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Method for Effective Increasing the Decomposition Rate of Ammonium Perchlorate in Solid Rocket Fuel

Ammonium perchlorate (AP) is a common oxidizer in solid rocket propellants. For devices, the most important parameter of which is the speed of movement, the key correlation is between the jet thrust and the combustion rate of fuels and, consequently, the rate of thermal decomposition of the AP. To increase the decomposition rate of AP, fuel, aluminum powder, is used in the form of nanoparticles. The aim of this work is to identify the decomposition mechanism of AP molecules under conditions where aluminum nanoparticles, in addition to acting as a fuel, also act as catalysts for the decomposition of AP. The result of spraying aluminum nanoparticles into multiple nanoclusters in the fuel combustion zone due to the melting of nanoparticle cores and the destruction of aluminum oxide shells is considered. In this case, aluminum nanoclusters become sources of terahertz (THz) radiation. Since the frequencies of vibrational and rotational oscillations in AP molecules are in the THz range, irradiation of AP molecules with THz photons promotes their decomposition. It is proposed to use emission of THz photons by aluminum nanoclusters, increasing its intensity by introducing 3*d* impurities into aluminum, which increase the density of electron states near the Fermi level of aluminum.

Keywords: aluminum nanoparticle, ammonium perchlorate, catalysis, nanocluster, terahertz.

Introduction

Improving the performance of solid rocket fuel by reducing the particle size scale of the oxidizer, ammonium perchlorate (AP) NH_4ClO_4 [1], and the fuel, dispersed aluminum [2], from the micrometric to the nanometric level has been the subject of research over the last decade. One of the main goals of the research was to find a way to effectively increase the rate of thermal decomposition of AP in fuel in order to increase jet thrust.

Of particular value are studies on the dispersion of aluminum nanoparticles into nanoclusters in the fuel combustion zone [3–6] — as a result of melting of the nanoparticle core, rupture of the oxide shell on them, and splashing of molten aluminum due to high internal pressure in the molten core. Nanoclusters are fragments of molten aluminum nanoparticles several nanometers in size. These works [3–6] suggest that in the fuel combustion zone, in addition to accelerating the decomposition of AP due to the grinding of aluminum nanoparticles (increasing the area of interaction of aluminum with the oxidizer), aluminum nanoclusters become sources of spontaneous terahertz (THz) radiation, which can be used to accelerate the decomposition of AP molecules. Although there is insufficient data on the absorption spectra of AP in the THz range, and the available information is contradictory and fragmentary, it is still known that the frequencies of the lattice vibrations of the NH_4ClO_4 crystal and the rotation of the NH_4^+ ion in the crystal [7–10] lie in the THz range.

Spontaneous emission of THz photons by aluminum nanoclusters

The physical mechanism of THz photon emission by an aluminum nanocluster is illustrated in Figure 1, where a Fermi electron with momentum $\boldsymbol{p}_F$ absorbs a vibrational mode (longitudinal phonon) with momentum $\boldsymbol{q}^*_{vm}$ propagating along the nanocluster diameter D. An excited electron with momentum $\boldsymbol{s}$ moves along a chord H, Figure 1(*a*). In the energy–momentum space, this process is illustrated in Figure 1(*b*), where the paraboloid is the dispersion surface of electrons, and the cone-shaped bells are the dispersion surfaces of longitudinal phonons. Relevant formulas to Figure 1 and numerical values of the parameters: $s = [2m\cdot(E_F + E_{vm})]^{1/2}$; $\gamma = \arccos[(2m\cdot E_{vm} + q^{*2}_{vm})/(2s\cdot q^*_{vm})]$; Fermi energy in Al: $E_F = 11.7$ eV [11; 51]; energy of dominant longitudinal phonons in Al: $E_{vm} \approx 34.8$ meV; magnitude of the momentum of dominant longitudinal phonons in Al: $q^*_{vm} \approx 1.2\ 10^{-19}$ g cm s^{-1}; with these parameters, the angle $\gamma = 71°$.

The excited electron, due to the Coulomb interaction with the positive aluminum ions, could induce a secondary longitudinal phonon with a momentum collinear to the momentum $\boldsymbol{s}$; and this would be a way of relaxation of the excited electron. However, in nanoclusters smaller than the electron mean free path, this mechanism is impossible, and relaxation occurs through photon emission. Other reasons that take into account the confinement of electrons and longitudinal phonons in nanoclusters are the following.

The first reason conditioning the emission is the difference in the quantization steps of momenta of longitudinal phonons propagating along the nanocluster's diameter D and the chord H, equal to h/D and h/H, respectively (here h is Planck's constant). Consequently, the steps of energy quantization for these two directions of phonon propagation also do not coincide. Due to the mismatch of quantized energy levels, the energy transfer from the excited electron to the secondary phonon is impossible (indeed, the Fermi electron received energy from the primary phonon quantized with a certain step, and it cannot generate a secondary phonon, energy of which would be quantized with a different step).

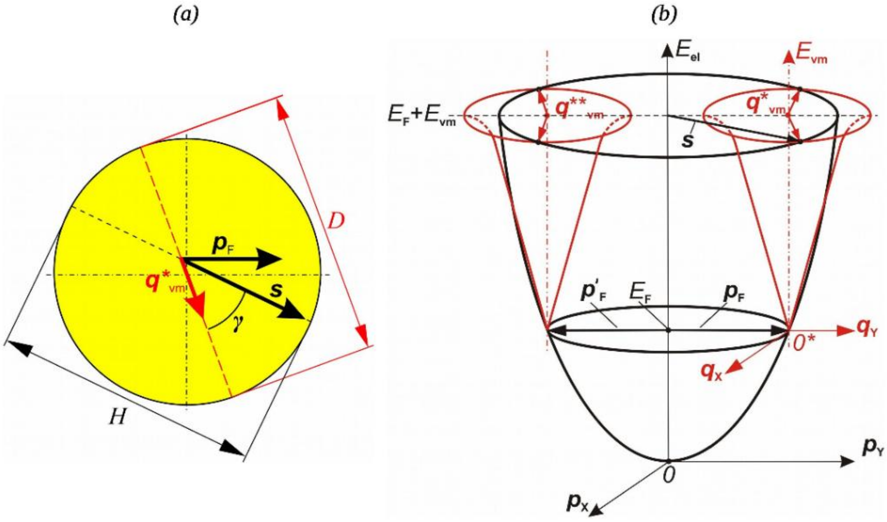

Figure 1. Absorption of a vibrational mode (longitudinal phonon) with momentum $\boldsymbol{q}^*_{\mathrm{vm}}$ by a Fermi electron with momentum $\boldsymbol{p}_{\mathrm{F}}$ in an aluminum nanocluster. The excited electron with momentum $\boldsymbol{s}$ moves along the chord H.

Another reason that excludes the excitation of a secondary phonon and, therefore, favors the emission of a photon is the following. As the nanoparticle diameter decreases, the gap between the energy levels of longitudinal phonons for the direction of propagation along the vector $\boldsymbol{s}$ increases, and eventually a situation may arise where the gap exceeds the full width at half maximum of the peak of the longitudinal phonon energy distribution $\mathrm{FWHM_L}$. Figure 2 shows the threshold state at which the energy step of vibration modes in a nanocluster $\Delta E_{\mathrm{vm}H}$, propagating along the chord H with momentum $\boldsymbol{s}$, exceeds the value of $\mathrm{FWHM_L}$. As a result, the energy level of the excited electron "hangs" between the levels of longitudinal phonons for the $\boldsymbol{s}$ direction: there are no levels to which the electron could transfer its energy. Consequently, the electron will relax, scattering at the boundary of the nanocluster, with the emission of a photon (the electron cannot leave the nanoparticle, since its energy is less than the work function of the electron in aluminum, ≈4.25 eV [11; 364]).

For the direction "along the chord H", the quantization steps of vibrational modes in momentum and energy are equal, respectively, to h/H and $\Delta E_{\mathrm{vm}H} \approx v^*_{\mathrm{L}} \cdot (h/H)$, where v^*_{L} is the propagation velocity of longitudinal phonons with energies within the FWHML region. The value of the velocity v^*_{L} is less than the nominal speed of sound in aluminum $v_{\mathrm{L}} = 6.5\ 10^5$ cm s^{-1} due to the curvature of the dispersion curve of longitudinal phonons near the boundary of the Brillouin zone, where the energies of longitudinal phonons corresponding to the $\mathrm{FWHM_L}$ are located.

Obviously, the gap between energy levels must take into account the consequence of Heisenberg's uncertainty principle. As a criterion for "complete divergence" of phonon levels, a situation was chosen in which two adjacent energy levels moved apart by an amount exceeding the $\mathrm{FWHM_L}$, taking into account the uncertainty in the energy of the levels. Such a threshold situation is shown in Figure 2, where the value of $\delta E_{\mathrm{vm}H}$ is calculated taking into account the Heisenberg uncertainty relation for the phonon momentum and coordinate, $\delta E_{\mathrm{vm}H} \geq v^*_{\mathrm{L}} \cdot h/(2\pi H)$. The inequality that determines the corresponding threshold chord length (such that at shorter chord lengths intense photon emission occurs) is as follows:

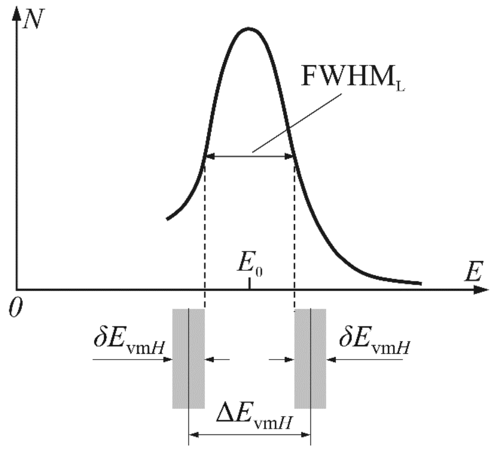

Figure 2. The threshold state at which the energy step of vibrational modes in a nanocluster ΔE_{vmH}, propagating along the chord H with momentum **s**, exceeds the FWHM$_L$ value for the energy distribution of longitudinal phonons in an aluminum nanocluster.

$$\Delta E_{vmH} > \mathrm{FWHM}_L + (\delta E_{vmH}/2) + (\delta E_{vmH}/2) \geq \mathrm{FWHM}_L + v^*_L \cdot h/(2\pi H) \qquad (1)$$

Substituting the value $\Delta E_{vmH} \approx v^*_L \cdot (h/H)$ into the left-hand side of inequality (1), we obtain:

$$v^*_L \cdot (h/H) > \mathrm{FWHM}_L + v^*_L \cdot (h/2\pi H)$$

$$\text{or } H < [1 - \cdot(1/2\pi)] \cdot v^*_L \cdot (h/\mathrm{FWHM}_L). \qquad (2)$$

If this inequality is satisfied, excited electrons will not be able to relax with the excitation of secondary phonons — they will emit photons. In this case, the energies of the emitted photons will correspond to the THz range, since the energies of the dominant primary phonons belong to the THz energy region: in aluminum, the FWHM$_L$ region of the longitudinal phonon energy distribution lies in the band ≈31–38 meV [12], that is, in the frequency range ≈7.5–9 THz.

It should be noted that so-called two-phonon processes can take place: an excited electron, if it cannot excite a secondary phonon with an energy exactly equal to the energy acquired E_1 from the primary phonon, can excite a secondary phonon of lower energy E_2, and transfer the difference in the energies of the primary and secondary phonons $\Delta E = E_1 \text{ — } E_2$ to the electron [13]. And the electron will not be able to relax with the excitation of the phonon and emits a photon. Then the region of frequencies generated by the nanocluster will expand and, possibly, cover a sufficient part of the phonon spectrum in the AP molecule.

Substituting the numerical values of the quantities ($v^*_L \approx 4{,}7 \cdot 10^5$ cm s^{-1}; FWHM$_L$ ≈7.9 meV) into inequality (2), we obtain an estimate of the chord lengths for which the vibration mode levels diverge by an energy gap $\Delta E_{vmH} > \mathrm{FWHM}_L$: $H < 2.1$ nm.

Let the “threshold” chord of length $H_0 = 2.1$ nm be the chord of minimum length of all chords that form an angle of $\gamma = 71°$ with the nanocluster diameter; it contacts the nanocluster diameter on its surface. Then the “threshold” diameter of the nanocluster $D_0 = H_0/\cos\gamma = 6.45$ nm. Aluminum nanoclusters are smaller than D_0 will be the most intense sources of THz photons.

Let $\Delta E_D \approx v^*_L \cdot (h/D)$ be the energy step for longitudinal phonons traveling along the diameter of the nanocluster. The greater the stacking multiplicity of the energy step ΔE_D within the FWHM$_L$ width (for example, with an increase in the nanocluster diameter D), that is, the greater the value of ($\mathrm{FWHM}_L/\Delta E_D$), the higher the probability of superposition of the energy level extended to δE_{vmH} on the energy level of the primary phonon, which will lead to relaxation of the excited electron with the generation of a secondary phonon (with the energy of the primary phonon). And the lower the intensity of spontaneous emission of photons, and the lower the catalytic activity of the nanocluster.

Method for increasing the intensity of THz photon emission by aluminum nanoclusters

Spontaneous emission of THz photons by aluminum nanoclusters can be used to accelerate the decomposition of AP molecules. To do this, it is necessary to use nanoparticles of aluminum containing impurity atoms of the so-called 3*d*-metals, elements of the 4th row of the Periodic Table: V, Cr, Mn. In such systems, the energies of the electron *d*-levels of impurity atoms are located near the Fermi level of aluminum, due to which the density of states of Fermi electrons increases significantly. The use of nanoparticles from the Al-

V, Al-Cr and Al-Mn systems would make it possible to obtain in the nanoclusters of these systems increased numbers of electrons participating in the processes of absorption of longitudinal phonons and emission of THz photons, due to which it would be possible to increase the intensity of irradiation of AP molecules with THz radiation and accelerate their decomposition.

Figure 3 shows a summary picture of the density of states of electrons in aluminum with impurities of 3*d* elements (based on the results of works [14–19]). The energy axis shows the position of the Fermi level E_F for the intermetallic compound FeAl.

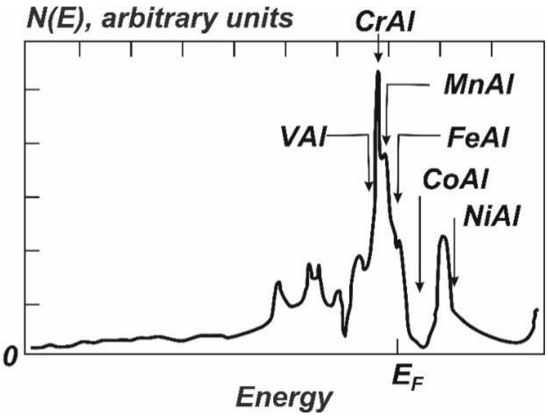

Figure 3. Summary picture of the locations of Fermi levels (indicated by arrows) in intermetallic compounds of Al and 3*d* metals on the distribution of the electron density of states by energy (based on the results of works [14–19]).

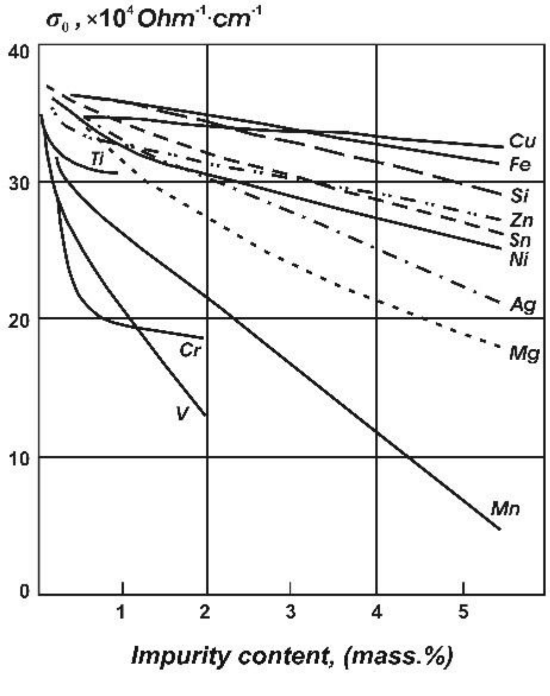

Figure 4. Change in the direct current specific electrical conductivity of Al when impurities are introduced into it [20].

The feasibility of the proposed approach is confirmed by data on the behavior of the specific electrical conductivity of aluminum when introducing even a small amount of impurities of V, Cr and Mn (~ 1–4 mass.%) [20] (Fig. 4).

From Figure 4 it is evident that with impurities of ~1 mass.% V or Cr the conductivity of Al decreases by approximately 2 times; this means that the mean free path of electrons l_{mfp} also decreases by 2 times. For bulk aluminum, $l_{mfp} \approx 18.9$ nm [21]. This means that for aluminum with 1 mass% V or Cr, the electron mean free path is $l_{mfp} \approx 9.45$ nm. Approximately the same length $l_{mfp} \approx 9$ nm will be for aluminum with

2 mass.% Mn. Therefore, if the size of aluminum nanoclusters-splashes containing such concentrations of impurity atoms of V, Cr or Mn is less than 9 nm, then they will emit THz photons and become catalysts for the decomposition of AP molecules. A rough estimate of the size of aluminum nanoclusters-splashes obtained as a result of dispersion of melts of 20–120 nm nanoparticles is known [3, 4]: 5–10 nm. Aluminum 5–10 nm nanoclusters with an unoxidized surface are already produced in the form of polymer nanocomposites (the binder is hydroxyl-terminated polybutadiene (HTPB) containing aluminum nanoclusters grown *in situ*) and demonstrate a high combustion rate, more than five times higher than that of conventional ALEX aluminum nanopowders [22].

The concept of *in situ* nanocluster formation in polymer nanocomposites [23], in principle, also includes the idea of obtaining nanoclusters-splashes of molten aluminum *in situ* — in the combustion zone, in already burning fuel, with fuel from a mixture of a polymer binder and aluminum nanoparticles, and an oxidizer, AP.

Unfortunately, we were unable to find data on the absorption of HTPB in the THz frequency range.

One of the possible ways to further increase the intensity of spontaneous emission of THz photons by nanoclusters is the use of *f*-element impurity atoms in aluminum instead of 3*d* impurities. So-called electron systems with “heavy fermions” are known [24, 25], characterized by a very high density of states of *f*-electrons near the Fermi level — more significant than in the case of using 3*d*-element impurities, for example, the compound $CeAl_3$. It seems appropriate to conduct studies of the decomposition rate of ammonium perchlorate using dispersed aluminum in the form of a mixture of nanoparticles of ordinary aluminum and $CeAl_3$ nanoparticles with a variation in the composition of the mixture.

Discussion

How to implement the approach using aluminum nanoparticles with 3*d* metal impurities? There are industrially produced aluminum alloys with an impurity element Mn (“alloying component”), of which the АМц1 alloy (Table), containing a sufficient amount of manganese, appears to be a promising alloy. This alloy could become a raw material for the production of nanoparticles.

Table 1

Composition of industrial aluminum alloys

lloy brand	Alloying components, mass%			
	Al	Cu	Mg	Mn
AMts [20]	Base of the alloy	–	–	1.0–1.6
AMts1 [26]	Same	?	?	2.0–4.5
MM [20]	Same	–	0.2–0.5	1.0–1.4
AMg6 [20]	Same	–	5.8–6.8	0.5–0.8
D16 [20]	Same	3.8–4.9	1.2–1.8	0.3–0.9

From Table 2 [26] it can be seen that, compared to other 3*d* metals, the solubility of Mn in Al is increased. Nanoparticles of aluminum intermetallic compounds could be produced from alloys obtained by the method of self-propagating high-temperature synthesis of aluminides [27–30] or by the method of exploding wires from the AMts1 alloy — this method of industrial production of metal nanopowders has been mastered [31].

Conclusions

Recently, the concept of forming nanoparticles *in situ* — directly in the matrix or binder — has been developed in the development of polymer composites. It has also found application in the production of polymer fuel in the form of 5–10 nm aluminum nanoclusters grown *in situ* in a polymer binder, hydroxyl-terminated polybutadiene (HTPB).

In this paper, it is proposed to develop this concept to obtain nanoclusters-splashes of molten aluminum containing impurity atoms of V, Cr or Mn, *in situ* — in **burning** fuel, with a fuel consisting of a polymer binder (hydroxyl-terminated polybutadiene) and 100–120 nm nanoparticles of Al-V, Al-Cr or Al-Mn intermetallic compounds, and an oxidizer (ammonium perchlorate).

Table 2

Maximum solubility of a number of 3*d* metals in aluminum [27]

System	Maximum solubility, mass.%	
	Equilibrium solubility	Nonequilibrium solubility
Al-Ti	0.24	0.35
Al-Cr	0.77	5.7
Al-Mn	1.82	10.2
Al-Fe	0.052	0.2

It has been shown that nanoclusters of aluminum containing impurity atoms of V, Cr or Mn, smaller than 9 nm in size, can become sources of terahertz radiation and contribute to the acceleration of the decomposition of ammonium perchlorate molecules in solid rocket fuel. This should result in increased jet thrust.

A promising development is the study of the decomposition rate of ammonium perchlorate using dispersed aluminum in the form of a mixture of nanoparticles of ordinary aluminum and nanoparticles of $CeAl_3$– with a variation in the composition of the mixture.

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Қатты ракета отынында аммоний перхлоратының ыдырау жылдамдығын тиімді арттыру әдісі

Аммоний перхлораты (АП) қатты зымыран отындарында кең таралған тотықтырғыш. Ең маңызды параметрі қозғалыс жылдамдығы болып табылатын құрылғылар үшін негізгі корреляция ағынның күші мен жанармайдың жану жылдамдығы, демек, АП термиялық ыдырау жылдамдығы арасында болады. АП ыдырау жылдамдығын арттыру үшін отын, алюминий ұнтағы, нанобөлшек түрінде қолданылады. Жұмыстың мақсаты алюминий нанобөлшектері отын ретінде әрекет етумен қатар, АП ыдырауының катализаторы ретінде де әрекет ететін жағдайларда АП молекулаларының ыдырау механизмін анықтау. Алюминий нанобөлшектерін нанобөлшектердің өзектерінің балқуына және алюминий оксидінің қабықшаларының бұзылуына байланысты жанармай жану аймағындағы көптеген нанокластерлерге шашырату нәтижесі қарастырылады. Бұл жағдайда алюминий нанокластерлері терагерц (ТГц) сәулелену көздеріне айналады. АП молекулаларындағы тербеліс және айналу тербелістерінің жиіліктері ТГц диапазонында болғандықтан, ТГц фотондарымен АП молекулаларының сәулеленуі олардың ыдырауына ықпал етеді. Алюминийдің Ферми деңгейіне жақын электрон күйлерінің тығыздығын арттыратын алюминийге 3*d*-қоспаларды енгізу арқылы оның қарқындылығын арттыра отырып, алюминий нанокластерлерінің ТГц фотондарының эмиссиясын пайдалану ұсынылады.

Кілт сөздер: алюминий нанобөлшегі, аммоний перхлораты, катализ, нанокластер, терагерц.

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Способ эффективного повышения скорости разложения перхлората аммония в твердом ракетном топливе

Перхлорат аммония (ПХА) — распространенный окислитель в твердых ракетных топливах. Для устройств, важнейшей характеристикой которых является скорость движения, ключевая корреляция — между реактивной тягой и скоростью горения топлив и, следовательно, скоростью термического разложения ПХА. Для повышения скорости разложения ПХА, горючее, порошок алюминия, применяют в виде наночастиц. Цель этой работы — выявление механизма разложения молекул ПХА в условиях, когда наночастицы алюминия, помимо выполнения роли горючего, являются и катализаторами разложения ПХА. Рассматривается результат распыления наночастиц алюминия на множество нанокластеров в зоне горения топлива из-за плавления ядер наночастиц и разрушения оболочек оксида алюминия. При этом нанокластеры алюминия становятся источниками спонтанного терагерцевого (ТГц) излучения. Поскольку частоты колебательных и вращательных осцилляций в молекулах ПХА находятся в ТГц диапазоне, облучение молекул ПХА ТГц фотонами способствует их разложению, так как вынужденные осцилляции молекул ослабляют внутримолекулярные связи. Авторами предложено использовать спонтанную эмиссию ТГц фотонов нанокластерами алюминия, повысив её интенсивность путём внедрения в алюминий *3d*-примесей, повышающих плотность состояний электронов вблизи уровня Ферми алюминия.

Ключевые слова: катализ, нанокластер, наночастица алюминия, перхлорат аммония, терагерц.

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