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## SELF-OSCILLATIONS IN SOLID METHANE IRRADIATED BY ELECTRONS

The formation of self-oscillations of temperature and concentration of radicals in an electron-irradiated methane film at low temperatures has been investigated experimentally and theoretically. Self-oscillations arise due to the activation nature of diffusion and radical recombination processes. Self-oscillations were studied experimentally by measuring the desorption of particles from an irradiated sample and theoretically by solving the kinetic equations for defects in a methane sample. Concentration self-oscillations of two types of particles have been found and investigated; namely, hydrogen atoms and CH<sub>3</sub> radicals formed during the irradiation of methane by electrons. It is shown that with an increase in the irradiation intensity, the oscillation periods decrease, and the calculation value are of the order of magnitude observed in the experiment. A model of a manifestation of the self-oscillation of hydrogen molecule concentration during desorption is presented.

*Keywords:* methane, electron irradiation, self-oscillations, temperature, defects.

### 1. Introduction

One of the consequences of the interaction between the fast-charged particles and solids is the accumulation of defects. Atoms displaced from the equilibrium position may occupy positions that are not optimal from the energy point of view and form various complexes. As the number of defects increases, energy accumulates in the material. This state is nonequilibrium and can have a long lifetime. For various physical reasons, the stored energy can be released. Depending on the time and nature of the irradiation, the type of material, and the conditions for the energy release, the arising effects can be very diverse. When a crystal is heated, the processes of atomic motion are intensified and atoms come to equilibrium positions, i.e. annealing of defects occurs. Upon annealing, defects disappear with the exception of very complex ones. The release of stored energy facilitates the annealing process. There may be positive feedback in the system when increased temperature leads to the energy release processes, which result in further temperature increases. In this case, when the material is irradiated and defects are accumulated, a fluctuation increase in temperature can lead to the annealing of some of the defects. The released energy will stimulate a further increase in temperature and annealing of other defects. Instability associated with the rapid release of energy may arise in the system and a temperature burst may occur. This process of abrupt heating of the system is called the

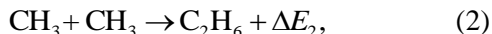
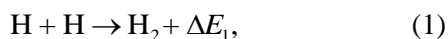
Wigner effect [1]. The effect can result in the destruction of the material and emergencies during prolonged exposure of the material.

However, instability may develop in a different scenario. Since the number of defects created by an external source is limited and decreases with time due to their annealing, the temperature increase process will slow down and stop after the number of defects is exhausted. In this case, the temperature drops to the initial value. With stationary irradiation, defects begin to appear again, and their concentration and temperature rise again, and the defects are annealed. Thus, the periodic fluctuations in temperature and the number of defects will be developed in the material with time. Such fluctuations are called temperature self-oscillations. Temperature self-oscillations were studied under nuclear irradiation and corresponding models are described in [2 - 5]. They were experimentally observed in jumps or the oscillatory dependence of the electrical conductivity of samples under stationary irradiation [6 - 8]. In [9], a theoretical study and experimental observation of the exciton density self-oscillations in a deuterobenzophenone crystal doped with benzophenone was carried out using the emission spectra obtained under optical pumping.

Self-oscillations in methane were first detected by John M. Carpenter upon irradiation of crystalline methane with neutrons [2]. Methane was used as a neutron moderator as being three times more effective than liquid hydrogen. During irradiation,

temperature bursts of several tens of degrees Kelvin were observed. The spontaneous release of energy, which ultimately leads to the destruction of the moderator's container, attracted considerable attention, and stimulated further research [10 - 14].

The phenomenon was explained by the accumulation of methyl radicals upon neutron irradiation. The most effective decay channel for a methane molecule  $\text{CH}_4$  under the influence of incident particles is the formation of a methyl radical  $\text{CH}_3$  and hydrogen atom  $\text{H}$ . Calculations of the processes of recombination of defects created by irradiation with heat release made in the approximation of a generalized type of defects [2] of the same type showed the occurrence of temperature and defects density self-oscillations in the system. Self-oscillations are determined by the activation nature of the defect recombination rate caused by the temperature dependence of the diffusion of radicals. To describe the experiment, the activation energy of defects in methane was taken equal to about 150 K. In [12], the results of studies of self-oscillations in methane under neutron irradiation are presented for the case of two types of defects created by irradiation. Two types of defects arising from reactions were considered



where  $\Delta E_1 = 218 \text{ J / mole}$ ,  $\Delta E_2 = 368 \text{ J / mole}$ .

Note that the radiation behavior of solid  $\text{CH}_4$  is also of interest to astrophysics due to the significant content of  $\text{CH}_4$  in the planetary and interstellar medium [15, 16] and this problem has become the topic of a large body of research e.g. [17 - 26]. The role of self-oscillations in the cryovolcanism of comets was considered in [2, 12]. In [2, 12], when studying methane irradiated with neutrons the temperature oscillations of only one type were found.

As far as we know, there were only a few studies in which a delayed in time burst of particles, the so-called "delayed desorption", from solid methane exposed to other types of ionizing radiation, was observed [27, 28]. Thus, solid  $\text{CD}_4$  was irradiated with MeV  $\text{He}^+$  and  $\text{H}^+$  [27]. When the beam was turned on, weak desorption of  $\text{D}_2$  first appeared. Upon reaching the threshold fluence density, the yield of  $\text{D}_2$  rapidly increased by more than an order of magnitude, and then gradually decreased. The threshold fluence values for irradiation with 1.5 MeV  $\text{He}^+$  ions and 1.5 MeV  $\text{H}^+$  were  $3 \cdot 10^{14} \text{ cm}^{-2}$  and  $9 \cdot 10^{15} \text{ ions cm}^{-2}$ , respectively. In [28], solid  $\text{CH}_4$  and  $\text{CD}_4$  were irradiated with 9.0 MeV  $\alpha$ -particles

and 7.3 MeV protons. Doses up to 145 eV per molecule caused pressure shocks rising the chamber pressure by several orders of magnitude. This process released up to 90 % of the molecules of the solid target into the gas phase. The authors concluded that the  $\text{H}$  and  $\text{CH}_3$  radicals play a major role in this phenomenon, and the observed explosion resembles a nonequilibrium process. However, in these experiments, no regular oscillations were observed.

In experiments [29, 30], when solid methane was irradiated with electrons at helium temperature, explosive delayed desorption of particles was detected. In contrast to the case of ion bombardment [27, 28] with high energy during the bursts stimulated by electron beam, the periodic oscillations of the desorption yield were also observed. The burst can be considered as an instability similar to that studied in [2, 12] upon methane irradiation with neutrons. The appearance of bursts and oscillations can be interpreted as the occurrence of self-oscillations of two types.

The possibility of the appearance of two types of oscillations during methane irradiation is studied in this paper. Further experimental studies of solid methane irradiated by electrons were carried out in order to elucidate the mechanisms and properties of self-oscillations (periods, dependences on excitation conditions). The relaxation characteristics of the methane irradiated in the subcritical and supercritical modes were measured. The corresponding model of self-oscillations in solid  $\text{CH}_4$  irradiated with an electron beam has been built.

## 2. Experimental observation of self-oscillations in irradiated solid methane

Samples of solid methane with a thickness of about 100  $\mu\text{m}$  were grown by condensation of gaseous methane onto a copper substrate cooled to a liquid-helium temperature of 4.2 K. Such thick films were used in order to reduce the influence of the substrate placed in a vacuum chamber with a base pressure of  $10^{-7}$  torr. The open surface of the samples allows the simultaneous registration of several relaxation emissions: electrons, photons, and desorbing particles. The samples were irradiated with an electron beam with an energy of 1 keV in a stationary mode at a beam current density of  $2.5 \text{ mA cm}^{-2}$ . The total yield of particles from the surface of solid methane was characterized by an increase in pressure in the vacuum chamber, as measured by an ionization sensor (a Bayard - Alpert gauge). The measurements were carried out in the dynamic pumping mode by LHe cryogenic and magnetic discharge pumps.

After a long exposure (about an hour) of an electron beam at LHe temperature, we first observed

an explosive emission of particles from an irradiated methane film. This “explosion” resulted in a drop in the chamber vacuum by two orders of magnitude (as shown in Fig. 1), despite continuous pumping. The

central peak of explosive particle emission was preceded by oscillations in the output of particles with an increasing amplitude as shown in Fig. 1, *b*.

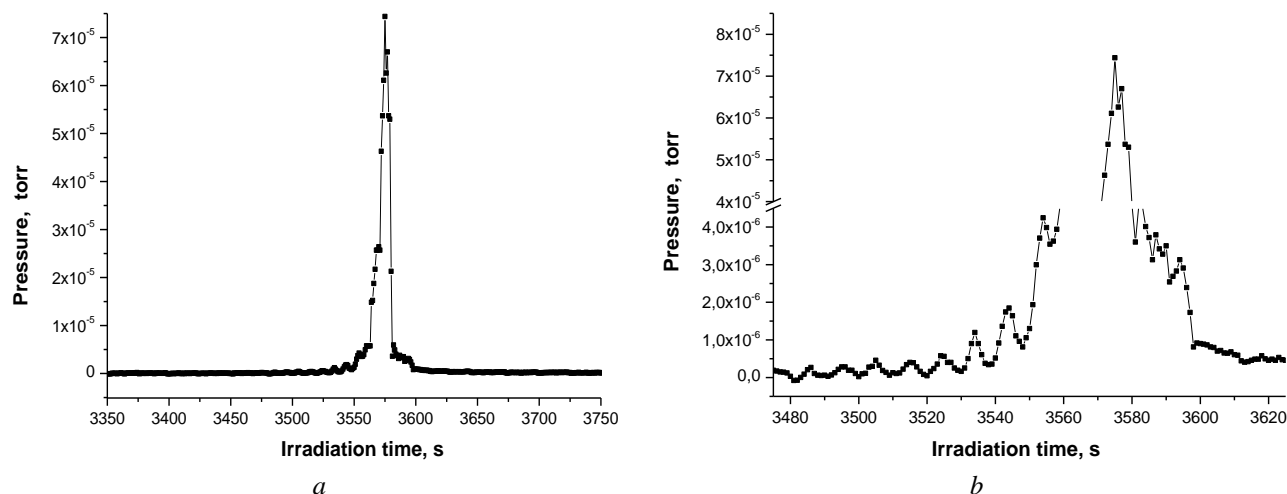


Fig. 1. Explosive particles emission from a methane film stimulated by electron beam irradiation (*a*); oscillations on an enlarged scale (*b*).

The characteristic oscillation period at the indicated beam parameters was  $\tau = 10$  s. It is of interest that oscillations with a short period were also observed at the beginning of irradiation, as shown in Fig. 2.

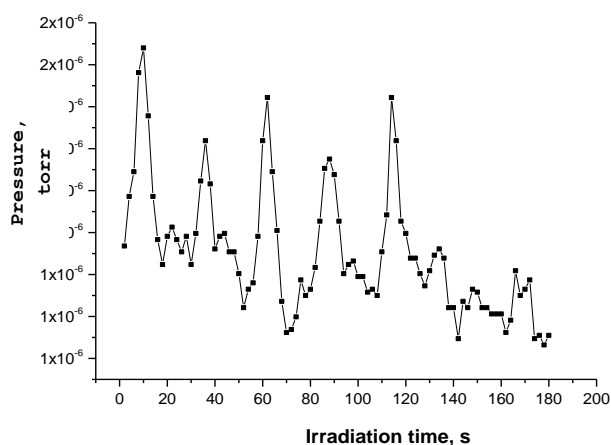


Fig. 2. Oscillations of pressure in a chamber at the beginning of irradiation.

It should be noted that the oscillation period  $\tau$  depends on the irradiation mode and decreases with an increasing current density of the electron beam. So, at a current density of  $1.5 \text{ mA}\cdot\text{cm}^{-2}$ ,  $\tau = 20$  s, whereas at a current density of  $3 \text{ mA}\cdot\text{cm}^{-2}$ ,  $\tau = 10$  s, and with an increase in current density up to  $5 \text{ mA}\cdot\text{cm}^{-2}$ ,  $\tau = 6$  s. The ejection of particles was accompanied by a sharp increase in the temperature of the methane film, followed by a slow decrease. Since the temperature sensor (Si diode) was mounted on the back of a massive substrate cooled by LHe, it was not possible to determine the actual

surface temperature of the methane film. However, its significant increase during explosive emission of particles is indicated by a drop in the thermally stimulated emission of exoelectrons (TSEE), measured after 5 min of irradiation after explosive emission of particles from the sample (curve 2 in Fig. 3).

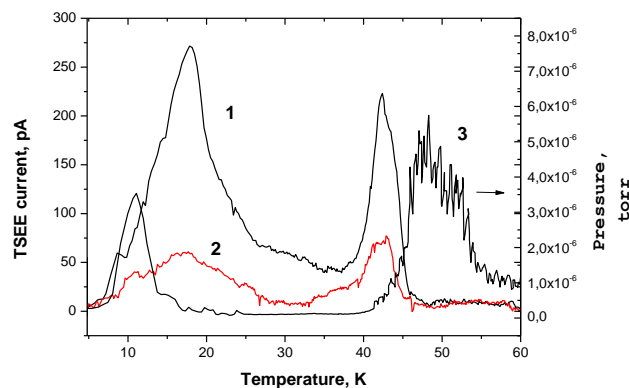


Fig. 3. Comparison of TSEE currents from the methane samples irradiated with subcritical dose (curve 1) and those with a supercritical one (curve 2). Curve 3 shows TSPD measured on a sample irradiated with supercritical dose.

It should be noted that a strong decrease in the TSEE yield from the sample irradiated with a supercritical dose is caused not only by the loss of part of the sample during the explosion but also by its partial annealing during the burst, as follows from the redistribution of the TSEE yield intensities at low and “high” temperatures (the drop in the low-temperature maximum is more pronounced). Because of the short duration of the explosion, the traps are annealed only partially.

We did not consider the threshold for current, at which the self-oscillation appears. But by experiment, it was established, that an explosive emission of particles from an irradiated methane film, occurs when the irradiation dose reaches 100 eV per molecule.

The beginning sublimation of the sample allows one to estimate only the lower boundary of the heating pulse – 45 K. In reality, the temperature rise in the pulse exceeds the triple point temperature of 90 K. The temperature-stimulated post-desorption (TSpD) of the samples irradiated with a supercritical dose is strongly suppressed. As can be seen from curve 3, when such a sample was heated, a recorded vacuum drop was only half an order of magnitude. It should be noted that its maximum does not coincide with the maximum of TSEE and is located at higher temperatures, as can be seen from Fig. 3, i.e. it is not associated directly with the recombination of charge centers. This indicates that the processes underlying such a strong suppression of TSpD after explosive desorption of particles are associated with the reactions of active neutral radiolysis products proceeding most efficiently at high temperatures.

### 3. Model and investigation method

In the system – solid methane irradiated by electrons – many processes leading to self-oscillations can be assumed: the accumulation of defects, and then their conversion with the release of energy, the accumulation of charges, and their subsequent release. We investigate temperature fluctuations associated with the accumulation of defects. At the electron energies used in the experiments [29, 30], of the order of 1 keV, the energy transfer to the hydrogen atom is small (less than the hydrogen binding energy in the molecule) and therefore its direct knocking from the molecule is unlikely. Methane dissociation occurs as a result of subthreshold processes, for example, during energy transfer from excited states, in particular, from the long-lived triplet states [31]. When a sample is excited by electrons, free electrons and holes are created. The number of electrons + hole pairs with a total spin of 1 (triplet) is three times larger than the number of singlet pairs with a spin of 0. Therefore, upon recombination, there is a high probability of the formation of methane molecules in an excited triplet state, the transition from which to the ground state, although allowed by the spin-orbit interaction, has a low probability. During the lifetime of the triplet state, a process of the hydrogen atom detachment from the molecule can occur, because the C – H binding energy (4.5 eV) is lower than the energy of the excited triplet state. The decay products of a methane molecule in a collision with an electron are

atomic and molecular hydrogen and radicals containing carbon and several hydrogen atoms [32]:  $\text{CH}_3 + \text{H}$ ,  $\text{CH}_2 + \text{H}_2$ ,  $\text{CH}_2 + 2\text{H}$ ,  $\text{CH} + \text{H}_2 + \text{H}$ . For temperature self-oscillations to occur, radical motion and recombination should take place. It can be assumed that of all the decay products of a methane molecule containing carbon, the largest diffusion coefficient is for hydrogen and the radical  $\text{CH}_3$  contained in the first of the above channels. The radical  $\text{CH}_3$  can move along the methane lattice without the movement of a carbon atom, but only by the transition of a more mobile hydrogen atom from a neighboring methane molecule. In this case, the  $\text{CH}_3$  radical moves to the lattice site, which the hydrogen atom has left. For such a movement of the  $\text{CH}_2$  radical, a transition of two hydrogen atoms is needed, which is a less likely process. Thus, we study the system already considered in [2, 12] and described by reactions (1), (2) and show that two types of self-oscillations are possible in it. Both the H atoms and  $\text{CH}_3$  radicals are assumed to have an activation character of diffusion, and when they are recombined according to Eqs. (1) and (2), energy is released. Then, with increasing temperature, diffusion, and recombination processes are accelerated. The energy released during recombination leads to a further increase in temperature. The stationary state of the system becomes unstable and self-oscillations occur.

A key feature of the experiments [29, 30] is the fact that the electron range (that is, the region in which defects are created by irradiation) at an electron energy of 1 keV is of the order of 0.1  $\mu\text{m}$  that is much less than the thickness of the sample. In this case, the temperature distribution in the sample will be heterogeneous and the study of self-oscillations is a difficult task. To detect self-oscillations of two types when the sample is irradiated with electrons, we will consider a simplified task – we will calculate self-oscillations in a thin methane layer with a thickness  $l$  of the order of the electron range. In this case, the temperature distribution can be considered homogeneous as in the case of neutron irradiation.

Let us denote the relative concentrations of H and  $\text{CH}_3$  related to the concentration of  $\text{CH}_4$  as  $\tilde{n}_1$  and  $\tilde{n}_2$ , the relative number of H and  $\text{CH}_3$  formed by irradiation with electrons per unit time, referred to the number of  $\text{CH}_4$  molecules as  $G_1, G_2$ .

The initial system of equations for defect concentrations resulting from the kinetics of their formation and destruction, as well as for temperature has the following form

$$\frac{\partial n_1}{\partial t} = G_1 - K_{01} \exp(-E_{a1}/(\kappa T)) n_1^2, \quad (3)$$

$$\frac{\partial n_2}{\partial t} = G_2 - K_{02} \exp(-E_{a2}/(\kappa T)) n_2^2, \quad (4)$$

$$lc(T) \frac{\partial T}{\partial t} = P - E_1 K_{01} \exp(-E_{a1}/(\kappa T)) n_1^2 l /$$

$$/v_0 - E_2 K_{02} \exp(-E_{a2}/(\kappa T)) n_2^2 l / v_0 - B (T - T_b), \quad (5)$$

where  $P$  is the part of the energy spent by the electron flux to the heating of a unit cross-section of a sample per unit time,  $E_{a1}$  and  $E_{a2}$  are migration activation energies of hydrogen atoms and  $\text{CH}_3$  radicals, respectively.  $B$  is the coefficient of energy transfer from the sample to the thermostat, and  $c(T)$  – is the heat capacity of a methane volume unit. In these calculations, we used the temperature dependence of the specific heat capacity from the experimental data given in [33, 34]. In the calculations, the heat capacity jump due to the presence of a phase transition in methane at  $T = 20.49$  K was taken into account. However, as follows from the calculations below, in view of the narrowness of the temperature region in which the jump is observed, its role in the processes under consideration is insignificant.  $v_0$  is the volume of  $\text{CH}_4$ .

The system of equations contains many unknown parameters. Since H and  $\text{CH}_3$  are created simultaneously and in one process, then  $G_1 = G_2$ . The probability of detachment of a hydrogen atom from a molecule  $\text{CH}_4$  with the formation of  $\text{CH}_3$  radical as a result of knocking out by electrons at electron energies of about 1 keV used in experiments is small due to the large difference between the masses of the electron and the hydrogen atom. Therefore, the main mechanisms of hydrogen atom detachment are various subthreshold processes involving excited states of molecules, and triplet long-lived states of  $\text{CH}_4$  can play an important role [31]. We will carry out calculations, considering the value  $G = G_1 = G_2$  as a parameter. The parameter  $P$  should be smaller in magnitude than the energy of the electrons entering the sample, since not all energy is converted into heat, some energy is used for cathode radiation, conventional desorption, and the formation of defects.

#### 4. Calculations and discussion

The densities of defects (H and  $\text{CH}_3$ ) were found from the numerical solution of Eqs. (3) - (5) with the initial conditions  $n_1 = n_2 = 0$ ,  $T = T_b$ . Self-oscillations are realized in a certain range of parameter values. The system of Eqs. (3) - (5) has many different solutions depending on the parameters  $G, P, K_{01}, K_{02}, B$ . For some parameters, solutions

are realized in which the sought physical quantities (defect densities and temperatures) reach saturation at a large period and take constant values. Depending on parameters, there are different types of solutions in which oscillations with one period are realized, as well as oscillations with two frequencies at all times and others. We will present the solutions describing oscillations with a large period and a sharp maximum in the temperature dependence of oscillations on time and oscillations having a short period and located in the vicinity of the maximum oscillations with a long period. This type of dynamics was observed experimentally in [29, 30].

Figs. 4 and 5 show the temporal dependence of the concentrations of hydrogen atoms,  $\text{CH}_3$  radicals, and temperature for various parameters of the system.

There are oscillations of two types. The figures show the dependence of the parameters (temperature and concentrations  $n_1$  and  $n_2$ ) on time for only one oscillation cycle with a large period. With increasing exposure time, the dependencies are repeated.

The qualitative picture of an oscillation appearance is following. During this time, the accumulation of  $\text{CH}_3$  radicals occurs (see Fig. 4, *c*). At a certain concentration of  $\text{CH}_3$ , the system becomes unstable. With the slightest increase in temperature, diffusion is accelerated leading to enhanced recombination of defects with the release of energy and a further increase in temperature. As a result, a sharp jump in temperature (see Fig. 4, *a*) and annealing of  $\text{CH}_3$  radicals occur. As the irradiation with electrons is continued, the concentration of radicals begins to grow again (see Fig. 4, *c*) and the process is repeated. The magnitude of the temperature jump strongly depends on the parameters of the system. With reasonable estimates of the coefficients  $K_{01}, K_{02}$ , the maximum temperature may be either lower or higher than the melting point of methane  $T_c$ . The calculations are given for the cases when this temperature is lower than  $T_c$ , since in Eqs. (1) - (3) the heat of fusion was not taken into account. On a time scale near the temperature jump, oscillations in the concentration of the hydrogen atoms  $n_1$  have been observed. Their origin is the same as that of the above-considered  $\text{CH}_3$  concentration oscillations with a large period, only the properties are determined mainly by the release of energy while hydrogen atoms are recombined to form a hydrogen molecule (reaction (1)). There is a deep and wide drop in the temporal dependence of  $n_1$  (Fig. 5, *d*). It is associated with the accelerated binding of hydrogen atoms into molecules with increasing temperature due to the

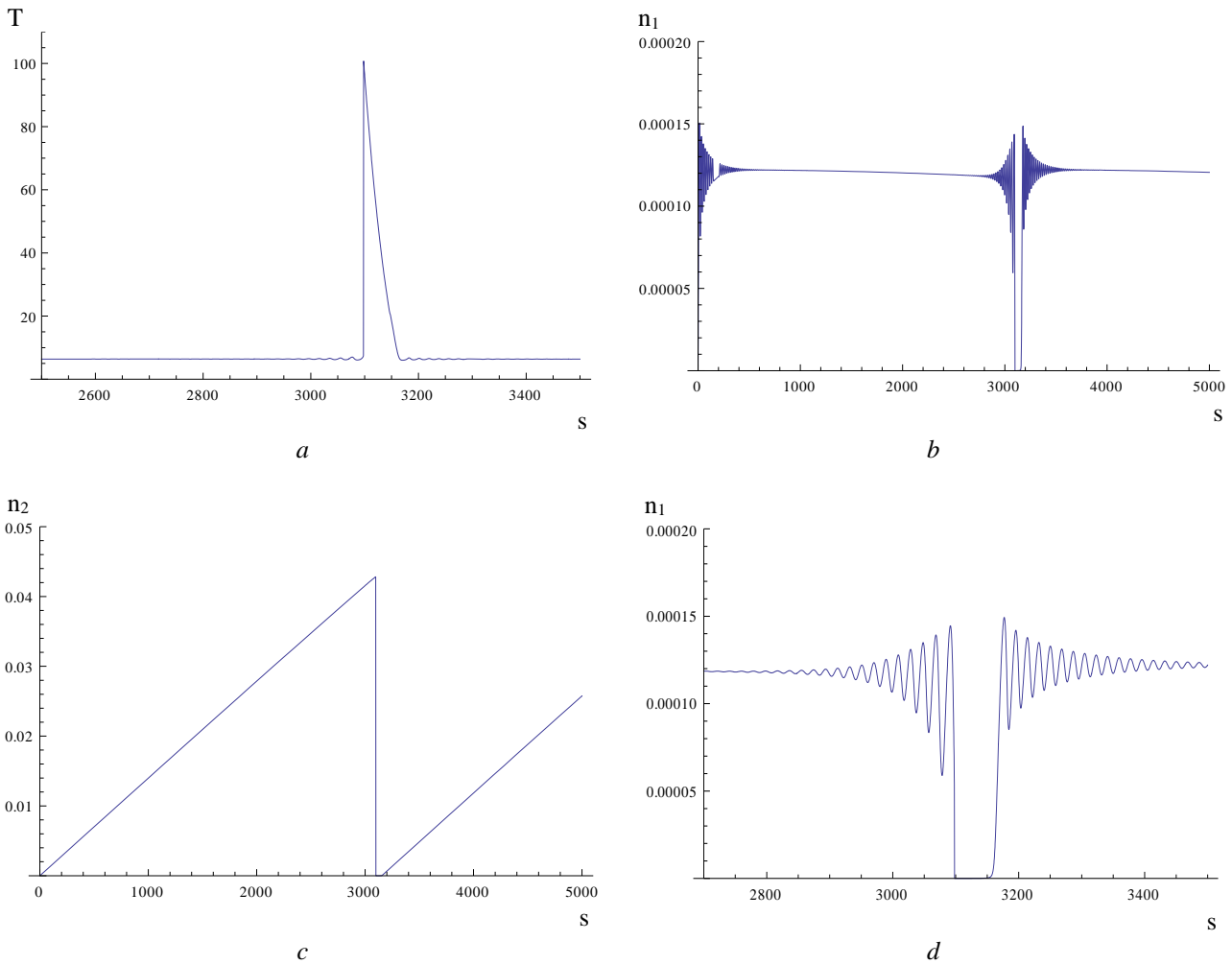


Fig. 4. Temporal dependence of: *a* – temperature; *b* – concentration of hydrogen atoms; *c* – concentration of CH<sub>3</sub> radicals; *d* – concentration of hydrogen atoms within a narrow time range. The calculations have been accomplished using the following parameters:  $G_1 = G_2 = 1.4 \cdot 10^{-5}$  ind/(atom·s),  $E_{a2}/\kappa = 200$  K,  $E_a/\kappa = 117.8$  K,  $K_{01} = 10^{11} s^{-1}$ ,  $K_{02} = 10^{10} s^{-1}$ , and is the ratio of the generated in the unit time defects to the numbers of molecules.

recombination of CH<sub>3</sub> radicals (see Fig. 4, *a*). Almost all hydrogen atoms are combined into hydrogen molecules. Thus, the two processes of self-oscillations are interconnected: instability in the system of CH<sub>3</sub> radicals affects the fluctuations in the concentration of hydrogen atoms.

Fig. 5 shows the temporal dependences of the concentration of radicals for self-oscillations at other values of the system parameters. In a qualitative sense, the results are similar: there are two types of oscillations; there is a sharp jump in temperature.

At a pump power corresponding to the generation of the number of defects  $G_1 = G_2 = 1.4 \cdot 10^{-5}$  per atom per second, the oscillation period of hydrogen atoms concentration is 19 s (see Fig. 4), when  $G = 2 \cdot 10^{-5}$  the period equals 11 s (see Fig. 5). These values are close to the

experimental ones [30], in which the period is of the order of 10 s. Generally speaking, it follows from the calculations that the period depends on many parameters of the sample and irradiation, but for the same parameters of the sample, the period decreases with increasing pumping, as noted in Section 2 and observed in our previous experiments [30]. The period of oscillations decreases with  $G$  increasing also for oscillations with a large period determined by the time before the outburst. It should also be noted that for all the variety of solutions of the system of Eqs. (3) - (5), in the case when oscillations appear in the solution in a certain limited time region near the outburst, self-oscillations with small periods always appear at the initial moments of the irradiation time (see Fig. 4, *b* and Fig. 5, *b*). In this case, self-oscillations are also observed at the beginning of irradiation in the experiment (see Fig. 2).

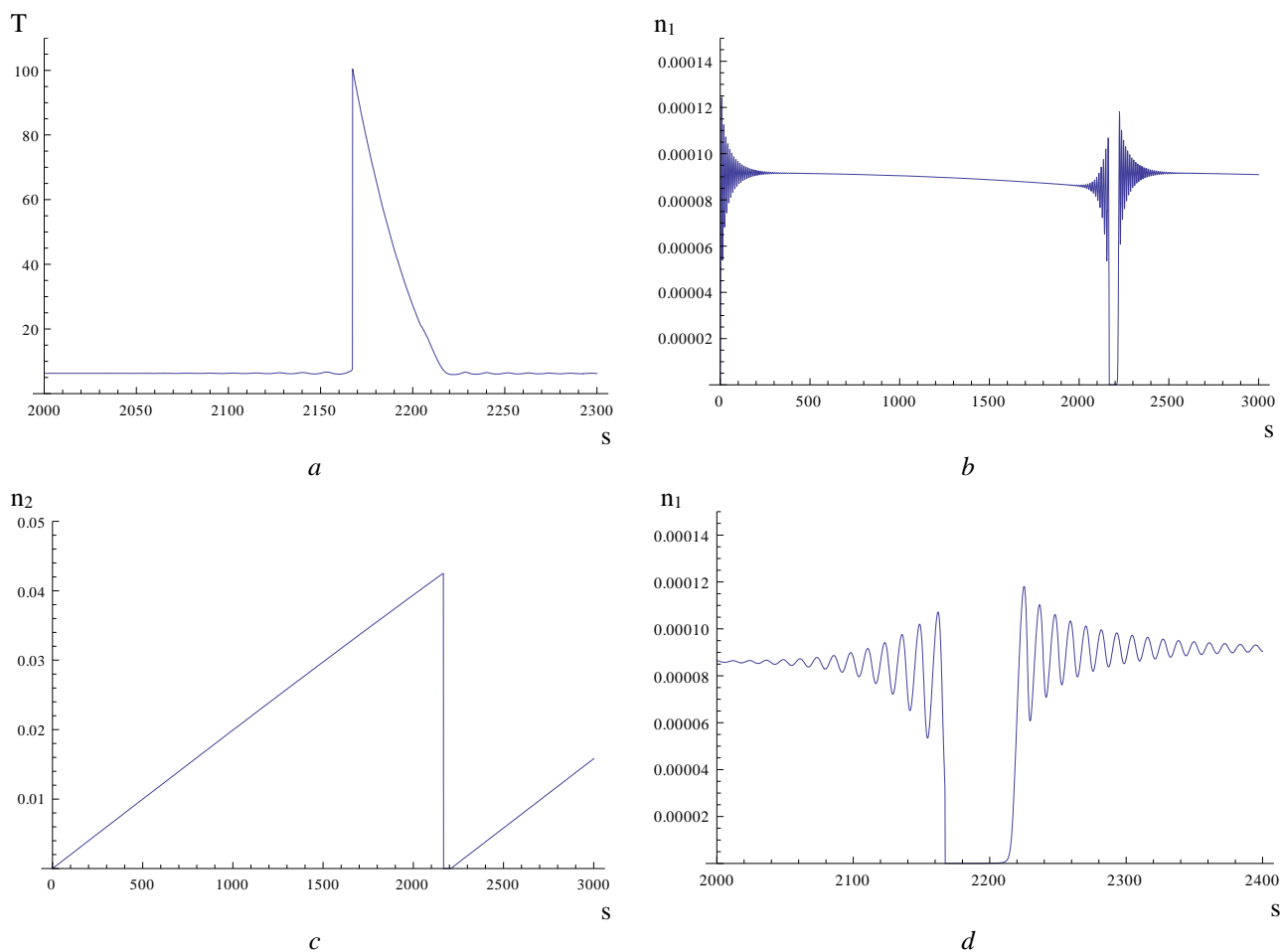


Fig. 5. Temporal dependence of: *a* – temperature; *b* – concentration of hydrogen atoms; *c* – concentration of  $\text{CH}_3$  radicals; *d* – concentration of hydrogen atoms within a narrow time range. The calculations have been accomplished using the following parameters:  $G_1 = G_2 = 2 \cdot 10^{-5}$  nd/(molecules·s),  $E_{a2}/\kappa = 170$  K,  $E_a/\kappa = 115.3$  K,  $K_{01} = 10^{11} \text{ s}^{-1}$ ,  $K_{02} = 3.5 \cdot 10^8 \text{ s}^{-1}$ .

It should be noted that in the results obtained, the self-oscillations occur at much lower values of the incident flux density than those observed in experiments [29, 30]. In our opinion, this is because of significantly smaller sizes of the irradiated region in the task being solved in comparison with the dimensions of the sample. Due to the faster heat transfer from the irradiated region to the depth of the sample compared to the periods of oscillation, the nonlinear relationship between an increase in temperature and diffusion and recombination rates of defects decreases. Therefore, in thick samples, if only a small region is irradiated, the appearance of self-oscillations requires a higher radiation intensity. An accumulation of charges in the sample may play a role.

We emphasize that in the process of irradiation, a part of the methane molecules is destroyed, besides mechanical destructions may occur during the temperature outburst. The destructions of devices took place at the neutron irradiation of methane [1]. As it is shown from our investigations the outburst at the electron irradiations may be greater than at

neutron irradiation. Therefore, the conditions for the formation of subsequent cycles of oscillations are changed, which can affect the frequency of oscillations. For the oscillations with short periods, this change was not observed and for oscillations with a long period, the process has not been considered.

In experiments [27, 28] the energies of incident particles ( $\alpha$ -particles, protons) were several MeV, which are much higher, than electron energies in our experiments. In the case of irradiation by heavy energetic particles both mechanisms of defect formation and desorption are at work – inelastic (through the electronic subsystem with  $\text{CH}_4$  molecule fragmentation) and elastic (by a direct impact). Irradiation by low-energy electrons creates defects only via electronic subsystem with methane molecule dissociation. (In this case, the irradiation turned off electrons from molecule  $\text{CH}_4$ , C, and H atoms and a formation of the different complexes of defects takes place.) So, the defect structure under irradiation with high energy particles differs from



the defect structure at irradiation with electrons of low energy in our experiment. Irradiation of solid methane with 9 MeV  $\alpha$ -particles and 7.3 MeV protons resulted in an explosive ejection into the gas phase more than 90 % of the ice target [28], so it was impossible to reproduce the cycle. It may be the reason why in the experiments [27, 28] were observed only delayed single pressure shocks and the self-oscillation were not observed.

### 5. Desorption of hydrogen molecules from a methane film irradiated by electrons

With increasing temperature, the decay products of methane molecules due to electron irradiation will come out of the surface of the methane film. In [29, 30], the pressure changes in the chamber created by their desorption served as one of the methods for detecting oscillation processes in an irradiated film. Desorption processes involving many components are diverse, complex, and contain many unknown parameters. We will consider some model tasks. Choosing different values of microscopic parameters, we will analyze how self-oscillations will manifest themselves in different desorption modes.

Let us consider the yield of hydrogen molecules from electron-irradiated methane film arising from the binding of hydrogen atoms (reaction (1)), which in turn are formed during the decay of methane molecules during the irradiation. As before, the film thickness is taken equally in order of magnitude to the electron range. We assume that during the period of self-oscillations, hydrogen has managed to uniformly distribute over the methane film, and, accordingly, the formation of hydrogen molecules is a homogeneous function of the coordinates inside the film. The exit of hydrogen molecules occurs from the surface by the activation law with activation energy  $E_d$ , the probability of the hydrogen molecule released from the film is proportional to  $\frac{\exp(-E_d / \kappa T)}{\tau_d}$ .

Denote the concentration of hydrogen molecules by  $n_3$ . According to the conservation law, for a portion of an irradiated film with a cross-section equal to the unit area, the equation follows

$$l \frac{dn_3}{dt} = \frac{l}{2} K_{01} \exp(-E_{a1} / (\kappa T)) n_1^2 - d \cdot n_3 \frac{\exp(-E_d / \kappa T)}{\tau_d}. \quad (6)$$

Here,  $d$  is the thickness of the near-surface layer shown in Fig. 6, from which the release of hydrogen molecules occurs (a magnitude of the order of the lattice constant).  $d \cdot n_3$  is the number of hydrogen molecules per unit of the surface layer.

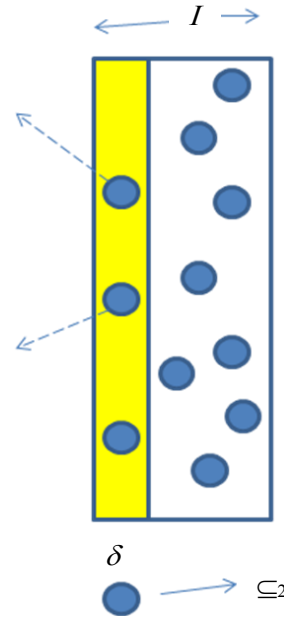


Fig. 6. Distribution of hydrogen molecules in methane film. The near-surface region from which the desorption of hydrogen molecules occurs is colored in yellow.

The dependence of the concentration of hydrogen atoms  $n_1$  and temperature  $T$  on time in this equation is determined from the solutions of equations for self-oscillations (3) - (5). For particular parameter values, they are presented in the captions to Fig. 4 and Fig. 5. The yield of hydrogen molecules (in relative units) from a unit surface per unit time determined by the ratio

$$P_{H_2} = d \cdot n_3 \frac{\exp(-E_d / \kappa T)}{\tau_d} \quad (7)$$

has been calculated. The calculations were performed at  $\tau_d = 10^{-11}$  s.

Since the values  $E_d$  are not known, the  $P_{H_2}$  was studied at various values of  $E_d / \kappa$ . Depending on the  $E_d / \kappa$  magnitude with respect to the activation energy  $E_{a2} / \kappa$  of the  $\text{CH}_3$  radicals' recombination, there are two modes of dynamics of the concentration of hydrogen molecules with time.

1. The activation energy of a hydrogen molecule detachment from the surface  $E_d / \kappa$  is of the order of magnitude of  $E_{a2} / \kappa$  or more. The calculation results for this case with  $E_d / \kappa = 190$  K and the parameters of the methane film irradiation which are given in the captions to Fig. 5 are presented in Fig. 7.

2. The calculation results for the case with  $E_d / \kappa = 130$  K, when it is significantly less, and the parameters are used which are given in captions to Fig. 5 are presented in Fig. 8.



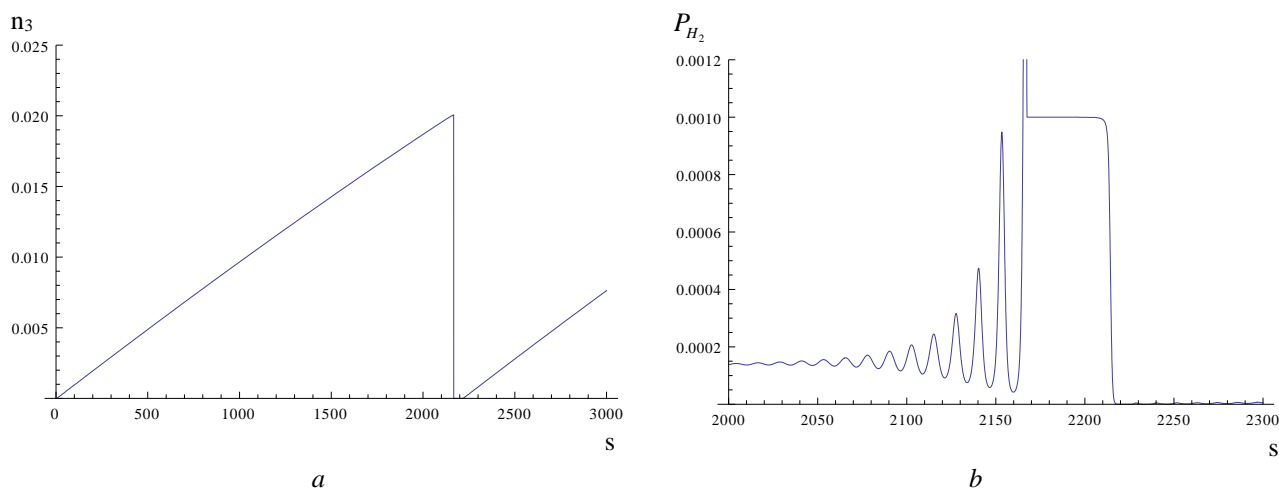


Fig. 7. Temporal dependence of: *a* – the time dependence of the concentration of hydrogen molecules in the near-surface methane layer being irradiated with electrons; *b* – yield of hydrogen molecules from a unit surface.  $E_{a2} / \kappa = 190$  K.

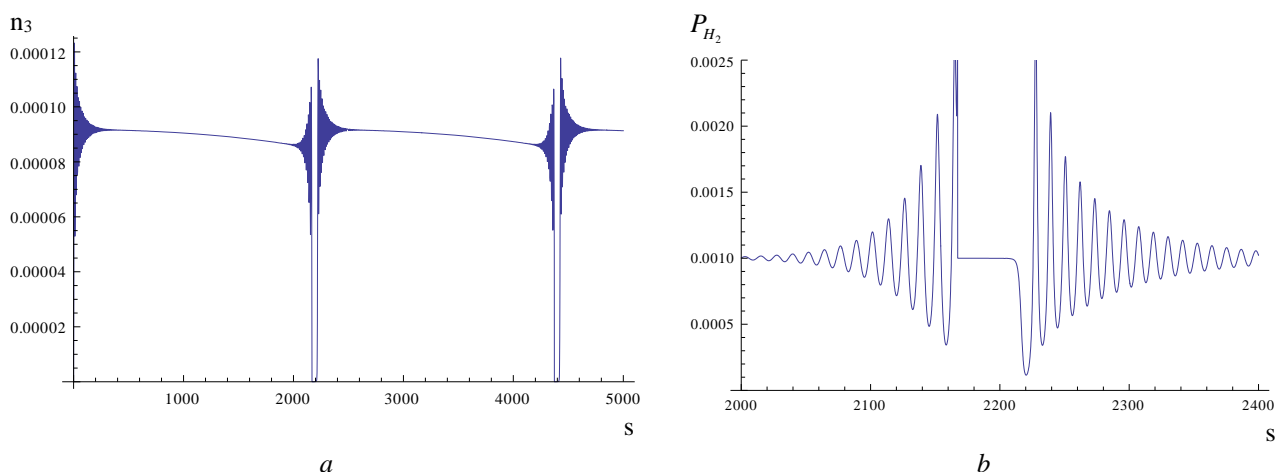


Fig. 8. Temporal dependence of: *a* – the concentration of hydrogen molecules in the surface layer of methane when irradiated with electrons; *b* – the release of hydrogen molecules from a unit surface.  $E_{a2} / \kappa = 130$  K.

It can be seen from Fig. 7 that at high activation energy of the detachment of hydrogen molecules from the sample surface (desorption), the concentration of hydrogen molecules formed by the merging of hydrogen atoms increases linearly with time during electron irradiation and drops sharply during a temperature flash due to self-oscillations. At lower activation energies of the release of hydrogen molecules from the film (see Fig. 8), a balance is established between the number of molecules formed upon recombination of hydrogen atoms and molecules leaving the sample, and the concentration of molecules weakly depends on time. However, in both cases, the temporal dynamics of desorption repeats the dynamics of self-oscillations.

The case considered is one example of a variety of desorption processes. Desorption is accompanied by the release of hydrogen atoms from methane and other methane decay products under the influence of an electron beam. Due to the diversity of the

processes and the lack of data on the diffusion of methane decomposition products and the activation energies of their release from the sample, these processes have not been considered.

## 6. Conclusion

Self-oscillations in methane irradiated by neutrons at low temperatures have been observed and studied for a long time [2, 12]. The effect consists of the appearance of a sharp jump in temperature. Investigations of methane irradiated by electrons in [29, 30] show also a sharp increase in the desorption of particles from the irradiated sample, that bear witness to a temperature jump. But besides temperature jump, the authors [29, 30] also observed periodic oscillations of the particle desorption with lower amplitude and frequency. So, they observed two types of oscillations. In the present paper, the manifestation of these oscillations is studied

experimentally, and a theory is being constructed, that describes the presence of two types of self-oscillations in methane irradiated by electrons. The self-oscillations arise due to two types of defects: the hydrogen atoms and the  $\text{CH}_3$  radicals, the

appearance of which is the result of methane molecule decay at electron irradiation. The calculations allowed determining the values of the kinetic parameters of the formed fragments (diffusion activation coefficients).

## REFERENCES

1. E.P. Wigner. Theoretical Physics in the Metallurgical Laboratory of Chicago. *Journal of Applied Physics* 17 (1946) 857.
2. J.M. Carpenter. Thermally activated release of stored chemical energy in cryogenic media. *Nature* 330 (1987) 358.
3. V.I. Sugakov. *Lectures in Synergetics, World Scientific Series on Nonlinear Science. Vol. 33* (Singapore: World Scientific, 1998) 220 p.
4. P.A. Selishchev, V.I. Sugakov. Self-organization phenomena in impure irradiated crystals. *Radiations Effects and Defects in Solids* 133(3) (1995) 237.
5. P.A. Selishchev, V.I. Sugakov. Temperature and defect density self-oscillations in thin plates under irradiation. *Sov. Phys. Solid State* 30 (1988) 1503.
6. G.A. Vikhliy, A.Ya. Karpenko, P.G. Litovchenko. Dose Dependence of Semiconductor Material Conductivity as a Means of High Fluence Dosimetry. *Radiation Protection Dosimetry* 66(1-4) (1996) 229.
7. P. Sen, G. Agarwal, U. Tiwan. Dissipative Structure Formation in Cold-Rolled Fe and Ni during Heavy Ion Irradiation. *Physical Review Letters* 80(1) (1998) 97.
8. R. Chatterjee et al. The observation of oscillatory behaviour in swift heavy ion irradiated quasicrystals. *Solid State Communication* 120(7-8) (2001) 289.
9. I.Yu. Golinei, I.Yu. Delyukov, V.I. Sugakov. Self-excited oscillations of the exciton density and temperature in an impurity molecular crystal. *JETP Letters* 49(4) (1989) 239.
10. E. Shabalin, On the Phenomenon of the Fast Release of Energy in Irradiated Solid Methane. Part I and II. *JINR Communications. E-17-95-141, E-17-95-142* (Dubna, 1995).
11. E. Kulaginet et al. Radiation effects in cold moderator materials: Experimental study of accumulation and release of chemical energy. *Nucl. Instrum. Methods. B* 215 (2004) 181.
12. O. Kirichek et al. Solid methane in neutron radiation: Cryogenic moderators and cometary cryo volcanism. *Cryogenics* 88 (2017) 101.
13. O. Kirichek et al. Recombination of radiation defects in solid methane: neutron sources and cryo-volcanism on celestial bodies. *Journal of Physics: Conf. Ser.* 969 (2018) 012006.
14. E.V. Savchenko et al. Relaxation processes in solid methane pre-irradiated with an electron beam. *Nucl. Instrum. Methods B* 433 (2018) 23.
15. R.N. Clark et al. Observed Ices in the Solar System. In: M.S. Gudipati, J. Castillo-Rogez (Eds.). *The Science of Solar System Ices* (New York: Springer, 2013).
16. K.I. Öberg. Photochemistry and Astrochemistry: Photochemical Pathways to Interstellar Complex Organic Molecules. *Chem. Rev.* 116(17) (2016) 9631.
17. G. Foti et al. Micrometre-sized polymer layers synthesized by MeV ions impinging on frozen methane. *Nature* 310 (1984) 126.
18. R.I. Kaiser, K. Roessler. Theoretical and Laboratory Studies on the Interaction of Cosmic-Ray Particles with Interstellar Ices. III. Suprathermal Chemistry-Induced Formation of Hydrocarbon Molecules in Solid Methane ( $\text{CH}_4$ ), Ethylene ( $\text{C}_2\text{H}_4$ ), and Acetylene ( $\text{C}_2\text{H}_2$ ). *Astrophys. J.* 503(2) (1998) 959.
19. C.F. Mejía et al. Cosmic ray-ice interaction studied by radiolysis of 15 K methane ice with MeV O, Fe and Zn ions. *Monthly Notices of the Royal Astronomical Society* 433 (2013) 2368.
20. M.E. Palumbo et al. Ion irradiation of astrophysical ices. *Journal of Physics: Conf. Ser.* 101 (2008) 012002.
21. R. Brunetto et al. Ion Irradiation of Frozen Methanol, Methane, and Benzene: Linking to the Colors of Centaurs and Trans-Neptunian Objects. *Astrophys. J.* 644(1) (2006) 646.
22. F.A. Vasconcelos et al. Ion irradiation of pure and amorphous  $\text{CH}_4$  ice relevant for astrophysical environments. *Phys. Chem. Chem. Phys.* 19 (2017) 12845.
23. A.L.F. de Barros et al. Cosmic ray impact on astrophysical ices: laboratory studies on heavy ion irradiation of methane. *Astronomy & Astrophysics* 531 (2011) A160.
24. C.J. Bennett et al. Laboratory Studies on the Irradiation of Methane in Interstellar, Cometary, and Solar System Ices. *Astrophys. J.* 653 (2006) 792.
25. M. Barberio et al. Experimental and Theoretical Study on the Ethane and Acetylene Formation from Electron Irradiation of Methane Ices. *World Journal of Condensed Matter Physics* 3(01) (2013) 14.
26. M.J. Abplanalp, B.M. Jones, R.I. Kaiser. Untangling the methane chemistry in interstellar and solar system ices toward ionizing radiation: a combined infrared and reflectron time-of-flight analysis. *Phys. Chem. Chem. Phys.* 20 (2018) 5435.
27. W.L. Brown et al. Delayed emission of hydrogen from ion bombardment of solid methane. *Nucl. Instrum. Methods B* 19-20(2) (1987) 899.
28. R.I. Kaiser et al. Theoretical and Laboratory Studies on the Interaction of Cosmic-Ray Particles with Interstellar Ices. II. Formation of Atomic and Molecular Hydrogen in Frozen Organic Molecules. *Astrophys. J.* 484 (1997) 487.
29. I.V. Khizhny et al. Explosive desorption of particles from solid methane induced by an electron beam. *Low Temperature Physics* 44(11) (2018) 1223.

30. E. Savchenko et al. Effects induced by an electron beam in methane ices. *Nucl. Instrum. Methods B* 460 (2019) 244.
31. E.I. Grigoriev, L.I. Trakhtenberg. *Radiation Chemical Processes in Solid Phase: Theory and Applications* (Boca Raton, Florida: CRC Press, 1996).
32. Young Song et al. Cross Sections for Electron Collisions with Methane. *Journal of Physical and Chemical Reference Data* 44 (2015) 023101.
33. J.H. Colwell, E.K. Gill, J.A. Morrison. Thermodynamic Properties of CH<sub>4</sub> and CD<sub>4</sub>. Interpretation of the Properties of the Solids. *J. Chem. Phys.* 39 (1963) 635.
34. G.J. Vogt, K.S. Pitzer. Entropy and heat capacity of methane; spin-species conversion. *J. Chem. Thermodynamics* 8(11) (1976) 1011.

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### **АВТОКОЛИВАННЯ У КРИСТАЛІЧНОМУ МЕТАНІ ПРИ ОПРОМІНЕННІ ЕЛЕКТРОНАМИ**

Проведено математичне моделювання та експериментальне дослідження процесів утворення автоколиваний температури та концентрації радикалів у плівці метану, що опромінюється електронами за низьких температур. Автоколивання обумовлені активаційним характером дифузії та процесами рекомбінації радикалів. Автоколивання вивчаються експериментально вимірюванням десорбції частинок з опромінюваного зразка і теоретично розв'язуванням кінетичних рівнянь для дефектів у зразку метану. Спостережено й досліджено автоколивання двох типів частинок, а саме атомів водню і радикала СН<sub>3</sub>, що формуються при опроміненні метану електронами. Показано, що зі збільшенням інтенсивності опромінення період осциляцій зменшується і його розраховане значення має порядок, спостережуваний в експерименті. Представлено модель прояву автоколиваний концентрації молекул водню під час десорбції.

*Ключові слова:* метан, електронне опромінення, автоколивання, температура, дефекти.

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