

## RADIATION-INDUCED MOTION OF LIQUID INCLUSIONS IN ALKALI HALIDE CRYSTALS

*A.P. Kulik<sup>1\*</sup>, O.V. Podshyvalova<sup>2</sup>, I.G. Marchenko<sup>1,3\*\*</sup>*

<sup>1</sup>*V.N. Karazin Kharkov National University, Kharkov, Ukraine*

<sup>2</sup>*N.E. Zhukovsky National Aerospace University*

*“Kharkov Aviation Institute”. Kharkov, Ukraine;*

<sup>3</sup>*National Science Center “Kharkov Institute of Physics and Technology”, Kharkov, Ukraine*

*E-mail: \* kulykop@gmail.com; \*\* march@kipt.kharkov.ua*

This scientific paper studies the effect of irradiation on the radiation-induced motion of liquid inclusions in KCl. It was shown that the inclusions exposed to the irradiation become mobile. It can result in the migration of such inclusions to the material boundary and release of radioactive elements by nuclear waste site. The trajectories of spontaneous migration of the inclusions of a different size in the crystals exposed to the irradiation with the electrons and  $\gamma$ -quanta have been studied.

### INTRODUCTION

The irradiation has a substantial influence on a change in the properties of original material [1]. Many processes are accelerated under the action of the neutron, -electron and gamma irradiation. The phenomena of radiation-accelerated diffusion, creep, embrittlement, etc. are well-known [2–5].

At the same time, the irradiation can affect not only the diffusion mobility of individual atoms or clusters but also the behavior of macroinclusions. Such inclusions are present in many virgin minerals, in particular in the depositions of a geological origin. Such minerals can be used for the nuclear waste disposal [6]. With time, nuclear reactions progress at nuclear waste sites. It can result in the activation of the processes of interaction of the matrix substance with land-buried products, in particular in the motion of inclusions that occupy vacant surfaces followed by their discharge into the atmosphere. In this connection, the studies of the influence of radioactive defects on the motion processes of liquid inclusions are of great interest.

The objective of this research paper was to study the radiation-induced motion of liquid inclusions in KCl monocrystals exposed to the irradiation with  $\gamma$ - quanta and electrons.

### SPECIMEN PREPARATION

Liquid inclusions were formed in KCl monocrystals using the crack healing method [7]. For this purpose the incomplete crack was formed in the specimen and that crack was filled with the distilled water exposed to the action of capillary forces. The specimen has been held at room temperature for about ten days to heal the crack and it was accompanied by the formation of the inclusions of saturated KCl water solution in the mouth of crack. The dimensions of formed inclusions varied in the range of 3 to 100  $\mu\text{m}$ .

The motion of liquid inclusions was studied in the temperature gradient field and the temperature gradient value varied in the range of  $2 \cdot 10^2$  to  $2 \cdot 10^4$  K/m. The temperature gradient was created in the specimen by contacting its opposite faces with the heater and the fridge that was cooled by the running water. To define

the temperature gradient value of ( $\nabla T$ ) the reference crystals of the same size as the specimens with inclusions were annealed. Two thermocouples were soldered into reference samples. Thermocouples' readings were taken to calculate the temperature gradient value for the specimens under certain distance between the thermocouples.

The motion of inclusions was observed using the optic microscope with the sight check. For this purpose, the heater, the specimen and the fridge were fixed on the microscope stage in such a way that the temperature gradient was oriented in the plane  $\{100\}$ , parallel to the direction  $\langle 100 \rangle$ .

The dislocation structure of studied crystals was controlled by chemical etching. The saturated methyl alcohol  $\text{PICl}_2$  solution was used as an etching agent. After the etching the specimen was rinsed by the mixture of ethyl and amyl alcohols.

### DISSOLUTION LAYER SOURCES

It is known that the layer-by-layer growth of crystals is realized either due to the two-dimensional crystal nucleation or due to the growth of dislocations that have a spiral component of the Burgers vector [8]. Assuming that the inclusion is a negative crystal the process of its motion can be viewed as a simultaneous growth of the frontal surface and the dissolution of the rear surface. In this connection, the dissolution of matrix on the frontal surface of the inclusion simulates the process of dislocation growth, because at driving forces that are realized in these experiments other sources of dissolution, except for the screw or Burgers dislocation fail to manifest themselves [2,9]. The growth of crystal at the rear surface of inclusion occurs due to the motion of stages that are formed in the angles between the rear surface and the lateral surface. This process simulates the dissolution of monocrystal when its edges act as the source of stages.

A dislocation mechanism of the dissolution of the frontal surfaces of moving inclusions is immediately confirmed by the following experiments. The dislocation structure of the most KCl crystals was studied to select the crystal with the inhomogeneous

distribution of dislocations. This crystal was used to chip out the specimen making the inclusions in it. The chipped off surface of a type (100) with the ensemble of inclusions near it that was selected for the observation was etched at the dislocation (Fig. 1,a). Afterwards, the specimen was placed into the temperature gradient field oriented in such a way that moving inclusions could cross both strongly and slightly dislocated areas of the specimen. The observations showed that moving inclusions stop as soon as they approach actually non-dislocated area of the crystal (Fig.1). It is evident that the inclusions that were not initially crossed by the dislocations should not move in general. The inclusions must also be motionless when the distance from the point of emergence of spiral dislocation to the face edge or to the point of emergence of the dislocation of an opposite sign is shorter than the threshold distance at specified motive forces [9].

### EXPERIMENTAL METHODS

The defects can be represented by electron and hole-type color centers formed under the action of ionizing radiation on alkali - halide crystals. These color centers are spot defects and these create no additional sources of stages on the crystal surface. However, their presence in the crystal can change the values of the kinetic characteristics of dissolution processes, in particular a kinetic coefficient of the stage that results in a change of the dissolution rate of crystal. In addition, the energy that was stored in the crystal during its irradiation should change the conditions of the thermodynamic equilibrium of the crystal and the solution. In other words, the solubility of irradiated crystal must be higher than that of unirradiated crystal.

The experiments were carried out using liquid inclusions for KCl crystals exposed to the irradiation with  $\gamma$ -quanta emitted by the  $\text{Co}^{60}$  source and the electrons of 10 MeV at the integral current density of  $5 \cdot 10^{-2} \text{ A/m}^2$  (a total dose reached the value of  $10^{21} \text{ m}^{-2}$ ). The irradiation resulted in colored specimens. The type and the concentration of color centers were defined from the spectra of the optic absorption of irradiated crystals using appropriate methods [10]. For all the experiments, the basic color centers were electron F-centers and hole-type  $\text{V}_3$ -centers. The concentrations of identified  $\text{R}_1$ -,  $\text{R}_2$ - and M-centers turned out to be much lower. Depending on the dose and the type of irradiation the concentrations of F- and  $\text{V}_3$ -centers were approximately the same and varied in the range of  $10^{21} \dots 10^{23} \text{ m}^{-3}$ .

A scheduled series of experiments was carried out using liquid inclusions in KCl monocrystals in which only electron centers were formed due to the additive coloring in the pairs of alkaline metal [11]. For this purpose, the plate was chipped out the KCl crystal and it was placed into the container made of stainless steel at the bottom of which the metal potassium was located. The container was tightly closed by the screwed cover. The temperature was controlled using the built-in thermocouple. The container was annealed in the argon atmosphere at a temperature of  $T = 600^\circ \text{C}$  during one hour. The specimen was cooled to the room temperature simultaneously with the cooling of the furnace.

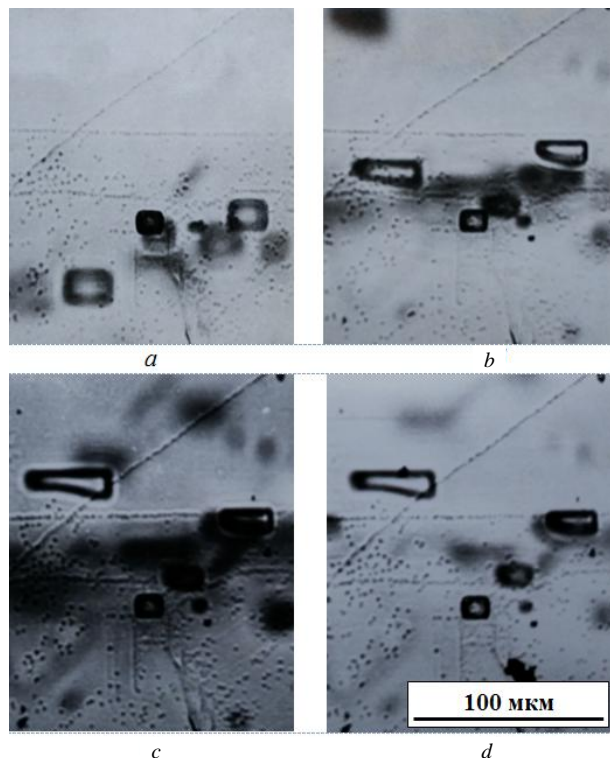


Fig. 1. Motion of the inclusions in the temperature gradient field of KCl crystal with the inhomogeneous distribution of dislocations: a is the initial state, b – 11; c – 16; d – 25 h

The inclusions in colored specimens were observed both in the temperature gradient field and under isothermal conditions. For additively colored crystals the direction of temperature gradient was preset perpendicularly to the crack plane. It is conditioned by the fact that the inclusions in the additively colored crystals turn out to be in the recrystallized region that contains no color centers during the crack healing in contrast to irradiated crystals (the crystals were exposed to the irradiation with already formed inclusions).

### MOVING AND RESHAPING INCLUSIONS IN THE CRYSTALS WITH COLOR CENTERS

Motion of the inclusion in the colored crystal is accompanied by the dissolution of the crystal with color centers on its frontal surface and the growth of crystal that has no such color centers on the rear surface. As a result, moving inclusions form brightened up traces behind them (Fig. 2). In this case we observe one more peculiarity of this process; in particular gas bubbles are formed inside liquid inclusions. The motion of such an inclusion can result in its decomposition into the liquid component and the gas-liquid component with a large amount of gas. Specifically, it can be explained by that the electrons localized in anion vacancies transfer to the solution during the dissolution of the crystal containing F-centers. These solvated electrons transfer hydrogen in the atomic state when bonding with  $\text{H}^+$  ions available in the solution [12].

Hydrogen formed in the inclusions saturates and oversaturates the solution and it forms the bubbles that can be seen in the inclusions.

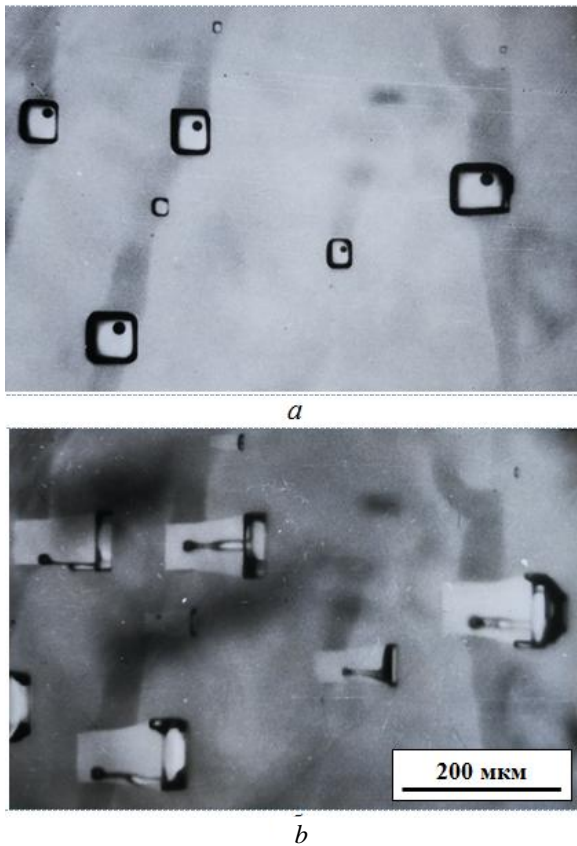


Fig. 2. Motion of the inclusions in the  $\nabla T$  field in irradiated KCl crystals: *a* is the initial state; *b* is the state after 5 hours

Motion of the inclusions both in irradiated specimens and in additively colored crystals occurred in the mode of boundary kinetics that is also peculiar for the motion of the inclusions in the crystals that contain no color centers [13]. It means that the diffusion transfer of the matrix substance through the inclusion volume will not limit the process of its motion. Alongside, the average values of velocities of the inclusions of the same size moving in the crystals with color centers turn out to be 30 to 50% higher in comparison to those in pure crystals, at other equal conditions. Such an increase can be related to a change in the crystal-solution boundary structure of colored crystals. The fact that such a change takes place confirms indirectly the difference in the etching patterns of colored and pure crystals (Fig. 3). It can also be clearly seen when etching the chipped off part of irradiated crystal over the inclusion passage plane (Fig. 4). The given patterns are indicative of the fact that not only the dislocations but also radiation defects and their clusters are the sites for the primary etching of the surface of KCl crystal. Similar etching patterns were observed on the surface of NaCl monocrystals irradiated with neutrons [14].

In contrast to the irradiation process of crystals that results in the formation of hole-type color centers in addition to electron centers the additive coloring of crystals results only in the formation of electron color centers. Hence, an increase in the motion velocity of the inclusions in the specimens of both types is indicative of the fact that particularly their influence on a change in the matrix-solution interphase structure can be considered as a defining factor.

In the absence of the external force fields that affect the crystal, nonisometric inclusions (the pores) spontaneously transform their shape approximating it to the equilibrium one [15,16]. These processes proceed to the extent of the difference of the chemical potentials of atoms (molecules)  $\Delta\mu = \gamma\Omega\Delta H$  conditioned by the difference in the local curvatures of surface  $\Delta H$  ( $\gamma$  is the surface tension,  $\Omega$  is the volume falling to one particle in the crystal). Since typical under saturations are low, the motion of stages that originate on spiral dislocations is only possible on condition that the distance from the point of emergence of the dislocation to the face edge or to the point of emergence of the dislocation of an opposite sign exceeds a diameter of the critical nucleus  $d_c = 2\alpha\Omega/\Delta\mu$  ( $\alpha$  is an effective surface tension of the stage defined as a ratio of its linear tension to the height). During the relaxation process the value of  $\Delta\mu$  is decreased and  $d_c$  is increased respectively and the dissolution (evaporation) process of the stages is stopped.

Hence, the shape relaxation process (equally as the motion process of inclusions (the pores)) is the threshold one for the layered mechanism in the crystals with no color centers. Attention should be paid to the fact that a motive force of the shape relaxation is defined by the surface tension  $\gamma$ , and the process hampering and its stoppage depend on the value of  $\alpha$ . Using the value of the residual degree of nonisometry of the inclusions (the pores) we can obtain information on the  $\alpha/\gamma$  ratio [15, 16] required for the understanding of many phenomena that occur on the crystal surface.

Available color centers have an essential influence on the relaxation process in isometric conditions of the shape of inclusions acquired during the motion in the temperature gradient field. In the pure crystal the relaxation of the shape of inclusion occurs through the dissolution of frontal and rear faces and the growth of lateral edges. In this case, the mass center of inclusion is not biased. In the irradiated crystal this process occurs mainly through the dissolution of the frontal edge only (Fig. 5). In addition, the degree of relaxation of the shape of inclusions in irradiated crystals is considerably higher in comparison to that of unirradiated crystals practically approaching very often the equilibrium shape.

Such a behavior of the inclusions can be conditioned at least by two reasons. The calculations and experiments [14] show that the concentration of equilibrium solution over the crystal is changed in most cases insignificantly depending on the extent of its defectiveness. However, for the liquid inclusion whose opposite faces are in inequivalent conditions (one face contains color centers and another face contains no color centers), and this difference can serve as an additional motive force ( $\Delta\mu_f$ ) of dissolution processes on frontal faces. The second reason can be related to the fact that the kinetic coefficients of the stages that characterize the emission rate of crystal particles by the stage (or the rate of their lining up to form the stage)



and define the rate of its motion have different values on the surfaces contiguous with the irradiated area of the crystal and with the recrystallized region. A value of the kinetic coefficient of the stage at other similar conditions is defined by the concentration of fractures on the stage. It is evident that the F-centers representing anion vacancies that captured an electron increase the values of the kinetic coefficients of elementary stages when appearing on the surface and increase the dissolution rate of the face as a whole.

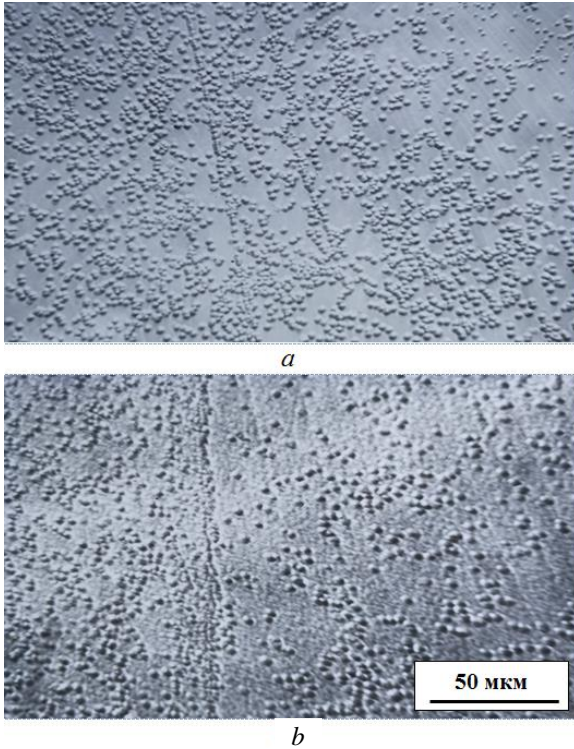


Fig. 3. The structure of the etched surface of KCl crystal before (a) and after (b) the irradiation

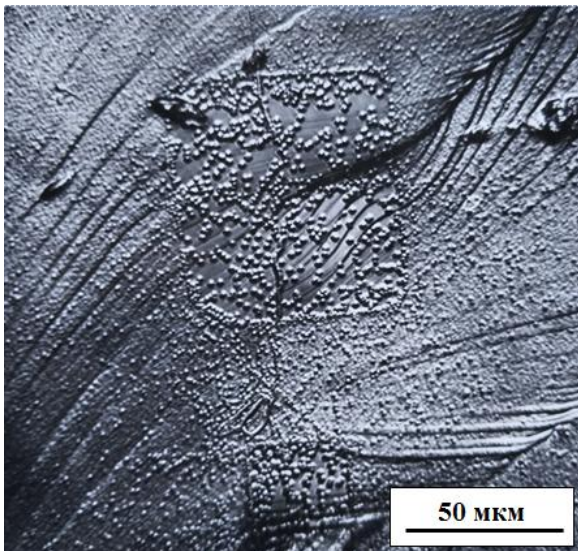


Fig. 4. Etching the crystal chip dislocation in the inclusion passage plane

Summing up, we can draw a conclusion that the motion of dissolution stages on the frontal surface contiguous with the defective area of the crystal will also be possible at a full relaxation of the inclusion shape on condition of the sufficient concentrations of

color centers in the crystal. However, in this case the crystallization will occur on the rear face and it won't be observed on lateral faces. In other words, the inclusion can shift as a whole in the absence of external force fields.

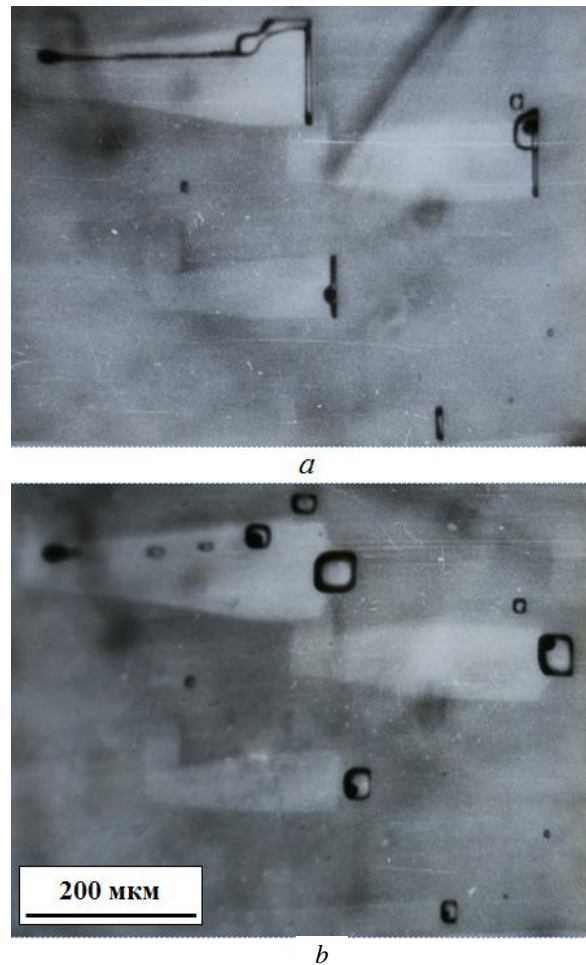


Fig. 5. Relaxation of the shape of inclusions in the irradiated crystal. The relaxation time is 34 hours

### SPONTANEOUS MIGRATION OF THE INCLUSIONS IN IRRADIATED CRYSTALS

Let's give consideration to the liquid inclusion in the irradiated crystal. Let's assume that the fluctuation or short-time external action (for example, that of the temperature gradient conditioned by the nonuniform cooling of the specimen and substrate after their irradiation) resulted in an insignificant recrystallization of the matrix substance from one surface of the inclusion to another. Since radiation defects are not reproduced we can observe the inequivalence of these surfaces conditioned by the difference in the chemical potentials of atoms  $\Delta\mu_F$  in the irradiated and recrystallized regions of crystal. If the value of  $\Delta\mu_F$  is sufficient to cause the motion of dissolution stages on any surface contiguous with the defective area of the crystal the motion of the inclusion as a whole is possible. The discussed type of the motion of the inclusions was observed in electron-irradiated KCl monocrystals in which the concentrations of basic color centers, i.e. electronic F-centers and hole-type  $V_3^-$

centers were approximately the same and these were equal to  $n \approx 2 \cdot 10^{23} \text{ m}^{-3}$ .

After the irradiation, the crystals were matured in isothermal conditions at room temperature in the absence of external force fields. It was accompanied by spontaneous motion of the inclusions (Fig. 6). The normal dissolution rate of the faces of inclusions given in Fig. 6 was about one monolayer per second. With time, the rate of inclusions was decreased and it is evidently related to the general decrease in the crystal defectiveness during its long-term maturing after the irradiation.

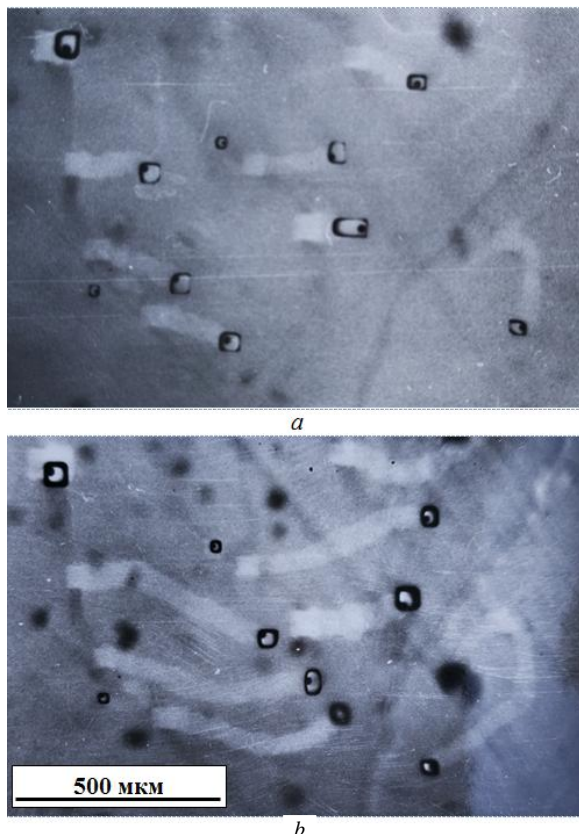


Fig. 6. Displacement of the inclusions in the electron-irradiated crystal in isothermal conditions: a – 9 days, b – 25 days after the irradiation

A motion trajectory of the inclusions can easily be judged from the brightened up traces that are formed behind them (Fig. 7). A chaotic behavior of the migration is evidently conditioned by the fact that only one (the rear surface) of six surfaces will be dissolved and as for the rest five surfaces the surface that has a more efficient source of the dissolution of stages will be dissolved. The most favorably located and oriented spiral dislocation is considered to be such a source. Different activity of dislocation sources can also explain an essential spread in the rates of inclusions due to the values of rates averaged by a sufficiently long time (up to one month) described in previous papers. Using the data on the motion kinetics we calculated an increase in the chemical potential of crystal atoms conditioned by the irradiation defects of  $\Delta\mu_f \approx qn\Omega$ , on the basis of which we estimated the stored energy  $q$  falling per one F-center.

The obtained value turned out to be much lower than that of the energy falling to one F-center during the irradiation of KCl crystal, according to the data of theoretical and experimental investigations described in B [14], –  $q \approx 5 \text{ eV}$ . A divergence was explained by a two-order difference in the concentration of color centers near the dissolution surface in comparison to that in the crystal volume. This difference was related to the perturbation effect of the solution on the pre-surface layer of the crystal of more than 10 nm thick in which the probability of tunnel recombination of electron and hole-type centers with each other is increased including also the donors and acceptors situated in the pre-surface layer of solution [17].

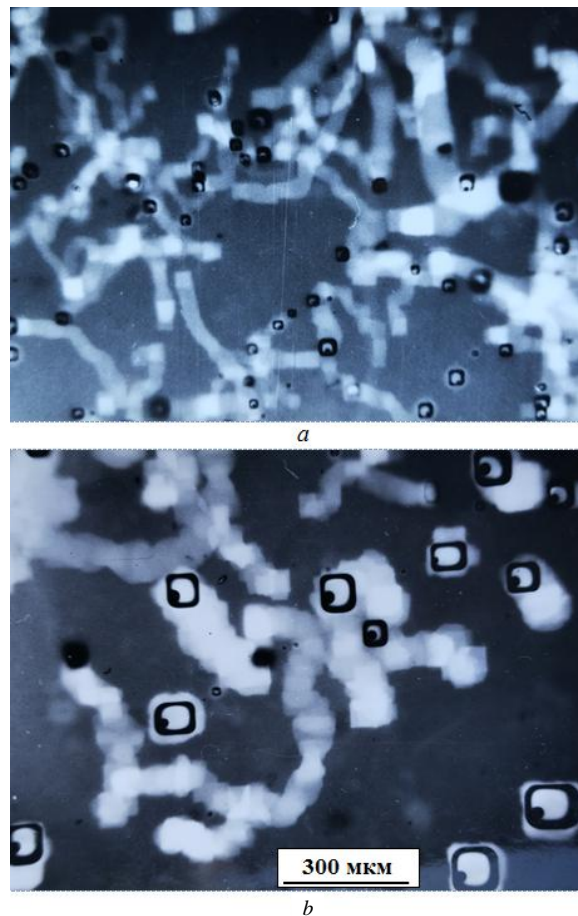


Fig. 7. The traces of spontaneous migration of the inclusions of a different size in the electron-irradiated crystal. The after-radiation time is one month

To look into the motive forces and the kinetics of the spontaneous migration of liquid inclusions in the crystals with spot defects of a radiation origin in greater detail we need to carry out additional investigations of the dynamics of these processes. In conclusion, we would like to note a fundamental difference in the role played by the color centers that are formed during the crystal irradiation and those that are formed during the additive coloring in the formation of the motive forces of spontaneous migration of the inclusions. The attempts made to induce spontaneous migration of the inclusions in the additively colored specimens turned out to be ineffective. Evidently, such an outcome is conditioned by the fact that in the second case the “matrix-color centers” system is thermodynamically



stable and in the first case it is thermodynamically unstable.

## CONCLUSIONS

This scientific paper looks into the effect the irradiation has on the radiation-induced mobility of liquid inclusions in KCl monocrystals. It is shown that these inclusions become mobile when exposed to the irradiation. It can result in the migration of such units to the material boundary and the release of radioactive elements from the sites of their disposal. The trajectories of spontaneous migration of the inclusions of a different size in the electron-irradiated crystal have been studied.

The obtained data are of great importance for the prediction of the properties of the storage sites of radioactive waste.

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## РАДИАЦИОННО-ИНДУЦИРОВАННОЕ ДВИЖЕНИЕ ЖИДКИХ ВКЛЮЧЕНИЙ В ЩЕЛОЧНО-ГАЛОИДНЫХ КРИСТАЛЛАХ

*А.П. Кулик, О.В. Подшивалова, И.Г. Марченко*

Изучено радиационно-стимулированное поведение жидких включений в монокристаллах KCl. Показано, что под действием облучения включения становятся подвижными. Это может приводить к миграции таких объектов на границу материала и выходу радиоактивных элементов из захоронения. Исследованы траектории самопроизвольной миграции включений различных размеров в кристаллах, облученных электронами и  $\gamma$ -квантами.

## РАДІАЦІЙНО-ІНДУКОВАНИЙ РУХ РІДКИХ ВКЛЮЧЕНЬ У ЛУЖНО-ГАЛОЇДНИХ КРИСТАЛАХ

*О.П. Кулик, О.В. Подшивалова, І.Г. Марченко*

Вивчено радіаційно-стимульовану поведінку рідких включень у монокристалах KCl. Показано, що під дією опромінення включення стають рухливими. Це може призводити до міграції таких об'єктів на межу матеріалу і виходу радіоактивних елементів із поховання. Досліджено траєкторії самочинної міграції включень різних розмірів у кристалах, опромінених електронами і  $\gamma$ -квантами.