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A possible reason for non-proportionality of response in NaI:Tl and CsI:Tl scintillation crystals

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It is known that the light yield L is not proportional to energy E for many scintillation materials under excitation by external γ-rays. In contrast, L is proportional to E for internal radiation sources. In this work, it has been shown that this contradiction can be eliminated if the non-proportionality is considered as a total result caused by two effects. First, the scintillation duration is shortened as the photon energy decreases, that results in increasing measured L/E value at fixed signal formation time. Second, the presence of dead layer results in the luminescence quenching near the crystal surface. In this concept, the response non-proportionality is considered as axial inhomogeneity of the scintillation efficiency depending on the radiation penetration depth H. It has been shown that the valley in L/E *vs* E dependence near the K-edge of iodine absorption (the jump-like H changing almost by ten times) disappears on the L/E *vs* H one.

Известно, что световой выход L непропорционален энергии электронов E для многих сцинтилляционных материалов при возбуждении внешними γ-квантами. В противоположность этому, L пропорционален E для внутренних источников радиации. В работе показано, что это противоречие можно устранить, если непропорциональность выхода рассматривать как суммарный эффект двух факторов. Во-первых, длительность сцинтилляций сокращается с уменьшением энергии квантов, что приводит к увеличению измеряемой величины L/E при фиксированном времени формирования сигнала. Во-вторых, наличие мертвого слоя приводит к тушению люминесценции вблизи поверхности кристалла. В таком подходе непропорциональность выхода трактуется как осевая неоднородность сцинтилляционной эффективности в зависимости от глубины H проникновения излучений. Показано, что провал на зависимости L/E *vs* E около K-края поглощения йода, где H изменяется скачком на порядок, исчезает на зависимости L/E *vs* H.

The light yield L is not proportional to the electron energy E for many scintillation materials under excitation by external radiation sources [1]. For NaI:Tl and CsI:Tl, the non-proportionality is characterized as an increasing scintillation efficiency dL/dE when the photon energy decreases [2]. As a first approximation, $dL/dE \approx L/E$, and the specific light yield L/E can be expressed as:

$$L/E = (1/\varepsilon)\beta SQ, \qquad (1)$$

where ε is the average energy of electron-hole pair formation; β, the light collection coefficient; S, efficiency of energy transfer from the host lattice to luminescence centers; Q, the quantum efficiency of a luminescence center. The coefficients β and Q are energy-independent. The non-proportionality of response is explained by differences in energy transfer conditions from host lattice to activator centers for electrons of different energies, i.e. energy dependence of the coefficient $S = S(E)$. More precisely, the explanation is connected with increasing specific energy loss dE/dx with decreasing electron energy [3]. The non-proportionality of response is postulated in [4] as an internal crystal property, which causes an essential deterioration of energy resolution.

Theoretical models [3, 4] based on concept of the light yield non-proportionality are generally accepted at present time. However, assumptions were made for a long time concerning possible distortion of light yield data for low-energy photons due to surface influence and its state [5, 6]. As an example, to correct the function L/E *vs* E in low-energy range, Meggitt [5] has supplemented the equation (1) with a coefficient η taking into account the L/E decrease caused by the surface negative influence:

$$\eta = 1 - \exp(-x/d_o), \qquad (2)$$

where x is the distance from surface; d_o, the characteristic layer depth. Essentially, Meggitt introduced the concept of the so-called "dead" near-surface layer [7, 8]. In this layer, the light yield either decreases essentially or is even zeroed. Such approach allowed to correct the L/E *vs* E curve for NaI:Tl in the lowest energy range [5] that was necessary to explain the McCann and Smith [9] results as to detection the events with energy of 0.84 keV. If $S = const$, then it follows from (1) and (2) that L/E is a function of penetration depth but not of energy, at least at a short distance from the scintillator surface. The surface influence can be neglected for sufficiently large crystals which contain internal sources, i.e. isotopes introduced to the crystal lattice during the crystal growth. Results of such studies are summarized in [10]. It turned out that the light yield is proportional to energy within a wide energy range from 0.345 to 1.33 MeV for internal radiation sources. This work is an attempt to eliminate contradictions between investigation data on the response non-proportionality obtained using external and internal radiation sources.

It is well known that the scintillation duration in NaI:Tl [11] and CsI:Tl [12] is shorter for α-particles than for γ-rays. Recently, the scintillation decay time has been found to shorten as the photon energy decreases [13]. The dependence of light yield on the signal formation time (τ_{RC}) under excitation by photons with various energies for CsI:Tl are given in Fig. 1. In this crystal, Tl concentration corresponded to the optimal value (0.11 mole %) both for γ-rays and α-particles. It is clearly seen from the data of Fig. 1 that the relative light yield at excitation by X-rays of 5.9 keV energy ($L_{5.9}$) as a function of τ_{RC} attains the saturation much faster than the similar curves for both L_{60} and L_{662}. We have observed this effect for NaI:Tl and CsI:Na, too [13]. It should be noted that for thin samples of 1.5 mm thickness, this effect is less pronounced than for crystals of 6 mm thickness. As far as both α-particles and 5.9 keV X-rays are absorbed in thin layer near the surface, these facts evidence a possible role of the crystal surface in the observed effect.

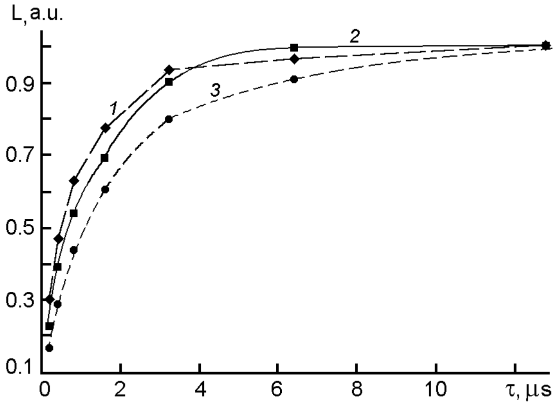

Fig. 1. Dependence of relative light yield on the signal formation time for CsI:Tl with 0.11 mole % of Tl. Excitation by 5.15 MeV α-particles (*1*), 5.9 keV X-rays (2) and 662 keV γ-rays (*3*)).

When being excited by external radiation sources, the light yield is not proportional to the photon energy. As it has been noted above, the mentioned non-proportionality is not observed for internal sources. To reconcile these experimental facts, let the free surface be assumed to influence the light yield both negatively and positively. According to [10], let us assume that in the crystal volume, the L/E depends neither on energy nor coordinate of an interaction point. We mean the "dead" layer as the negative influence of surface while the positive surface influence is believed to be associated with shortening of scintillation decay time, i.e. with a purely kinetic light collection effect. In other words, in the whole crystal volume except for a thin dead layer, the luminescence intensity is coordinate-in-

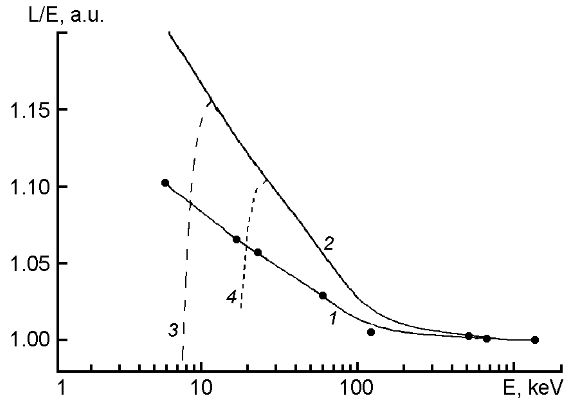

Fig. 2. Specific light yield as a result of shortening of decay time (*1*, *2*) and sum effect (*3*, *4*). The L/E is normalized to τ_{RC} = 12.8 μs (*1*) and 25 μs (*2*). Parameter d_0 = 5 μm (*3*) and 40 μm (*4*).

dependent and the light yield is defined by kinetic parameters of scintillation.

In the proposed model, all the $L(t)$ *vs* τ_{RC} dependences are possible to be normalized to the same relative yield when the $\tau_{RC} \to \infty$, as it is shown in Fig. 1. These data show that the lower is the energy (in the range of 662 to 5.9 keV), the higher is the relative light yield at a selected signal formation time. Such trend is typical of any t_{RC} values really used when the crystal is excited by an external source. Let us assume that $L/E = 1$ at $E = 662$ keV, as it is considered as normalizing condition in the works aimed at the non-proportionality of response. So, from data of Fig. 1, we obtain the measured response value L/E for a selected τ_{RC} and various E. For example, at τ_{RC} = 1.6 μs, the response will be 15 per cent higher for 5.9 keV than for 662 keV. Such data for 511; 122; 59.5; 22.6; 17 and 5.9 keV energies are presented in Fig. 2, curve *1*. That curve makes it possible to explain a main feature of the L/E *vs* E dependence, namely, increase of the L/E as the photon energy decreases, without using conception of energy transfer by excitons.

The L/E in values low energy region are less than the known ones. According to [14, 15], L/E has a maximum at $E_\gamma \approx 15$ keV (+20 % as compared to L/E at 662 keV). The dependence L/E *vs* E for 662 keV in Fig. 1 shows no saturation at $\tau_{RC} > 6$ μs, so its extrapolation to τ_{RC} = 25 μs causes L/E values in low energy region increased nearly twice (curve *2* in Fig. 2). Curve 2, in its physical sense, is the coefficient η_1 taking into account the response increase due to shortening of τ. The maximum η_1 value is limited by the radioluminescence yield. The ratio of scintillation yield to luminescence one is 0.6 for NaI:Tl and 0.5 for CsI:Tl [6]. As to scintillation yield, it is a maximum for protons [16]. The L/E values for protons are approximately 35 to 40 % higher than for γ-rays (E_γ = 662 keV) [14, 16]. So, the elevation of curve *2* on Fig. 2 towards the low energy seems to be limited to $L/E = 1.38$.

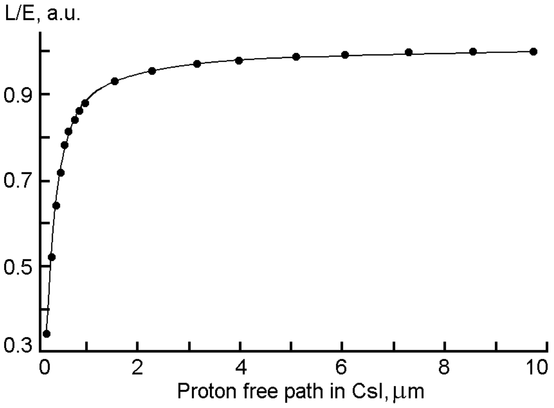

Fig. 3. The dependence of L/E on the proton free path in CsI single crystal.

Let us introduce the coefficient η_2 taking into account the dead layer influence. The multiplication of these two coefficients just defines the scintillation response near the surface:

$$L/E = (1/\varepsilon)\beta S Q \eta_1 \eta_2. \qquad (3)$$

We assume the coefficients β, S and Q to be energy-independent. This is a distinction of our approach, since in many works, it is assumed that $S = S(E)$ [3]. It is somewhat difficult to take into account the dead layer effect, since this term itself assumes a dependence of the coefficient η_2 on penetration depth H but not on energy. The information on the dead layer profile can be obtained best of all from the L/E dependence on proton energy E_p. For protons, L/E has maximum value and almost independent of energy [16] if $E_p > 500$ keV. In [17], the light yield and energy resolution of thin-film CsI:Na and CsI:Tl detectors have been investigated under excitation by protons with $20 \le E_p \le 540$ keV. The obtained dependences for thin-films and single crystals are similar to one another but are in a sharp contradiction with data from [14]. It is important that in [17], the measurements were carried out on aged samples. This allows to neglect the influence of polishing on the scintillation efficiency near the surface

[18]. The results from [17] for single crystal are presented on Fig. 3. Unlike that work, we have presented the data for L/E as a dependence on the proton free path l_p in CsI, not on energy. It is seen that $L/E = const$ if the $l_p > 5$ μm ($E_p > 100$ keV), while for protons of lower energy, the L/E value decreases sharply.

Proton has a maximum value of specific energy loss ($dE/dx = 230$ keV·cm^2/mg) when its energy is equal to 100 keV [3] and proton free path is about 3.5 μm. The dE/dx value decreases with decreasing energy (and proton free path) from 100 to 20 keV, therefore, the drop of the L/E *vs* l_p curve should be addressed to dead layer effect near the surface and not to increasing dE/dx. The L/E *vs* l_p dependence in Fig. 3 is described well by equation (2) with parameter $d_o = 0.2$ μm. This value agrees well with $d_o = 0.4$ μm obtained in paper [8] for dead layer depth in CsI:Tl. This result was obtained in experiments with mono-energetic α-particles hitting the surface at acute angles. Thus, we confirm the prediction [7] that the dead layer profile can be described by exponential dependence (2). For CsI:Tl crystal with Tl concentration of 0.11 mole %, it is possible to suppose that d_o is 0.2 to 0.4 μm. For strongly hygroscopic NaI:Tl crystal, the d0 value depends on the surface state. According to [19], NaI:Tl make it possible to detect the events with energy of 1.7 keV (K_αAl), i.e. for cleavage plane, the d_o seems to be thinner than 1 μm. For polishing entrance surface, the d_0 may attain 30 nm or even 40 μm [20, 21]. The causes of the dead layer formation in alkali halide crystals are considered in detail in monograph [20].

Knowing the behavior of η_1 and η_2 coefficients, we can construct the resulting curve in Fig. 2. To that end, the curve *2* is multiplied by coefficient η_2. First, the penetration depth H_i has been calculated for each photon energy E_i. The coefficient $\eta_2(H_i)$ has been found from equation (2) for two dead layer profiles: $d_o = 5$ μm and $d_o = 40$ μm, these values corresponding to real d_o thickness for NaI:Tl. Results are presented by curves *2* and *3* in Fig. 2. It is seen that the resulting curves reflect the behavior of the dependence L/E *vs* E_γ, see for instance [14, 15, 22]. It is just the curve shape (with the exceptions for the features in the region of iodine K-edge) that is widely discussed in literature [1, 10]. From data of Fig. 2, it is seen that as d_o increases, the maximum of the resulting curve shifts towards higher energies. In our opinion, this fact can explain the discrepancy of experimental data concerning position of the maximum on the curve of response non-proportionality [22]. Basing on obtained results, a possible cause of response non-proportionality can be explained easily. It is also possible to eliminate the contradiction between data from works where the non-proportionality was studied using external and internal radiation sources [10]. The scintillations occurring near the surface are of shorter duration, and this results in L/E increase. The cause of scintillation duration shortening consists most likely in elastic stresses. These stresses can penetrate to the crystal depth to the distances of hundred micrometers if the surface electric properties are not uniform over area [23].

The elastic stresses are known to influence the light yield and energy resolution of NaI:Tl crystals [24]. The uniaxial compression influences the luminescence of self-trapped excitons in CsI [25]. Internal tensile stresses in CsI caused by impurity of a small radius reduce the exciton luminescence duration [26]. To describe the excited state relaxation of a luminescence center, the concept of local surrounding change of that center is used (Jan-Teller effect). Therefore, it is clear that in elastic-stressed crystal, displacement of ions surrounding the luminescence center depends on the acting force value and direction. Near the scintillator surface, the dead layer exists. Electrons and holes arisen in this layer can recombinate on the surface at a high probability. At this region, their energy is spent for radiolysis of adsorbed water molecules [20]. In CsI:Na, Na$^+$ solid solution decomposition also occurs with formation of NaI inclusions at the surface and sodium precipitates in the near-surface layer [7]. Thus, the non-proportionality of response as a matter of fact is the axial non-uniformity of L/E depending on penetration depth of radiation. Such concept allows to explain the L/E *vs* E_γ curve dip near the iodine adsorption K-edge. The fact is that penetration depth changes almost ten times at K-edge. Above the K-edge, the crystal area with increased scintillation efficiency is excited. When E_γ becomes such that H reaches the same value as that immediately before K-edge, L/E values coincide with each other. In Fig. 4, the data from [15] concerning to L/E *vs* E_γ curve are presented. We have

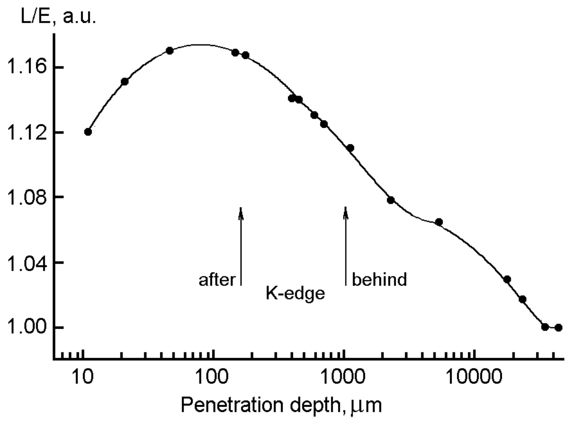

Fig. 4. Specific light yield as a function on penetration depth. Data on *L/E vs E* dependence are taken from [15]. Arrows indicate the *H* values before and behind K-edge.

recalculated these data into *L/E vs H* dependence except for several points lying above the K-edge, to which it is senseless to ascribe definite *H* values. For these excepted points, the excited scintillator volume is not characterized by penetration depth of normal hitting photons with the energy E_γ but by secondary X-rays absorption (emission of K_α and K_β X-rays with ~28 keV energy) taking into account the X-ray escape out of the crystal. It is a reason why the *L/E* has constant values just over K-edge [27], i.e. *H* is defined by secondary photons absorption. From Fig. 4 data, it is seen that the *L/E vs H* dependence is characterized by a smooth curve where the dip near the iodine adsorption K-edge disappears.

In conclusion, for NaI:Tl or CsI:Tl crystals, typical *L/E vs* E_γ curves measured with external radiation sources are defined by influence of two effects. Those are (i) shortened scintillation duration for low energy quanta resulting in increasing measured light yield value at fixed signal formation time and (ii) the dead layer influence characterized by quenching of the light yield near the crystal surface. The dead layer existence or absence as well as its thickness define the position of maximum on the curve of response non-proportionality as a function of energy. *L/E vs* E_γ dependence reflects not the peculiarities of radiation interaction with crystal but existence of axial light yield non-uniformity near the scintillator entrance surface. Such concept allows to eliminate the contradiction between experimental data obtained with external or internal radiation sources as well as to explain the *L/E vs* E_γ curve discrepancy near the iodine adsorption K-edge.

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References

1. P.Dorenbos, J.T.M.De Haas, C.W.E.van Eijk, *IEEE Trans.Nucl.Sci.*, **42**, 2190 (1995).
2. D.Engelkmeir, *Rev.Sci.Instr.*, **27**, 589 (1956).
3. R.B.Murray, A.Meyer, *Phys.Rev.*, **122**, 815 (1961).
4. C.D.Zerby, A.Meyer, R.B.Murray, *Nucl.Inst. Meth.*, **12**, 115 (1961).
5. G.C.Meggitt, *Nucl.Inst.Meth.*, **83**, 313 (1970).
6. E.D.Aluker, V.V.Gavrilov, R.G.Deych, S.A.Chernov, Fast Prosesses Stimulated by Radiation in Alkali Halide Crystals, Zinatne, Riga (1987) [in Russian].
7. G.H.Rozenberg, Yu.T.Vyday, G.V.Ptitsyn et al., *Izv.AN SSSR, Ser.Fiz.*, **41**, 2365 (1977).
8. V.V.Averkiev, V.K.Lyapidevsky, V.A.Prorvich et al., *Prib.Tekhn.Exper.*, **3**, 152 (1982).
9. M.F.McCann, K.M.Smith, *Nucl.Instr.Meth.*, **65**, 173 (1968).
10. H.Leutz, C.D'Ambrosio, *IEEE Trans.Nucl. Sci.*, **44**, 190 (1997).
11. R.B.Owen, *Nucleonics*, **17**, 92 (1959).
12. L.Piro, E.Massaro, S.Fiacconi et al., *Nucl. Instr.Meth.*, **A257**, 429 (1987).
13. A.M.Kudin, A.A.Anapenko, Yu.T.Vyday et al., *Functional Materials*, **9**, 229 (2002).
14. R.Gwin, R.Murray, *Phys.Rev.*, **131**, 501 (1963).
15. D.W.Aitken, B.L.Beron, G.Yenicay et al., *IEEE Trans.Nucl.Sci.*, **NS-14**, 468 (1967).
16. T.Doke, E.Shibamura, S.Kubota, *J.Phys.Soc. Jap.*, **68**, 2433 (1999).
17. Yu.I.Usikov, Yu.T.Vyday, G.I.Primenko et al., *Prib.Tekhn.Exper.*, **2**, 86 (1983).
18. A.M.Kudin, E.P.Sysoeva, E.V.Sysoeva et al., *Nucl.Instr.Meth.*, **A 537**, 105 (2005).
19. D.E.Persyk, T.E.Moi, *IEEE Trans.Nucl.Sci.*, **NS-25**, 615 (1978).
20. A.B.Alexandrov, E.D.Aluker, I.A.Vasil'ev et al., Introduction to Radiation Physics and Chemistry of Surface of Alkali Halide Crystals, Zinatne, Riga (1989) [in Russian].
21. Yu.T.Vyday, L.B.Zagariy, Yu.A.Tsirlin, *Prib. Tekhn.Exper.*, **2**, 74 (1990).
22. F.T.Porter, M.S.Freedman, F.Wagner et al., *Nucl.Instr.Meth.*, **39**, 35 (1966).
23. V.I.Solunsky, M.N.Shpigelman, *Functional Materials*, **7**, 47 (2000).
24. R.Hill, A.Collinson, *Brit.J.Appl.Phys.*, **17**, 1377 (1966).
25. V.Babin, A.Elango, K.Kalder et al., *Phys. Stat.Sol.(b)*, **212**, 185 (1999).
26. M.N.Karklinya, L.E.Nagli, *Izv.AN Latv.SSR, Ser.Fiz.i Tekhn.Nauk*, **3**, 114 (1990).
27. T.H.Jones, *Nucl.Instr.Meth.*, **15**, 55 (1962).

Можлива причина непропорціональності відгуку у сцинтиляційних кристалах NaI:Tl та CsI:Tl

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Відомо, що світловихід *L* не є пропорціональним енергії електронів *E* для багатьох сцинтиляційних матеріалів при збудженні зовнішніми γ-квантами. У протилежність цьому, *L* є пропорціональним *E* для внутрішніх джерел радіації. У роботі показано, що це протиріччя можна усунути, якщо непропорціональність виходу розглядати як сумарний ефект двох чинників. По-перше, тривалість сцинтиляцій скорочується зі зменшенням енергії квантів, що приводить до збільшення вимірюваної величини L/E при фіксованому часі формування сигналу. По-друге, наявність мертвого шару спричиняє гасіння люмінесценції поблизу поверхні кристалу. При такому підході непропорціональність виходу трактується як осьова неоднорідність сцинтиляційної ефективності в залежності від глибини *H* проникнення радіації. Показано, що провал на залежності L/E *vs* E поблизу K-краю поглинання йоду, де *H* змінюється стрибком на порядок, зникає на залежності L/E *vs* H.