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STUDY OF FAST NEUTRON RADIATION EFFECTS IN COLD MODERATOR MATERIALS

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A phenomenon of spontaneous release of energy accumulated in some hydrogenous materials under fast neutron irradiation at low temperature was studied at a cryogenic irradiation facility of the IBR-2 reactor in Dubna for the purpose of cold neutron moderator development. Spontaneous release of energy occurred in water ice after $5\div11$ h of fast neutron irradiation at a temperature of less than 34 K and at an absorbed dose rate of 0.4 MGy/h. In contrast with previous data, no spontaneous burp was observed in solid methane.

На низкотемпературной облучательной установке реактора ИБР-2 в Дубне исследован эффект спонтанного саморазогрева некоторых водородосодержащих соединений при облучении быстрыми нейтронами для целей разработки холодных замедлителей нейтронов. В водяном льде саморазогрев возникал после облучения в течение $5\div11$ ч при температуре менее 34 K и мощности поглощенной дозы 0,4 МГр/ч. В отличие от ранее опубликованных данных в твердом метане спонтанный саморазогрев не наблюдался.

INTRODUCTION

Cryogenic moderators of neutrons (with temperature of hydrogenous moderating media $15\div100$ K) are presently a matter of scientific enquiry of neutron scattering community, as neutrons with a long de Broglie wavelength are particularly attractive for study of macromolecules and biological objects. Efforts are in action at various places to improve the performances of cold moderators in one way or the other. In particular, such combinations as of water ice and hydrogen, methane and water ice (clathrate) are considered to be effective for pulsed advanced neutron sources. It is, however, not easy to use such compounds at high-power neutron sources because of their bad resistance to radiation with dose rates as high as 10–1000 Gy/s that are characteristics of advanced neutron sources.

The most serious of radiation problems is caused by «frozen» radicals which are produced intensely under fast neutron radiation and diffuse too slow at low temperature to dissipate before reaching high concentration. Their accumulation gives rise to the stored chemical energy in an irradiated sample. Usually, the process of fast recombination of radicals can be stimulated by heating of a sample but under specific condition, the stored energy may be released spontaneously, with no perturbation in cooling condition [1–6]. Naturally, sudden leap of temperature has an ill effect on a yield of cold neutrons from a moderator.

This phenomenon was originally revealed by solid methane in the temperature range 15–25 K. Keeping up the tradition started by J. Carpenter [1], the authors refer to this phenomenon

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as «a burp» or «burping». Unlike solid methane, only a little is known about burping of water ice under neutron irradiation, except thermally induced burps in a cold moderator of the NIST reactor [7]. As to methane clathrate, there was no information about its radiation resistance properties.

1. EXPERIMENTAL TECHNIQUES

The irradiation facility and techniques of irradiation are described in [8], see Fig. 1. Samples were irradiated inside a capsule with a spherical cavity of diameter 30 mm made of copper M1. Samples of solid methane can be prepared either by condensing gas onto the

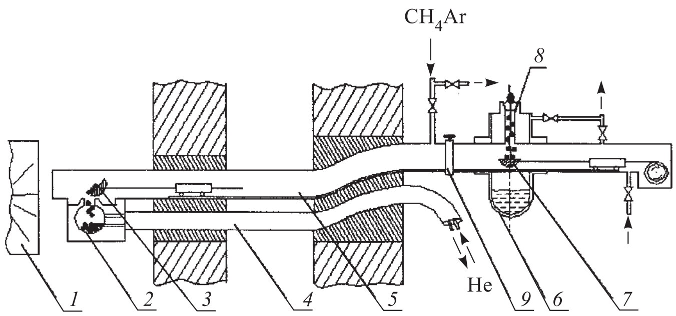


Fig. 1. Sketch of the URAM-2 cryogenic irradiation facility: *1* — the IBR-2 reactor; *2* — irradiation capsule; *3* — carrying bowl with a cart in «near the reactor» position; *4* — helium pipelines; *5* — evacuated transport passage; *6* — nitrogen cryostat; *7* — carrying bowl with a cart in «out of the reactor» position; *8* — charging tube with a plug; *9* — vacuum lock

inner surface of the capsule or by freezing liquid methane in the form of spherical segment up to 15 mm height. Samples of ice were prepared by two ways: by freezing of distilled water inside the irradiation capsule and by dropping water into liquid nitrogen. In the latter case, beads of ice were charged into the capsule at $T \approx 120{\div}140$ K with the aid of charging device (Fig. 1) and then solid argon was condensed into the capsule to increase the thermal conductivity of the pile of beads. The same procedure was used for preparation of methane hydrate samples; beads of hydrate were made by breaking a lump of hydrate ice. In the former case, ice samples (and samples of tetrahydrofuran hydrate, $C_4H_8O{\times}17\ H_2O$) had a shape of spherical segment of height 7.5 mm or of hemisphere 30 mm in diameter.

The energy released in a burp was estimated within 15 % error by different ways depending on the form of a sample: by making balance of energy in a sample and copper walls, by integrating a heat removed by helium, or directly from records of a thermocouple installed inside a sample. The temperature stability of a sample during irradiation was within ± 0.3 K. The dose rate in solid methane was $0.2{\div}0.23$ W/g (about 10 % of that due to gamma radiation); in water ice and hydrates, $0.1{\div}0.115$ W/g. The fast neutron flux was $2 \cdot 10^{12}$ cm^{-2}·s^{-1} with an averaged neutrons energy of about 0.3 MeV.

2. RESULTS AND ANALYSIS

2.1. Solid Methane. Twenty-three runs of irradiation of nine types of samples (layers of methane with thickness of 0.28, 1, 1.3, 1.6, 2.2 mm and spherical segments of height 4.6, 7.5, 9, and 14.3 mm) were performed. The irradiation time was from 3 up to 22 h. The principal results may be formulated as follows:

- No spontaneous burp was observed.
- For irradiation time ≥ 4 h and for size of samples ≥ 1 mm, thermally induced burps were always registered, see Fig. 2, with no effect of the size of a sample on ignition condition; the smallest samples displayed burps after 10–12 h of irradiation.
- Maximal (initial) rate of energy accumulation in solid methane (at temperatures more than 20 K) was estimated to be as high as 1.6 ± 0.2 % of absorbed dose rate, that is, ≈ 3.5 mW/g.

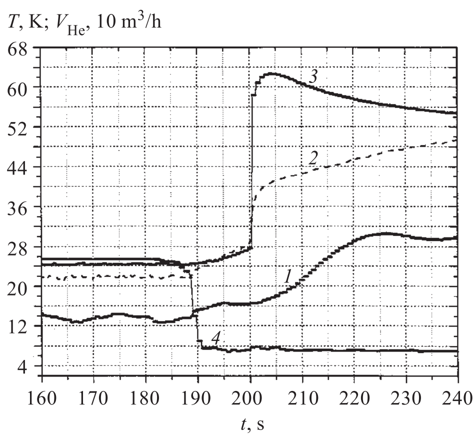


Fig. 2. Induced, fast release of stored energy in solid methane: temperature excursion versus time. *1* — temperature of cooling helium; *2* — temperature of copper walls of the irradiation capsule; *3* — temperature of methane at 8 mm off the walls; *4* — helium flow rate, 10 m^3/h

The simplest equation which defines a molar concentration of radicals n during irradiation is

$$\partial n/\partial t = R - RK_1(T)n - K_2(T)n^2, \qquad (1)$$

where R is radical production rate; T is temperature of a sample, and $K_i(T)$ are recombination reaction rate coefficients that are assumed to increase with temperature. The first-order term on the right describes a rate of recombination of stabilized radicals caused by hot tracks of recoil protons, and the term of the second order is a rate of recombination due to diffusion. As we have a deal with low-temperature samples and very high dose rates, the diffusion term seems to be negligibly small during irradiation. In this case, saturated value of concentration of radicals (and saturated energy value Q_∞ subsequently) is independent of a dose rate, as is evident from Eq. (1). This assumption was confirmed by comparison of saturated values of stored energy in solid methane moderators operated in the world. Having different dose rates in the range 10–200 Gy/s, they showed identical values of Q_∞ being equal to 45–55 J/g at an irradiation temperature of 25–26 K. Basing on a host of experimental data of the URAM-2 project, Q_∞-value was estimated with a precision of about ± 10 % for temperature range 21–28 K, that is, for phase I of solid methane. The temperature dependence can be described in Arrhenius form with $T_{\rm act} \approx 100$ K, see Fig. 3:

$$Q_\infty \approx 45 \exp\left(\frac{T_{\rm act}(26 - T_{\rm irr})}{26 T_{\rm irr}}\right) \text{J/g}. \qquad (2)$$

The energy storing rate R was found to be equal to (13±1) J/(g · h). There was one experiment at $T = 10$ K which showed a higher energy storing rate for phase III of methane — 20–30 J/(g · h).

A lack of spontaneous burps in the given experiments contradicts previously reported data on radiation effects in solid methane [3–5]. The conditions were almost identical in URAM-2 and in cold moderators at the IBR-2, IPNS, and KENS facilities where spontaneous burps were recorded: the same irradiation temperatures, identical cooling condition and characteristic size of samples. Differences were only in masses of methane and in the material of walls (Al and Cu). In the URAM-1 experiments [4] where the mass of methane was small (about 16 g), no spontaneous burp was also registered. The mass of methane (exactly mass, not size!) may be a significant factor if the nonuniformity of the radical spatial distribution plays an important part in the process of fast recombination of radicals. Then, instability can arise in a small region with density of radicals much higher than averaged over a sample. An interesting regularity was observed for induced burps: stored energy is close to be linear to temperature difference between the temperature of ignition and some constant $T_{\rm cl}$, see Fig. 3. In the equation of line

$$Q_{\rm ign} = C(T_{\rm cl} - T_{\rm ign}) \tag{3}$$

factor $C \approx 10$ J/(g · K) and $T_{\rm cl} \approx 34-35$ K, which is consistent with the temperature of the threshold of mobility of radicals [10, 11]. The same linear relation between the critical value of stored energy and the temperature of burping was deduced assuming cluster distribution of radicals [5, 9]. In there $T_{\rm cl}$ value was interpreted as a temperature of ignition of a small region enriched with radicals.

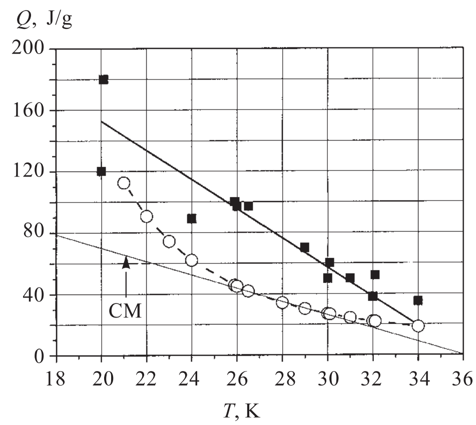
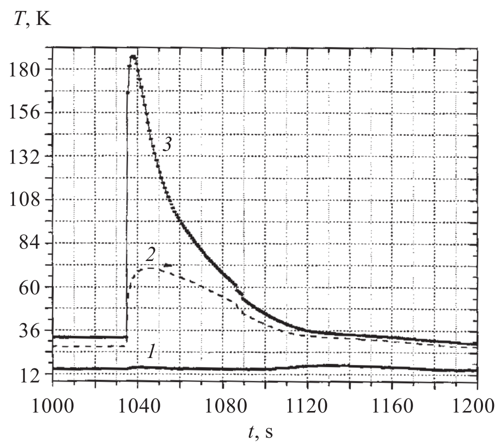


Fig. 3. Chemical stored energy in solid methane Q versus temperature of methane T. Black squares — amount of stored energy in induced burps versus temperature of ignition; open circles — saturated quantity of stored energy versus irradiation temperature; line CM — amount of stored energy in spontaneous burps of IPNS moderators [3], linear approximation of the authors

2.2. Water Ice. A considerable body of work existed in the science literature on the radiolysis of water ice under γ radiation and charged particles (for example, [12–16]). However, most of information falls into the region of low dose rates and nothing exists essential to our purpose — fast release of stored energy under strong irradiation with fast neutrons. The authors could find no presentation of observation of spontaneous burps in ice but for burps induced by small perturbation in cooling condition [7].

Twenty runs of irradiation with three types of samples (spherical segments of height 7.5 and 15 mm and beads of ice in argon matrix) were performed. The irradiation time was from 3 to 15 h. Spontaneous burps occurred after $5{\div}11$ h of irradiation of icy samples at 20–24 K (temperature of copper walls) and after longer irradiation at 30–34 K. Warming-up of a sample during a burp reached almost 200 K for a time less than 1 s (see Fig. 4). At higher temperature, spontaneous burping was not observed though the concentration of radicals at the end of irradiation was close to saturation.

After short time of irradiation (3–5 h), induced burps were always stimulated by increasing cooling helium temperature, and stored energy was estimated by the methods described above.



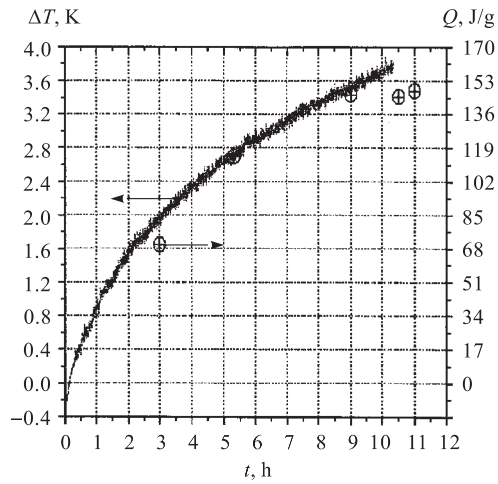


Fig. 4. Spontaneous release of stored energy in water ice: temperature excursion versus time. *1* — temperature of cooling helium; *2* — temperature of copper walls of the irradiation capsule; *3* — temperature of methane at 8 mm off the walls

Fig. 5. Evolution of the temperature difference between copper walls and ice (8 mm off the walls) in the process of irradiation (left vertical scale). The crosses inside the circles are amounts of stored energy (right vertical scale)

It appeared to be as high as 5.4 ± 0.4 % of absorbed dose rate, that is, $20 \div 24$ J/(g · h) for URAM-2 irradiation condition ($2 \cdot 10^{12}$ cm$^{-2} \cdot$ s^{-1}).

It was observed that the radical production rate, or the rate of energy accumulation, depends on methods of ice preparation. If ice samples (5-mm beads) are prepared by freezing water droplets in liquid nitrogen, then the rate of energy accumulation is factor of $2 \div 2.3$ less than that of the ice prepared by slower cooling of a water bathe. The same observation was earlier referenced for luminescence of ice after gamma irradiation [16]. This phenomenon may be a reason why Q quantity sometimes varied from experiment to experiment under identical condition of irradiation: the cooling rate of water sample was not identical. The procedure of water freezing affected also a critical concentration which appeared lower for an ice sample being frozen faster.

Another unexpected phenomenon which water ice displayed under fast neutron irradiation is fast increase of thermal resistance in the process of irradiation, see Fig. 5. The plot in the figure represents an evolution in time of a difference in reading of thermocouples, one of which was installed inside a hemispherical sample of ice $D = 30$ mm at $r = 7.5$ mm and the other measured the temperature of the copper walls of the irradiation capsule. The initial difference is close to zero due to the high thermal conductivity of ice at low temperature [16], but just after the beginning of irradiation it started going up steeply. The saturated value of thermal conductivity was estimated to be as low as ≈ 0.5 W/(m · K), which is close to that of solid methane. After a burp thermal resistance recovers.

2.3. Hydrates (Clathrates). From eight experiments with tetrahydrofuran hydrate and methane hydrate it can be deduced that these substances behave similarly to water ice but with lower radical production rate (or «energy storing rate»), which in these cases was close to 10 J/(g · h) (like for the ice beads prepared by freezing water in liquid nitrogen). Spontaneous burps with $Q \approx 100$ J/g occurred in both hydrates after 13 h of irradiation at $T = 20$ K. At higher temperatures (up to 35 K) there were no burps even after one day of irradiation when stored energy was saturated.

CONCLUSION

Spontaneous release of energy after irradiation at low temperature (20–35 K) in fast neutron field was observed for the first time in water ice and hydrates of methane and tetrahydrofuran. The temperature of samples after fast release of energy has reached 200 K. This phenomenon is due to thermal instability of a sample with accumulated concentration of radicals of an order of 1 %. Answers to the next questions seem to be essential both for practical use (construction of cold moderators) and for the theory of fast recombination of radicals:

— Does the mass of methane affect spontaneous release of stored energy in solid methane or not?

— What is a critical concentration of radicals in water ice at temperatures below 20 K?

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