}\sum_{i=1}^{F} m_{ij}\cdot V_{ijx},\\
V_{jy} &= \frac{1}{M_\Sigma}\sum_{i=1}^{F} m_{ij}V_{ijy},\\
V_{jz} &= \frac{1}{M_\Sigma}\sum_{i=1}^{F} m_{ij}V_{ijz},\\
j &= 1, 2, \ldots N.
\end{aligned} \tag{1}
$$

The double index *ij* denotes the atom with *i* number in the molecule with *j* number.

Thus, the components of center of mass velocity for each cross-sectional volume were determined by the following expressions:

$$V_x = \frac{1}{N}\sum_{j=1}^{N} V_{jx}, \quad V_y = \frac{1}{N}\sum_{j=1}^{N} V_{jy}, \quad V_z = \frac{1}{N}\sum_{j=1}^{N} V_{jz}. \tag{2}$$

The kinetic energy of the molecular thermal motion relative to the center of mass of the specified cross-sectional volume is determined by the following expression:

$$E_K = \frac{M_\Sigma}{2}\cdot\sum_{j=1}^{N}\left[(V_x - V_{jx})^2 + (V_y - V_{jy})^2 + (V_z - V_{jz})^2\right]. \tag{3}$$

Thereafter, the temperature of molecular translation motion (or the temperature of intermolecular vibrations) was calculated in accordance with the relationship

$$T = \frac{2E_K}{3kN}, \tag{4}$$

where *k* is the Boltzmann constant.

The kinetic translation motion energy can be also introduced in x, y, and z directions using the following relationship:

$$\begin{aligned} \mathrm{E_{Kx}} &= \frac{\mathrm{M_{\Sigma}}}{2}\sum_{\mathrm{j=1}}^{\mathrm{N}}\left(\mathrm{V_x} - \mathrm{V_{jx}}\right)^2, \\ \mathrm{E_{Ky}} &= \frac{\mathrm{M_{\Sigma}}}{2}\sum_{\mathrm{j=1}}^{\mathrm{N}}\left(\mathrm{V_y} - \mathrm{V_{jy}}\right)^2, \\ \mathrm{E_{Kz}} &= \frac{\mathrm{M_{\Sigma}}}{2}\sum_{\mathrm{j=1}}^{N}\left(\mathrm{V_z} - \mathrm{V_{jz}}\right)^2. \end{aligned} \tag{5}$$

Corresponding to these energies temperatures T_x, T_y, and T_z are calculated in accordance with the following relationship:

$$\mathrm{T_x} = \frac{2\mathrm{E_{Kx}}}{\mathrm{k}\cdot\mathrm{N}}, \quad \mathrm{T_y} = \frac{2\mathrm{E_{Ky}}}{\mathrm{k}\cdot\mathrm{N}}, \quad \mathrm{T_z} = \frac{2\mathrm{E_{Kz}}}{\mathrm{k}\cdot\mathrm{N}}. \tag{6}$$

When calculating the atomic vibration temperature, atoms were considered as structureless classical particles having three degrees of motion freedom. The temperature is calculated for each type of atom of the ensemble under consideration. The calculation sequence of the atomic vibration temperature is as follows:

1. In the specified volume, the center-of-mass velocity is calculated for the ensemble of the type of atoms involved.
2. The velocity of each atom of the given type is calculated relative to the center of mass for the type of atoms involved.
3. The full kinetic energy of chaotic motion of atoms is calculated relative to the center of mass for the type of atoms involved.
4. The kinetic energy is recalculated into the temperature.

Let the specified cross-sectional volume hold N atoms of the given type with mass m. Obviously, the center-of-mass components for the considered ensemble of atoms of the given type are determined by the following expressions:

$$\mathrm{V_x = \frac{1}{N}\sum_{i=1}^{N} V_{xi}, \quad V_y = \frac{1}{N}\sum_{i=1}^{N} V_{yi}, \quad V_z = \frac{1}{N}\sum_{i=1}^{N} V_{zi}.}$$

The kinetic energy of the thermal motion relative to the center of mass is equal to

$$\mathrm{E_K = \frac{m}{2}\sum_{i=1}^{N} V_i^2,}$$

where

$$\mathrm{V_i^2 = (V_x - V_{xi})^2 + (V_y - V_{yi})^2 + (V_z - V_{zi})^2.}$$

Recalculation of the kinetic energy to the temperature is performed according to the relationship

$$\mathrm{T = \frac{2 \cdot E_K}{3 \cdot k \cdot N} = \frac{m}{3 \cdot k \cdot N} \cdot \sum_{i=1}^{N} V_i^2.} \tag{7}$$

If the temperature is known for each type of atom within the specified volume, the average temperature after equilibrium is established can be calculated using the relationship

$$\mathrm{\langle T \rangle = \sum n_i \cdot T_i,} \tag{8}$$

where n_i is a numerical fraction of atom of the i type, $\mathrm{n_i = N_i / \sum_{i=1}^{N} N_i}$, and T_i is the temperature of the ensemble of atoms of the i type.

For testing the force field from Smith and Bharadwaj [1], initially we have performed calculations of the P-V_o/V curve for an isotropically compressed RDX crystal at $T = 300\,\mathrm{K}$. The calculated results based on this force field were compared to the experimental data and to the results of other calculations [3–6]. The results of this comparison are shown in Fig. 1.

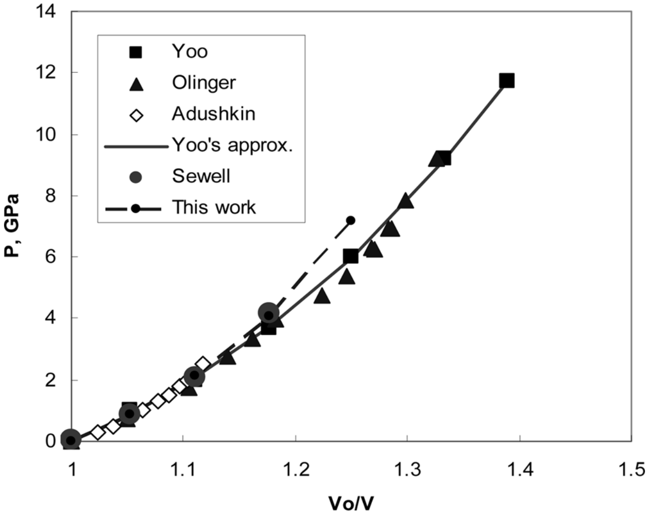

Figure 1. Pressure as a function of hydrostatic compression of RDX molecular crystal.

As can be seen from the given comparison, the calculated data based on the potential from Smith and Bharadwaj [1] agree well with the experimental data up to a compression value of 1.2 corresponding with the phase transition at 4 GPa.

A D-U diagram obtained by the MD simulation method is given in Fig. 2. The same picture shows the experimental dependence [7]. As is seen from the given data, with the use of potential from Smith and Bharadwaj [1] the dependence of the shock wave velocity on the value of particle velocity is reproduced reasonably well within the wide range of changing particle velocity values.

The results of MD simulation allowed us to determine the width of the shock jump in an RDX crystal. Figure 3 presents a visual representation of one of the versions of simulation and the shock jump width. Initial temperature of RDX crystal was 300 K, and particle velocity was 2 km/s.

Figure 4 shows one of the calculation versions related to the time dependence of molecular and atomic vibration temperatures in the specified volume. As is seen from the given data,

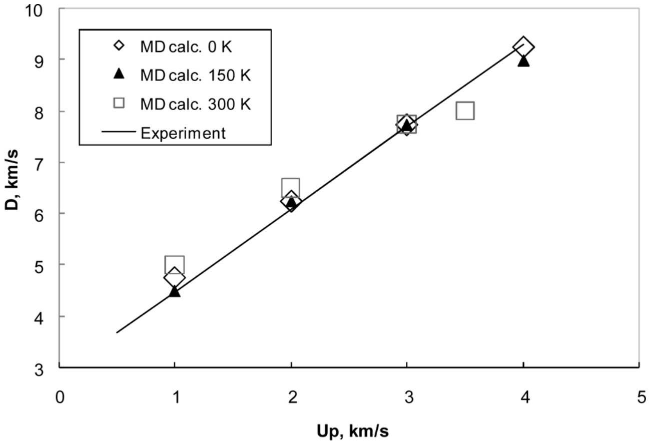

Figure 2. Shock wave velocity as a function of particle velocity.

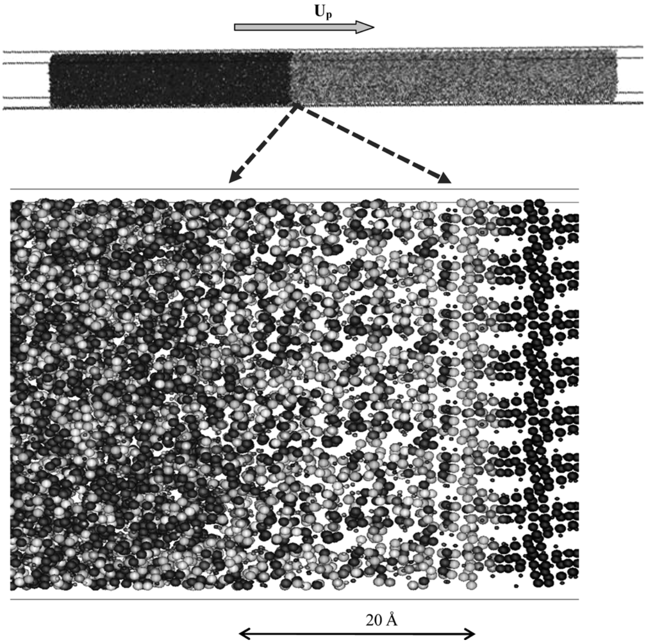

Figure 3. Shock jump width in RDX crystal.

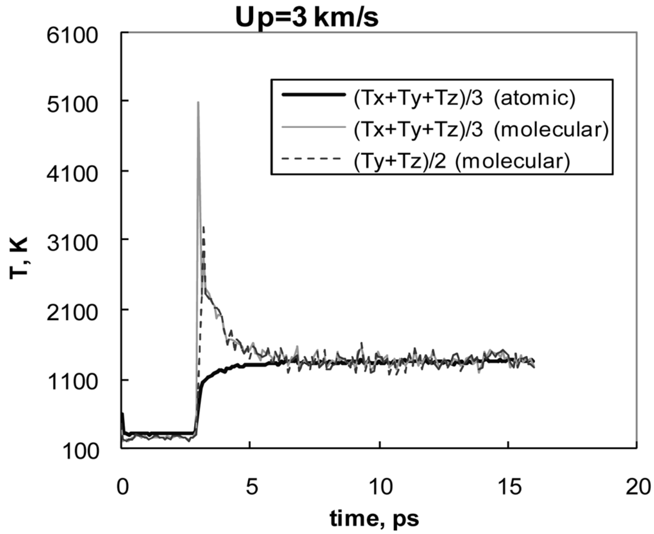

Figure 4. Molecular and atomic vibration temperature as a function of time.

the method of direct MD simulation related to shock wave propagation in RDX crystal allows the registration of the "overheat" of molecular vibrations behind the shock wave front. This effect was qualitatively and quantitatively examined in the literature [8–12].

The results of MD simulation allow us to determine the relaxation time of the energy of RDX molecular ordered motion behind the shock wave front in all vibrational degrees of freedom of a molecular crystal, which is practically the time of phonon–vibron relaxation. Figure 5 shows the dependence of the phonon–vibron relaxation time on the particle velocity of RDX molecules behind the shock wave front. The phonon–vibron relaxation time was calculated as time from maximum intermolecular vibrations temperatures until the moment of equilibration of intermolecular vibrations temperature and temperature of atomic vibrations.

Selezenev et al. [13] provided the calculation of kinetic energy redistribution time throughout intramolecular vibrational

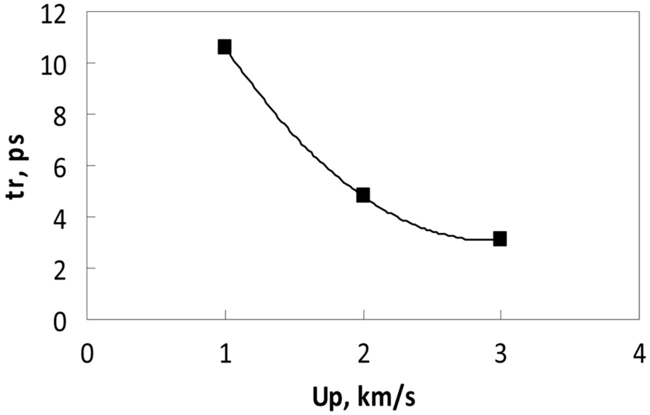

Figure 5. Phonon–vibron relaxation time as a function of particle velocity of high-explosive molecules behind a shock wave front.

modes of the isolated RDX molecule. This time is ~ 3.5 ps. As is seen from Fig. 5, with high intensities of shock waves the phonon–vibron relaxation time becomes limited by the time of energy redistribution throughout intramolecular vibrational modes of molecules.

Using the ratio $\Delta X_r = D \cdot t_r$ one can estimate the spatial width of a phonon–vibron relaxation zone (ΔX_r). Figure 6 shows the phonon–vibron relaxation zone vs. particle velocity of RDX molecules behind the shock wave front.

The values of the molecular vibration maximum temperature and the atomic vibration equilibrium temperature behind the shock wave front are given in Fig. 7.

Figure 8 shows the ratio between the values of the maximum temperature of molecular vibrations and the equilibrium temperature behind the shock wave front as a function of RDX molecular particle velocity.

As can be seen from the results, the maximum values of molecular vibration overheat obtained by the method of MD simulation makes up the value $T_{mol}/T_{eq} \cong 4$, which is significantly lower than the maximum theoretically possible value.

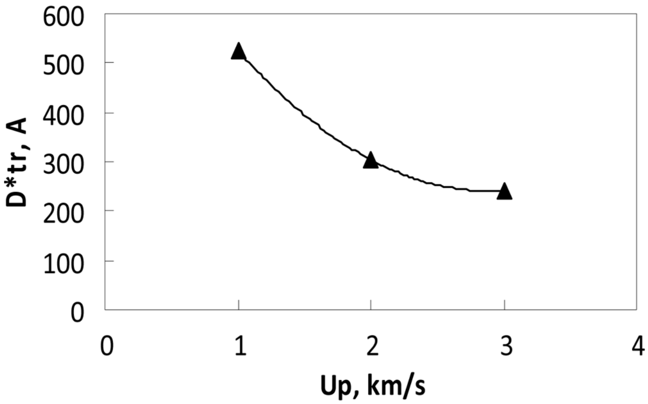

Figure 6. Phonon–vibron relaxation zone as a function of particle velocity of RDX molecules behind shock wave front.

The maximum temperature of molecular vibrations can be obtained from the following considerations [7,8]. Assuming that at the initial stage of the crystal compression at a shock front

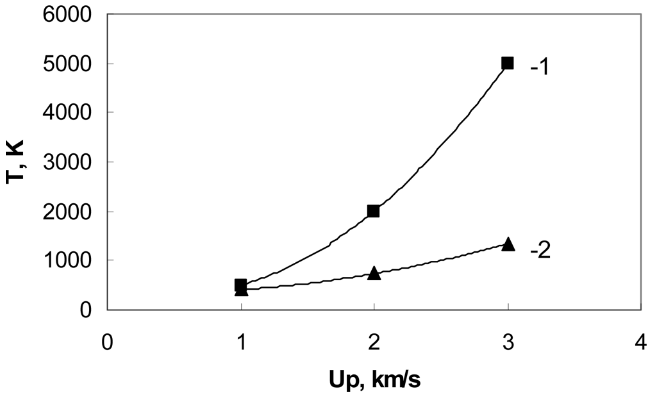

Figure 7. Values of molecular vibration maximum temperature and atomic vibration equilibrium temperature behind the shock wave front as a function of RDX molecule particle velocity. (1) Molecular vibration maximum temperature and (2) equilibrium temperature behind shock wave front.

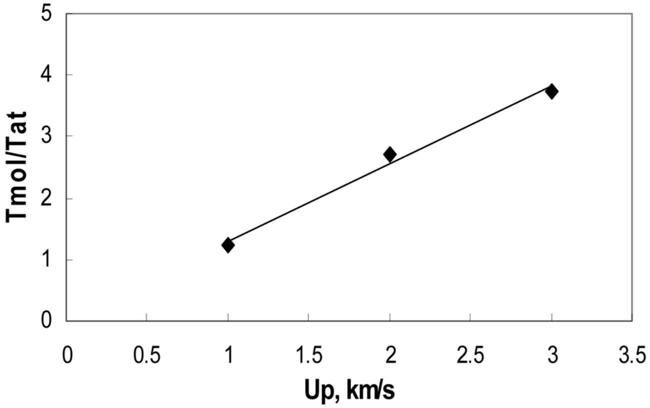

Figure 8. Ratio between the values of the maximum temperature of molecular vibrations and the equilibrium temperature as a function of RDX molecular particle velocity.

the thermal energy is concentrated only at molecular vibrations, one can write the following relationship:

$$\frac{1}{2}\cdot\frac{\mathrm{M}_{\Sigma}\cdot\mathrm{U}_{\mathrm{P}}^{2}}{2}=\frac{3}{2}\mathrm{kT}_{\mathrm{mol}}-\frac{3}{2}\mathrm{kT}_{0}, \tag{9}$$

$$\frac{1}{2}\cdot\frac{\mathrm{M}_{\Sigma}\cdot\mathrm{U}_{\mathrm{P}}^{2}}{2}=\frac{3}{2}\mathrm{N}\cdot\mathrm{kT}_{\mathrm{eq}}-\frac{3}{2}\mathrm{N}\cdot\mathrm{kT}_{0}, \tag{10}$$

where U_P is the RDX molecular ordered velocity behind the shock wave front, M_Σ is the mass of one molecule, k is the Boltzmann constant, T_{mol} is the molecular vibration temperature, T_0 is the crystal initial temperature, N is the number of atoms in an RDX molecule, and T_{eq} is the equilibrium temperature behind the shock wave front.

From the relationship (9), (10)

$$\frac{T_{mol}-T_0}{T_{eq}-T_0}=N$$

was found or

$$\frac{\mathrm{T_{mol}}}{\mathrm{T_{eq}}} = \mathrm{N} \cdot \left(1 - \frac{\mathrm{T_0}}{\mathrm{T_{eq}}}\right) + \frac{\mathrm{T_0}}{\mathrm{T_{eq}}}. \tag{11}$$

With regard to numerical values of parameters included into the relationship (11), $N = 21$, $T_0 = 300\,\mathrm{K}$, $T_{eq} \cong 1300\,\mathrm{K}$, we obtain $T_{mol}/T_{eq} \cong 16$. Obviously the understated value of the maximum molecular vibration temperature obtained with MD simulation is a consequence of the classical approximation used in this method when simulating vibrations and collisions of molecules.

Using the relationship $P = \rho \cdot D \cdot U_p$, where ρ is the density of a crystal ahead of the shock wave front, D is the shock wave velocity, and U_P is the particle velocity behind the shock wave front, the temperature dependence on particle velocity U_P, given in Fig. 7, can be transformed depending on the pressure value at the shock wave front. The dependences of the maximum temperature of molecular vibrations and the equilibrium

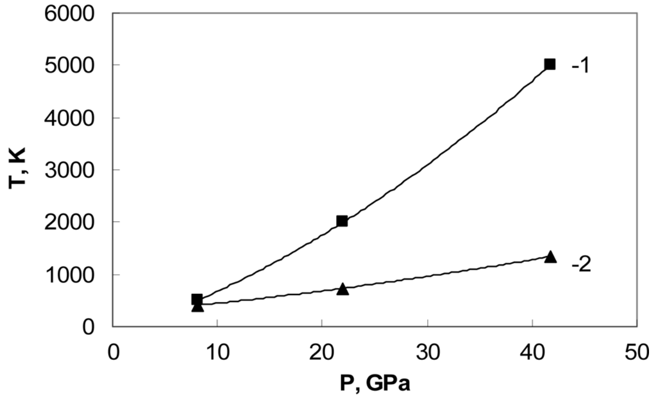

Figure 9. The maximum temperature of molecular vibrations and the equilibrium temperature of atomic vibrations behind the shock wave front as a function of pressure behind the shock wave front. (1) Maximum temperature of molecular vibrations and (2) equilibrium temperature behind the shock wave front.

temperature of atomic vibrations behind the shock wave front on the pressure value are presented in Fig. 9.

As is seen from the results presented in Fig. 9, the maximum temperature of molecular vibrations begins to exceed the value of the equilibrium temperature behind the shock wave front starting from a pressure value of about 10 GPa.

Conclusion

The method of nonequilibrium molecular dynamics has been used to calculate the Hugoniot and to determine the width of a shock jump range for an RDX molecular crystal. Using the MD method we determined the maximum temperature values of molecular vibrations behind the shock wave in single-crystal RDX. We obtained the curves of the molecular vibration maximum temperature and the atomic vibration equilibrium temperature behind the shock wave front as a function of shock wave pressure. The method of nonequilibrium MD simulation has been used to obtain the phonon–vibron relaxation time as a function of the particle velocity value.

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