PACS
УДК 539.1.074.5: 620.179.152

# Dead layer in living CsI crystal

A.M. Kudin[1], D.I. Zosim[2], A.Yu. Yemelyanov[2]

*1. National University of civil protection of Ukraine, 94 Chtrnyshevska str., 61023 Kharkiv, Ukraine*
*a.m.kudin@gmail.com*
*2. Institute for scintillation materials National Academy of Science, 60 Nauki ave., 61001, Kharkiv, Ukraine*

Representations of dead layer (DL) nature in CsI:Na crystals are considered. To eliminate the contradictions between the models of DL, degradation of the conversion efficiency (η) for surface layers has been studied. Simultaneously, the DL profile and its evolution under aging were studied using X-rays of different energies. It has been shown that immediately after surface polishing the η is increased for 5.9 keV photons (depth of 90% attenuation is equals ~7.6 μm). Anion vacancies are responsible for η increase, whose concentration in the disturbed layer is comparable with the concentration of the activator $C_A$. Decay of supersaturated vacancy solid solution results in extremely inhomogeneous distribution of the η due to the local distortion of the $C_A$. The consequence of this is the disappearance of the full absorption peak in the pulse height spectrum. Despite the loss of energy resolution and detection efficiency (at photopeak) the total counting rate remains constant for α-particles. The dead layer itself (the loss of full detection efficiency) is formed after the diffusion of sodium to the free surface, approximately after 6 months and more.

**Keywords:** dead layer; detection efficiency; conversion efficiency; light yield non-uniformity.

Розглянуто уявлення про природу мертвого шару (МШ) в кристалах CsI:Na. Для усунення розбіжностей між моделями МШ вивчено деградацію конверсійної ефективності (η) поверхневих шарів. Одночасно з цим вивчено профіль МШ і його еволюцію під час старіння, використовуючи рентгенівські кванти різної енергії. Показано, що безпосередньо після полірування поверхні η збільшена для фотонів з енергією 5,9 кеВ (глибина 90% послаблення ~ 7.6 мкм). За збільшення η відповідають аніонні вакансії, концентрація яких у спотвореному шарі порівняна з концентрацією активатора $C_A$. Розпад пересиченого розчину вакансій призводить до вкрай неоднорідного розподілу η через локальні порушення $C_A$. Наслідком цього є зникнення піку повного поглинання в амплітудному спектрі. Незважаючи на втрату роздільної здатності а також пікової ефективності реєстрації, швидкість рахунку α- часток по всьому спектру залишається постійною. Власне МШ (втрата повної ефективності реєстрації) утворюється через 6 місяців і більше, після дифузійного виходу натрію на вільну поверхню.

**Ключові слова:** мертвий шар; ефективність реєстрації, конверсійна ефективність; неоднорідність світловиходу.

Рассмотрены представления о природе мертвого слоя (МС) в кристаллах CsI:Na. Для устранения противоречий между моделями МС изучена деградация конверсионной эффективности (η) поверхностных слоев. Одновременно с этим изучен профиль МС и его эволюция при старении, используя рентгеновские кванты разных энергий. Показано, что непосредственно после полировки поверхности η увеличена для фотонов с энергией 5,9 кэВ (глубина 90% ослабления ~7.6 мкм). За увеличение η ответственны анионные вакансии, концентрация которых в нарушенном слое сравнима с концентрацией активатора $C_A$. Распад пересыщенного раствора вакансий приводит к неоднородному распределению η из-за локальных нарушений $C_A$. Следствием этого является исчезновение пика полного поглощения в амплитудном спектре. Несмотря на утрату разрешения и пиковой эффективности регистрации, скорость счета α-частиц по всему спектру остается постоянной. Собственно МС (потеря полной эффективности регистрации) образуется через 6 месяцев и более, после диффузионного выхода натрия на поверхность.

**Ключевые слова:** мертвый слой; эффективность регистрации; неоднородность светового выхода

## Introduction

The figurative expression "living crystal" has long been firmly established in the scientific literature [1] with the easy hand of Ya.E. Geguzin. The term "dead layer" (DL) is also widely used in technology for functional materials and implies the absence of a useful signal from the surface layers of the active element. For example, the concept of DL was introduced in [2] for semiconductor crystal phosphors and is explained by the distortion of the band structure near the surface.

Despite the fact that the term DL has firmly entered the scientific lexicon, seems that different authors put into this concept a somewhat different meaning. First of all it should be noted that spectrometry is the most important section of scintillation technique. As to spectrometry in our opinion the term DL means a sharp decrease (by one order or more) of the registration efficiency ε at the peak of total absorption, as this concept is used in [3, 4] especially for weakly penetrating radiations.

On the other hand, it is known that the conversion efficiency η is reduced commonly for low-energy photons. This fact was discovered long ago, for the first time in [5] for NaI:Tl scintillator. It was a decrease of η by approximately 20% (without a change in the ε) and there were no grounds for using the term DL. Since this decrease concerned only the region of soft X-ray radiation and did not affect the volume characteristics of scintillator, the nature of this phenomenon was not dealt with in detail.

Nature of the DL and mechanism of its formation were considered in [6, 7] for hygroscopic crystals of NaI:Tl. In present paper, let us dwell on the features of the DL manifestation in the CsI:Na scintillation material. The goal of our present consideration is to review modern ideas about the nature of the dead layer, its evolution over time, and also about measures to prevent its occurrence.

**The dead layer manifestations in CsI:Na**

Initially, the DL idea and its effect on the detection of short-range radiation arose on the basis of a study of light yield degradation. It is well known, that CsI:Na crystals, despite its successful application for γ-ray detection, are not recommended as an α-particle counter. Let us explain this conclusion by two examples. Fig. 1 shows the pulse height spectra excited by α-particles in the CsI:Na scintillation material [8]. It is clear seen that the degradation of the light yield $L_\alpha$ begins immediately after manufacturing (finishing polishing) of the sample and continues until the crystal is almost completely lost by the ability to register short-range particles**.** A distinctive feature of pulse height spectra at a late stage of degradation is that, the peak of the total absorption (see curve 4) is not so much shifted to the low-energy region as it spreads to such an extent that it is practically impossible to correctly determine the half-width. After a few days, depending on the temperature and relative humidity, the full absorption peak disappears.

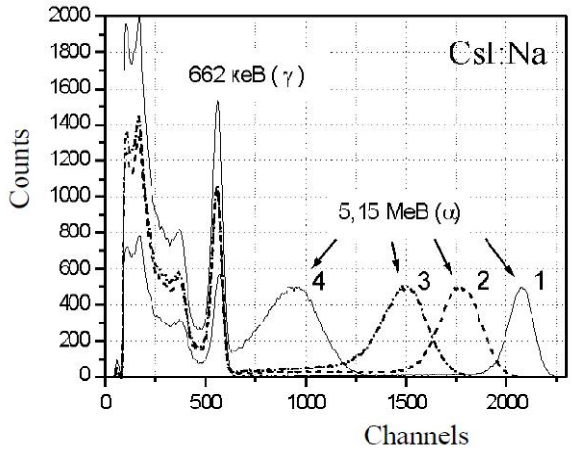


Fig.1 – Change of pulse height spectrum during the crystal storage at ambient conditions. Spectra are recoded after one hour (1) of finishing polishing, 12 hours (2), 3 days (3) and 6 days (4). Note that position of the photopeak for 662 keV γ-rays do not change [8]

The aging degradation kinetics of the light yield is shown in Fig. 2. Curve 1 presents the change in light yield for α-particle $L_\alpha$ at temperature of 18°C and relative humidity of ~ 80%. It is clear seen that the $L_\alpha$ is continuously reduced and after 25 days is only 30% of the initial value.

A distinctive feature of the degradation process is not so much a reduction in light yield as a significant deterioration in the energy resolution ($R$). The measurements were terminated due to the fact that the $R$ values exceeded 50% and it was impossible to determine correctly the position of the maximum and the peak half-width. This means that the CsI:Na crystal loses the ability to identify the particles on energy (by the position of the full absorption peak) after three weeks of aging (see curve 1 in Fig. 2). It should be noted that a collimator with a hole diameter of 0.5 mm was used in our experiments. It means that the α-particles penetrated into the crystal perpendicular to its surface. Apparently, the registration of oblique particles leads to the fact that the degradation of $L_\alpha$ occurs in a few days [10] under normal conditions.

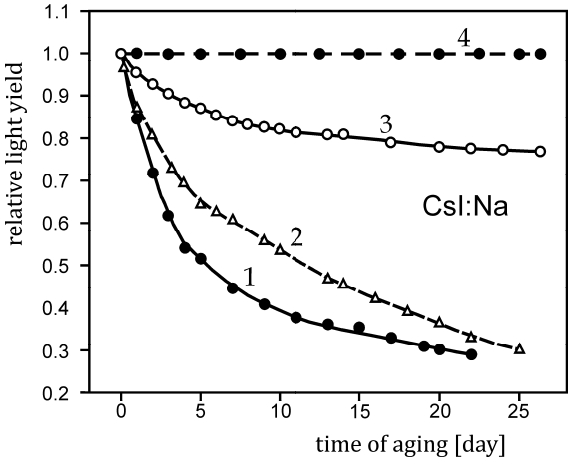


Fig. 2 – Relative light yield degradation during CsI:Na crystals aging at 25°C and relative humidity 70 (1), 30 (2) and 5% (3). Curves 1, 2 and 3 correspond to excitation by α-particles ($^{239}$Pu), curve 4 by γ-rays ($^{137}$Cs)

**Diffusion model of the DL in CsI:Na**

Representations of the DL formation mechanism due to the $Na^+$ diffusion from the crystal volume to free surface were originally formed when studying thin-film detectors [11], which have obvious advantages in the detection of α-particles, protons and soft X-rays, when the thickness of the scintillator is sufficiently small. The development of works in this direction [12] led to the creation of production for CsI:Tl epitaxial layers, which have been successfully used so far.

It turned out, however, that CsI:Na thin films are not stable and degrade in a short period of time in contrast to CsI:Tl one which exhibit the stability of the spectrometric characteristics. To explain this phenomenon, a diffusion mechanism for DL formation due to the sodium release from the volume to surface has been proposed in [3, 13].

The experimental facts underlying the mechanism are the following:

- during the aging of CsI:Na films, the parameters η and ε deteriorate sharply during 2-4 days;
- distribution profile of activator in the aged sample shows a sharp Na concentration increase at the surface;
- the NaI phase is formed on the surface itself;
- sodium precipitates are formed in the near-surface layer.

It was concluded in [13] that all these facts also hold for single crystals taking into account that the diffusion processes are inhibited. The typical time needed for NaI phase formation on free surface is 6 months or more. A visual experimental confirmation was obtained in [14], see Fig.3. When the aged CsI:Na crystal is excited, a strong dependence of the spectral composition of the luminescence on the penetration depth of X-rays is observed. It has been shown that a 304-nm emission, typical for CsI-pure, rather than 420 nm, characteristic of the CsI:Na, is excited near the surface. According to our data, a sample of 3.8-mm-thick loses its spectrometric properties at excitation by 662 keV γ-rays after 13 years of storage under ambient conditions. When this sample is excited with 60-keV X-rays (90% depth of attenuation is ~0.65 mm) the 420 nm luminescence of CsI:Na does not appeared, but only 304 nm emission is clearly recorded.

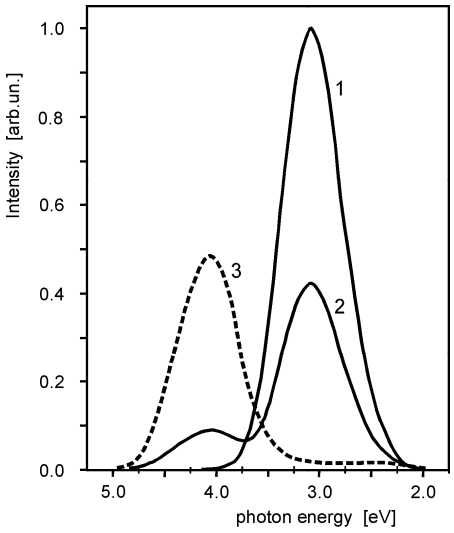


Fig.3. Radioluminescence spectra of CsI:Na crystal at aging. 1 – one day of storage; 2 – 10 years; 3 – 14 years of storage, curve 3 is multiplied by factor 5. Emission is excited by 60 keV γ-rays from $^{241}$Am source.

On the surface of aged samples, there is an appearance of matte areas with a characteristic size of up to one millimeter. The micro-X-ray analysis of such areas shows that they are a film of baking soda ($NaHCO_3$) on the polished surface [15]. The $NaHCO_3$ product is observed in centers of nucleation, where the formed NaI phase actively adsorbs water and dissolves in it. The arid puddles of a saturated solution are visible to the naked eye like the shiny spines of a clamping hole [16]. In our opinion, it is with this fact that the concepts of the hygroscopicity of CsI: Na crystals are related. In solution, NaI hydrolyses to form NaOH, this process is especially active in the light [7]. Then the carbonization process proceeds according to a known reaction:

$$NaOH + CO_2 = NaHCO_3, \quad (1)$$

as a result of which baking soda is formed. Similar results on the nature of the precipitates on the surface of CsI:Na crystals are presented recently in [17].

The diffusion model of DL proposed by Tchaikovsky and Rosenberg [3, 13] can be considered proven, since both the formation of the NaI phase on the surface and the depletion of the near surface layer by the activator, are observed experimentally.

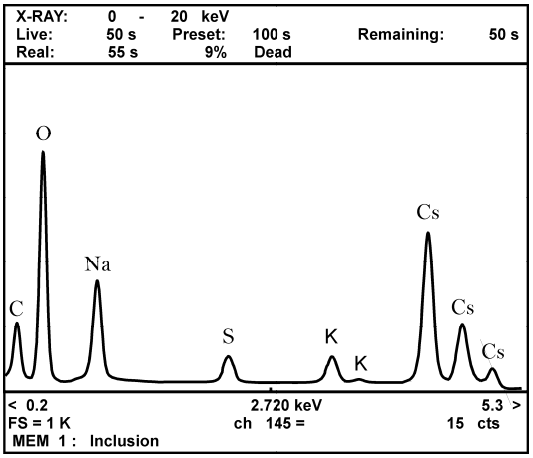


Fig.4. Spectrum of characteristic X-ray emission which excited in matted regions formed by the inclusion of new phase on internal surface of crystal

However, it soon became clear that the loss of crystal spectrometric properties does not coincide in time with the diffusion of sodium to the free surface of sample. The light output decrease at excitation by α-particles in the course of aging follows the exponential law $L_\alpha \sim \exp(-t/\tau)$ with the parameter $\tau \approx 4$ days [4], which is clearly not enough for a noticeable enrichment of the surface with sodium. The essential signs of sodium enrichment appeared after a few months of storage. The authors of [4] explained their results from the opposite point of view they proposed the diffusion of quenching impurities (like $OH^-$ ions) into the crystal lattice. Note that our results (see Fig. 2) confirm both the data [4] as well as [3, 13] (see Fig. 4).

**Distorted layer in living crystal**

To solve this contradiction a DL profile and its evolution in time have been studied. Simultaneously the degradation of light output $L_\alpha$ has been studied too. To obtain the profile we replaced $L_\alpha$ by $\eta$, using first approximation: $\eta = L_\alpha/E_\alpha$. We expected that a sharp decrease in the conversion efficiency will be observed near the surface, as it follows from the data of [18], where the dependence of $\eta$ *vs* $E_p$ was studied in the range of proton energy $20 \le E_p \le 540$ keV.

Fig. 5 shows the data [18], but the original energy scale was recounted by us into the proton range. It can be seen that the η decrease is observed for protons of the lowest energies. Characteristic depth $d_0$ of DL ($d_0$ corresponds to attenuation of the $\eta$ in 2,71 times) is approximately 2 μm for CsI:Na and only 0.2 μm for CsI:Tl crystal. It should be noted that conversion efficiency is normalized in Fig. 5, the $\eta$ value is equal to unity for protons of biggest energy.

In present work the DL profile has been investigated using X- and low energy γ-rays. Obtained profiles of DL are shown in Fig.6 for CsI:Na crystal at different stages of aging. Original data are presented in paper [9],

here we have recalculated energy scale to a depth of 90% attenuation ($d_{90}$) of X-rays. It should be noted that dependence $\eta$ *vs* $E_\gamma$ (where $E_\gamma$ is an energy of X-ray) has a nonmonotonic character in the region of the K-edge of iodine (~ 30 keV). It has been shown, however, that after scale replacement ($E_\gamma \rightarrow d_{90}$) this feature is smoothed out [19].

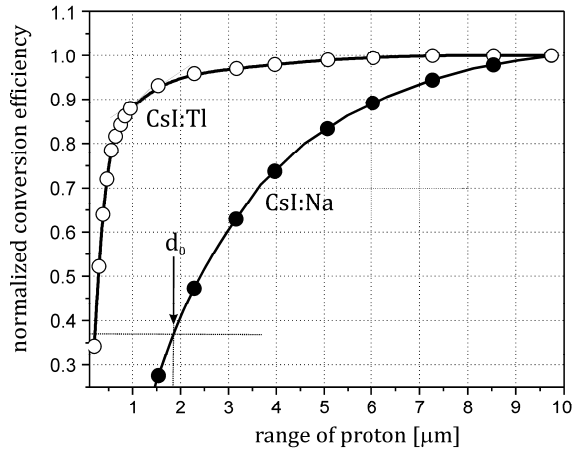


Fig.5. Profile of dead layer in CsI:Na and CsI:Tl crystals after 10 months of aging. Excitation by protons [18]

The course of the dependence $\eta$ *vs* $d_{90}$ for X-rays after 20 days of storage is similar to curves 1 and 2 in Fig. 5. A distinctive feature of curve 1 in Fig. 6 is that for the quanta of the lowest energies (5.9 keV with the $d_{90}$ = 7.6 μm), an increase in the $\eta$ value is clearly seen. This increase in conversion efficiency is temporary and disappears after several days of aging. As can be seen from the data in Fig. 6, the alignment of the $\eta$ values occurs after 19 days.

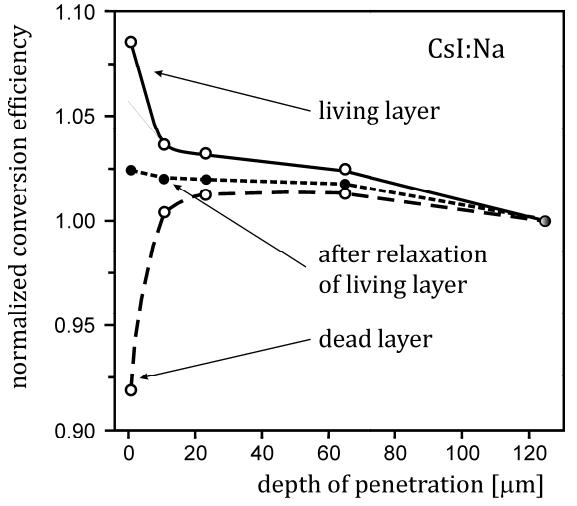


Fig. 6. Dead layer profiles at different stage of CsI:Na crystal aging. 1 – one day of storage; 2 – 19 days; 3 – 22 days of storage

Contrary to curve 3 in Fig.6 which corresponds to profile of the DL, the curve 1 illustrates the layer with increased conversional efficiency. By analogy with [1] we propose that such a profile be called a ″living layer″. During aging the living layer relaxes and after some days the η values correspond to conversion efficiency in volume, after that the actual dead layer is formed. After 25 days of storage, the crystal practically loses its ability to detect weakly penetrating radiation, which is manifested in the sharp degradation of ε and *R* for photons with energy of 5.9 keV.

The nature of the living layer is associated with an increase in the number of luminescence centers in the near-surface distorted layer. The fact is that the blue luminescence of CsI:Na crystals is associated not only with the activator ($Na^+$), but also with anion vacancies [20]. Cation ($V_C^+$) and anion ($V_A^-$) vacancies easily arise during plastic deformation [20] of CsI crystal. Well known that mechanical treatment causes the plastic deformation in near-surface layer. It was shown that, with a greater degree of deformation, a greater yield of blue luminescence [15, 20]. Estimates made in [15, 21] show that the concentration of vacancies ($C_V$) in the living layer after ″soft polishing″ is comparable to the sodium content ($C_A$) in the volume of crystal.

**Two-stage mechanism of DL formation**

The DL model in CsI:Na crystals, proposed by Tchaikovsky and Rosenberg [3, 13], is schematically shown in Fig. 7. Curve $C_A(d)$ denotes the profile of activator distribution on the depth of crystal. It is well known that sodium diffusion towards free surface results in formation near boundary of the zone depleted by the activator. Boundary between *CsI pure* layer and *CsI:Na* volume has to shifts towards crystal depth according low $d_0 \sim t^{1/2}$ [22]. However, as we saw above for single crystals $d_0 \sim 1–exp(–t/\tau)$. According data [4] as well as our results shown in Fig. 2 the parameter $\tau$ is equal to 4 days for sample stored at ambient condition and 6 days for aging at dry room. These values of $\tau$ are in good agreement with data [10, 15] also.

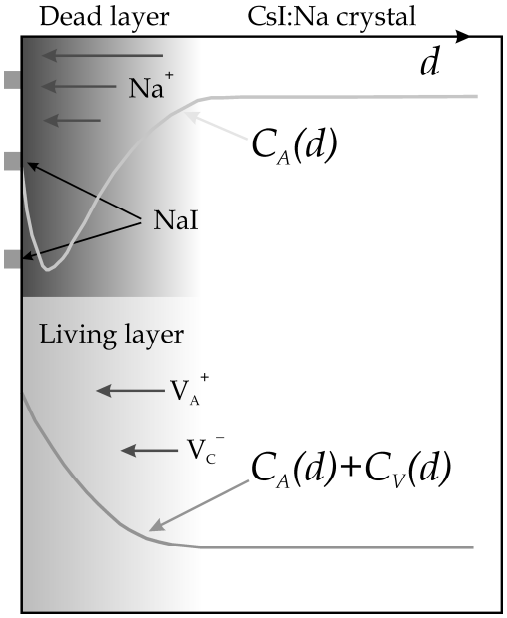


Fig.7. Model of Dead Layer in CsI:Na crystal after aging [13], curve ″$C_A(d)$″ shows the distribution profile of Na. Proposed model of Living Layer, curve ″$C_A(d) + C_V(d)$ ″ shows profile of distribution of emission centers

A decrease in the light yield by 30% (see curve 3 in Fig. 2) cannot lead to a significant broadening of total absorption peak and to a catastrophic deterioration in energy resolution (see Fig. 1). It is natural to assume that in the near-surface layer an inhomogeneous distribution of emission centers is formed not only along the depth of layer, but also in the cross-sectional area. An obvious sign of such non-uniformity is the presence of sodium precipitates, which appear in the DL [3, 13]. Sodium precipitates are not typical for crystals with an optimal Na concentration: $C_A = 9.5 \cdot 10^{17}$ см$^{-3}$. It should be noted that we used an ingot with uniform activator distribution in whole volume, sodium concentration in all samples was: $C_A = 8{,}6 \cdot 10^{17}$ см$^{-3}$.

Existence of the living layer near the surface at initial stage of aging implies a revision of mechanism of DL formation, since a supersaturated solid solution of vacancies should disintegrate first of all. Obvious sinks for vacancies are the free surface and dislocations. Let's explain the above with a simple example.

Free surface itself is a natural sink for excess vacancies. Within a few days towards the interface, a gradual weakening flow of vacancies will be directed. Vacancy flow will lead to a predominant shift of $Na^+$ cation in the opposite direction. Another consequence of the living layer relaxation is, perhaps, the penetration of foreign impurities, for example, $OH^-$ ions, from the surface into the crystal lattice. A similar displacement of impurity ions occurs in any part of the crystal where there is a directed vacancy flow [22].

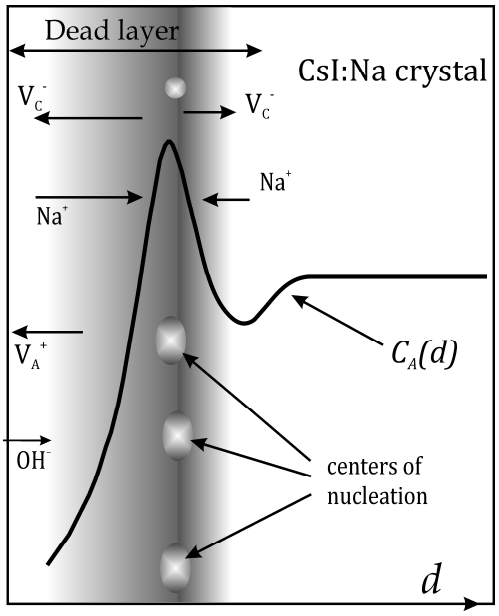


Fig.8. Profile of dead layer in CsI:Na. Curve *"$C_A(d)$"* shows the proposed distribution of Na after relaxation of supersaturated solid solution of vacancies

As a result, the sodium distribution along depth will change. Schematically, the change in the profile of sodium distribution is shown in Fig.8. In disappearing living layer the zone enriched by sodium should form. Since even a small (within + 20%) increase in Na concentration causes the decay of solid solution [23], in noted zone the sharply inhomogeneous activator distribution is appeared. Sodium precipitates are just an experimental manifestation of such non-homogeneity on microscopic level [3]. Vacancy claster can play role of nucleation center for decay of solid solution. It is known that such clasters appeared easy in CsI [24] after plastic deformation as a result supersaturated vacancy solution decay.

So, proposed model of DL and mechanism of living layer transformation to dead one can be checking experimentally. New model supposes that the formed dead layer (peak of total absorption in which is absent on the pulse height spectrum) is still a solid solution of sodium in CsI. It means that α-particles should be detected even in course of the decay of solid solution. So, CsI:Na crystal can detects α-particles in counting mode but cannot identify them on energy.

To check this assumption the pulse height spectra have been measured. To select needed level of discrimination the pulse height spectrum was measured for CsI-pure crystal. Then the high discrimination threshold was chosen such that the total absorption peak in spectrum disappeared. Figuratively speaking, we made artificially the CsI crystal dead. As for the CsI:Na crystals, they still recorded and distinguished α-particles at such a high threshold. The measurements were continued after 30 days. Despite the absence of a full absorption peak in the spectrum, the crystal registered the α-particles in counting mode, the total detection unchanged.

So, the term DL means first of all a loss of energy resolution, rather than a light output or detection efficiency. The scintillation technique distinguishes the total and peak detection efficiency. Returning to the meaning of term DL, one can concretize that a crystal with a dead layer loses its peak not total registration efficiency. Total efficiency of α-particles registration CsI:Na loss throughout the year formation a CsI-pure layer. The thickness of the CsI-pure layer should not be less than the range $\ell$ of α-particles in CsI ($\ell = 32\ \mu m$ for energy 5.15 MeV from $^{239}$Pu source).

**Conclusion**

Representations of dead layer nature in CsI:Na crystals are considered. To eliminate the contradictions between two existing models of DL, degradation of the conversion efficiency in near surface layer has been studied. Simultaneously, the DL profile and its evolution under aging were studied using X-rays of different energies. It has been shown that immediately after surface polishing, the η is increased for 5.9 keV photons (depth of 90% attenuation is equals ~7.6 μm). Anion vacancies are responsible for η increase, whose concentration in the disturbed layer is comparable with the concentration of the activator $C_A$. Decay of supersaturated vacancy solid solution results in extremely inhomogeneous distribution of the η due to the local distortion of the $C_A$. The consequence of this is the disappearance of the full absorption peak in the pulse height spectrum. Despite the loss of energy resolution and detection efficiency (at photopeak) the total counting rate remains constant for α-particles. The dead layer itself (the loss of full detection efficiency) is formed after the diffusion of sodium to the free surface, approximately after 6 months and more.

## Literature


1. Ya.E. Geguzin. Living crystal, 2-nd ed., Nauka, Moscow (1987), 192 p.
2. A.M. Gurvich. Introduction to physical chemistry of crystal-phosphors, Vysshaya shkola, Moscow (1971), 336 p.
3. G.Kh. Rosenberg, Yu.T. Vydai, G.V. Ptitsyn, E.F. Tchaikovsky. Bul. Academy of Science of USSR, phys., 41, 2365 (1977).
4. V.V. Averkiev, V.K. Lyapidevsky, V.A. Prorvich, A.V.Sartory. Instr. & Exp. Technique, 3, 152 (1982).
5. W.G. Kaizer, S.I. Baiker, A.J. MacKay and I.S. Sherman. IEEE Trans. Nucl. Sci., 9, 3, 22 (1962).
6. A.M. Kudin. In: Scintillation materials. Obtaining, Property, Application, ed. by B. Grinyov, Ukraine, Kharkov, Institute for Single Crystals (2007), p. 320.
7. K.A. Kudin, A.V. Shkoropatenko, A.Yu. Voloshko, D.I. Zosim, A.M. Kudin. Phys. Surface Engineering, 9, 256 (2011).
8. A.M. Kudin, E.P. Sysoeva, L.N. Trefilova, D.I. Zosim. NIMA, A537, 105 (2005).
9. A.M. Kudin, A.A. Ananenko, Y.T. Vyday, V.Yu Gres', B.G. Zaslavsky, D.I. Zosim, Problems of Atomic Science and Technology, 4, 111 (2001).
10. K.V. Shakhova, A.N. Panova, V.I. Goriletsky, Y.A. Prikhod'ko, V.P. Gavrylyuk, S.P. Korsunova, N.N. Kosinov. Rad. Measurements, 33, 769 (2001).
11. Yu.T. Vyday, G.V. Ptitsyn, G.Kh. Rosenberg, E.F. Tchaikovsky. Single Crystals and Tech., Ukraine, Kharkov, VNII Monokristallov, 17, 228 (1976).
12. A. Fedorov, A. Gektin, A. Lebedynskiy, P. Mateychenko, A. Shkoropatenko. Rad. Measurements, 56, 163 (2013).
13. G.Kh. Rosenberg. Autoreferat diss. candidate fis.-mat. nauk: 01.04.10. – Kharkov, 21 p. (1980).
14. L.E. Dinca, P. Dorenbos, J.T.M. de Haas, NIMA, A486, 141 (2002).
15. V.Yu. Gres'. Autoreferat diss. candidate tech. nauk: 05.02.01. – Kharkov, 18 p. (2002).
16. B.V. Grinyov, V.P. Seminozhenko. Scintillation detectors of ionizing radiation for hard operation conditions, Osnova, Kharkov (1998), 155 c.
17. Pin Yang, Charles D. Harmon, F. Patrick Doty, and James A. Ohlhause. IEEE Trans. Nucl. Sci., 61, 2, 1024 (2014).
18. Yu.I. Usikov, Yu.T. Vyday, G.I. Primenko, Yu.A. Tsyrlin. Instr. & Exp. Technique, 1, 86 (1984).
19. A.M. Kudin, B.V. Grinyov, V. Yu. Gres, A.I. Mitichkin. Functional Materials, 13, 54 (2006).
20. A.V. Gektin, N.V. Shiran, V.Y. Serebryannyi, T.A. Charkina. Opt. & Spectroscopy, 72, 1061 (1992).
21. A.M. Kudin, L.A. Andryushchenko, V. Yu. Gres', A.V. Didenko, T.A. Charkina. J. Opt. Technology, 77, 300 (2010).
22. Ya.E. Geguzin. Diffusion zone, Nauka, Moscow (1979), 343 p.
23. A.N. Panova, E.L. Vinograd, V.I. Goriletsky, S.P. Korsunova, N.N. Kosinov, K.V. Shakhova. Func. Materials, 5, 480 (1998).
24. A.V. Gektin, T.A. Charkina, N.V. Shiran, V.Ya. Serebryanyi, Opt. & Spectroscopy, 67, 1075 (1989).