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WATER MOLECULES ROLE AND IMPACT ON RECOMBINATION PROCESSES IN LITHIUM SULFATE MONOHYDRATE

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Curves of a thermal luminescence in $Li_2SO_4H_2O$ *are studied. For an explanation of the received results quantum and chemical calculations are carried out. It is shown that radiolysis products molecules of water lead to disintegration of sulphatic anions. On the other hand they "switch off" defects of a sulphatic subsystem from recombination processes.*

Keywords: thermal luminescence, lithium sulfate monohydrate, "switch off" defects, recombination processes.

When heated, lithium sulfate crystal-hydrates lose water; this permits to define the problems of studying the role and impact of water molecules on radiation stimulated processes behavior. It is known [1] that in lithium sulfate monohydrate the curve of thermal luminescence (TL) consists of two strongly overlapping luminescence peaks with their maximum at 100К and 130К. After monohydrate thermal decomposition the peak of recombination luminescence at 100К disappears [1]. Thus, the TL peak at 100К is related to the recombination of crystal water radiolysis products recombination, and at 130К with recombination of radiation defects in the sulfate subsystem. Besides, it was established experimentally that X-ray luminescence intensity in waterless sulfate in by 3 to 4 orders higher than in monohydrate.

In Figure 1 there is shown the TL curve after lithium sulfate monohydrate irradiating with UV light. In Figure 1 it is seen that there is observed a single expressive luminescence peak with its maximum in the realm of 135К. On its low-temperature wing there is a distortion showing this luminescence peak non-elementary character. The specimen isothermal annealing at 100К after UV irradiation at the temperature of liquid nitrogen permitted to separate the luminescence peak at 130К. Thus, under the action of UV light there form defects in the sulfate subsystem and there takes place water molecules photolysis. It’s worth noting that in waterless specimens of lithium sulfate there is no accumulation of light sums.

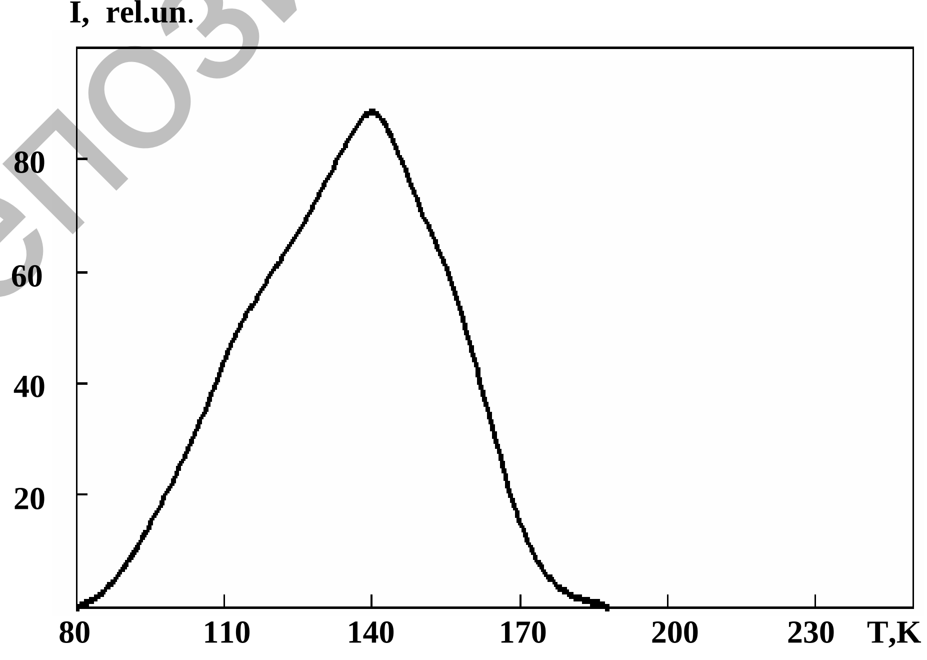

Fig.1. TL curve of lithium sulfate monohydrate after UV irradiation

Thus, crystal water molecules help defects to form in the sulfate subsystem and depress strongly X-ray luminescence intensity.

One of the products of photolysis or radiolysis of crystal water molecules is atomic hydrogen. We supposed that atomic hydrogen helps sulfate anions to decompose. To check this supposition we carried out the computer modeling of hydrogen atom with SO_4^{2-}ion.

The modeling was carried out on $(SO_4^{2-}2Li^+H^0)$ cluster by semi-empiric quantum-chemical method of MNDO computation. The computation method selection is based on the fact that this scheme gives sufficiently well the energy characteristics of molecules forming and decomposing [2]. In $(SO_4^{2-}2Li^+H^0)$ cluster lithium atoms located near the sulfate anion in accordance with crystallographic data. The hydrogen atom approached the oxygen atom of the sulfate anion. The sulfate anion original geometry had symmetry of the point group T_d. At each stage of the hydrogen atom movement it did not change, as there is supposed that the characteristic time of interaction is of order of a single in-molecule oscillation. Within such time there does not occur the geometrical structure relaxation.

In Figure 2 there is presented the computed potential curve. In Figure 2 it is seen that hydrogen atoms joining the sulfate anion is an energy-wise profitable process, as the cluster general energy reduces significantly. To join the hydrogen atom to SO_4^{2-} it is necessary to overcome a small energy barrier. This barrier height is about 0.2 eV. Such a barrier can be overcome by the hydrogen atom due to its thermal movement.

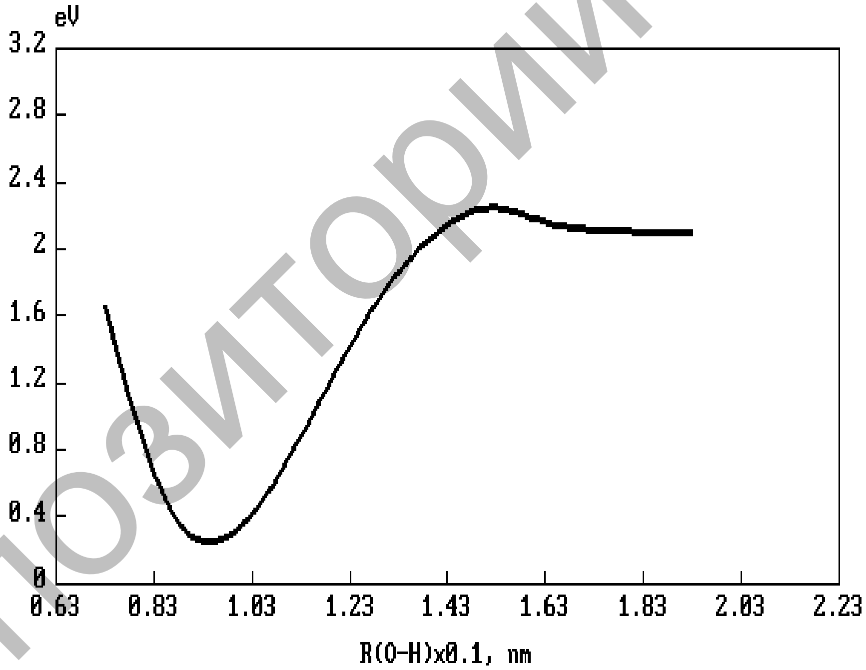

Fig.2.Potential curve of interaction between atomic hydrogen and sulfate anion SO_4^{2-}

Optimization of $(SO_4^{2-}H^0)$ complex geometrical structure showed that it decomposes without activation with forming SO_3^- and OH^-ions. It is known [3] that SO_4^{2-} ion is subject to non-activation decomposition when captured by the electron sulfate anion. Here there takes place a similar process. Oxygen atoms are more electrically negative, therefore electronic density shifts from the hydrogen atom to the oxygen atom. The analysis of electronic density distribution in $(SO_4^{2-}H^0)$ cluster proved this statement. In dissociative decomposition of the sulfate anion there form SO_3^{2-} ions and an oxygen ion. In our case the hydrogen atom plays the role of electron-excess center, and there from SO_3^- and OH^-ions.

The main known radiation defects in sulfates are: an auto-located hole SO_4^-, SO_3^-, SO_3^{2-} and O^- ions [4,5]. In order to explain the suppression of X-ray luminescence intensity, we simulated the interaction of the known radiation defects in the sulfate subsystem with a hydrogen atom.

It is obvious that atomic hydrogen that occurs due to photolysis or radiolysis of crystal water molecules interacting with O^- ion, form OH^- defect. This ion has sufficiently large bond energy. So, as a result of such an interaction a part of O^- ions is “turned off” from recombination processes. However, in our opinion, the abovementioned channel is not the only that explains such a great difference in recombination luminescence intensity in mono- and dehydrated crystals of lithium sulfate.

Atomic hydrogen taking the inter-node position or anion vacancy forms U-type centers. In haloid of alkali metals, in the zone of transparence these centers have characteristic absorption bands [6]. Above we indicated that under the action of ionizing radiation lithium sulfate crystal-hydrates are not colored. By the EPR method in these compounds the centers of atomic hydrogen were not fixed either [7]. This shows indirectly that atomic hydrogen forms in sulfate matrixes non-paramagnetic complexes.

When modeling the interaction of SO_3^- and SO_4^- radicals with atomic hydrogen it is necessary to consider two possible spin states. The total spin can be equal to 1 (triplet state) and 0 (singlet state).

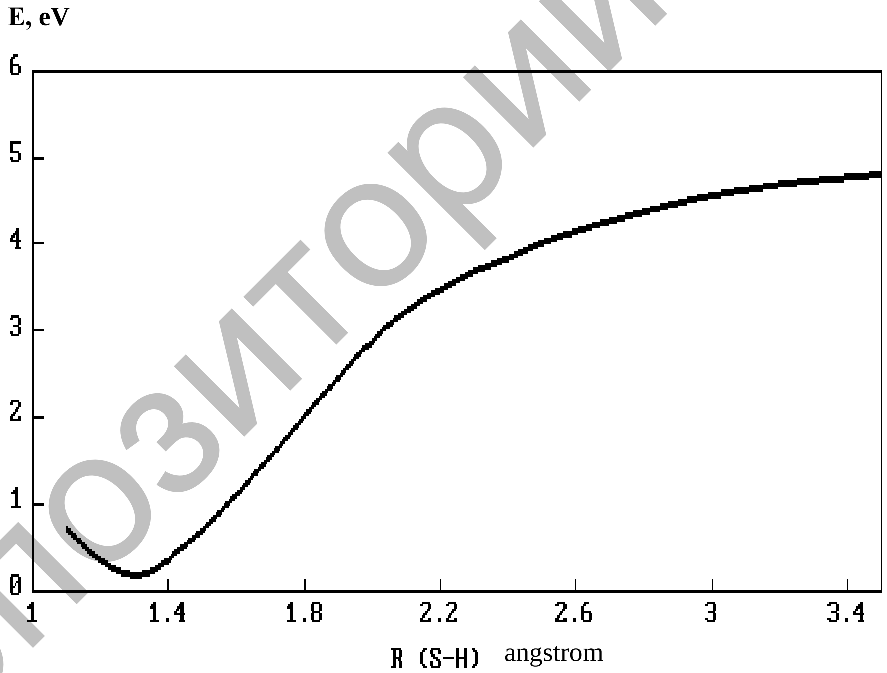

Fig.3. Potential curve for $(SO_3H)^-$ complex with the hydrogen atom tearing

The hole center SO_3^- has a pyramidal structure with symmetry of the point group C_{3V}. This center geometrical structure and bond energy were computed earlier by the methods of quantum chemistry in work [8]. These results were taken as the starting ones for the further computation. Computing the energy of interaction of SO_3^- defect with the hydrogen atom show that the optimal way of the reaction runs on the symmetry axis C_3 with H^0 approximation to the sulfur atom. We established that in the triplet spin configuration the hole center SO_3^- does not capture the hydrogen atom. On the potential curve of their interaction there is no minimum proving the presence of the bound state. In the singlet configuration on the potential curve there is an energy minimum which indicates the forming of $(SO_3H)^-$ complex. The formation of this non-paramagnetic complex has no energy barrier and is energy-wise profitable, as it leads to reducing the system general energy. When the hydrogen atom joins SO_3^- ion, the geometrical parameters of the latter change. That's why we carried out a complete optimization of the geometrical parameters of $(SO_3H)^-$ complex. After its geometry optimization we computed the potential curve of the hydrogen atom tearing. The result of computation is presented in Figure 3. The analysis of electronic density distribution on the atoms permitted to establish that this complex decomposition takes place by the reaction:

$$(SO_3H)^- \rightarrow SO_3^0 + H^- .$$

The energy needed for this reaction is equal to 4.7 eV. Thus, it cannot be thermally activated. In the singlet state, when SO_3^- anion interacts with atomic hydrogen, there forms a stable complex.

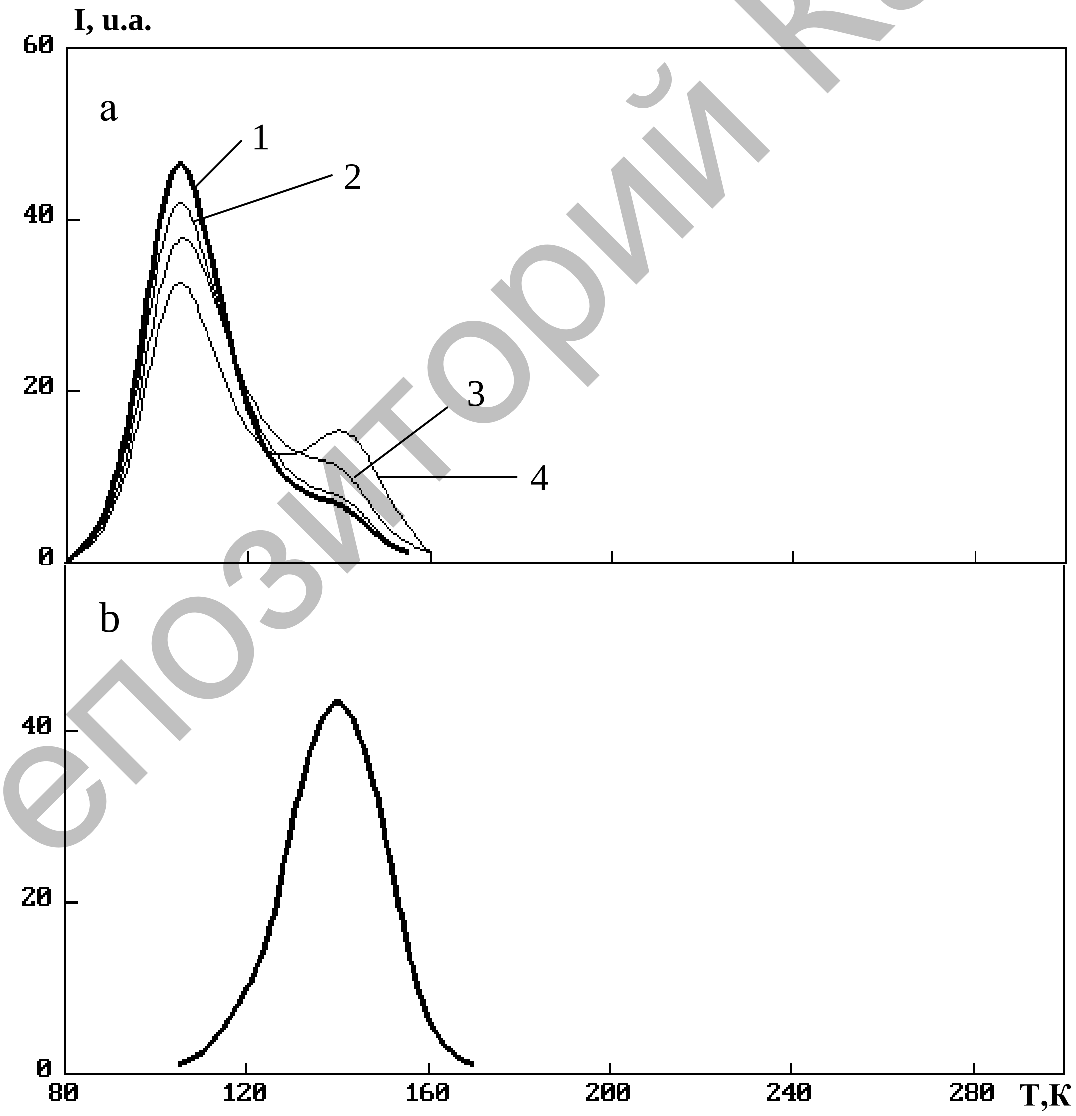

Fig.4. a – TL curves for $Na_2SO_4 \bullet 10H_2O$ after irradiation by X-rays of doses 100 kGr (1), 150 kGr (2), 200 kGr (3), 300 kGr (4); b – TL curve for waterless potassium sulphate. Dose of irradiation 50 Gr.

Similar computations were carried out for $(SO_4H)^-$ complex. It was established that for the hydrogen atom it is energy-wise profitable to join SO_4^-ion. Here there is formed a stable complex both in the singlet and in the triplet states.

For $(SO_4H)^-$ complex there was carried out a complete optimization of geometry for establishing its stability. In the singlet state the following reaction is the most energy-wise profitable:

$$(SO_4H)^- \rightarrow SO_3^- + OH^0 .$$

For its running there is needed energy equal to 3.5 eV. Such a process cannot be activated thermally in the temperature range up to the temperature of crystal melting.

The direct optimization of the $(SO_4H)^-$ complex geometrical structure in the triplet state showed that it is unstable. This complex decomposes without activation with forming defects SO_3^0 and OH^-.

The last of the known defects in sulfates whose interaction with atomic hydrogen was considered was SO_3^{2-}. It presents a pyramid, and its symmetry relates to group C_{3V} [9]. It was established that it is profitable for the hydrogen atom to join this ion along C_3axis. This process leads to reducing the general system energy and takes place without activation. There was carried out optimization of $(SO_3^{2-}\ H^0)$ complex geometrical parameters. The complex complete energy minimum corresponds to the S–H bond length, equal to 1.6 Å. There was computed the energy needed for the hydrogen atom tearing from this complex. It made about 0.5 eV. This process can be thermally activated. Thus, SO_3^{2-} ions are traps for atomic hydrogen.

Thus, when the hydrogen atom interacts with the known radiation defects in the sulfate subsystem, they are partly “turned off” from the recombination processes, as they form rather stable complexes.

Similar results are received when studying a recombination luminescence of crystals of Na_2SO_4. In figure 4a curve TL for this connection at radiation by X-rays at 80K is shown. It is visible that there are 2 TL peaks at 95K and at 140K. For accumulation surely measured lightsum it is necessary a dose of radiation order 50kGr. In waterless sulphate of sodium on TL curve one peak of a luminescence is observed. Its maximum is at 140K. The received result is given in figure 4b at a radiation dose 50Gr. Therefore the exit of recombination luminescence in waterless sulphate of sodium in comparison with crystal-hydrates is 3 orders higher. It is explained by influence of crystal water, products radiolysis which "switch off" defects of a sulphatic subsystem from participation in recombination processes.

Thus, crystal water photolysis or radiolysis leads to occurring a new channel of sulfate anions decomposition. This allows explaining the TL peaks occurring when lithium sulfate monohydrate is irradiated with UV light. On the other hand, the hydrogen atom joins the sulfate subsystem defects, forming stable complexes. This permits to explain strong suppression of X-ray luminescence intensity in the monohydrate.

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