Abstract—Europium activated \(^6\)LiI crystal (enriched to 96% \(^6\)Li) has been studied in neutron and \(\gamma\)-ray spectrometry. Two crystals of \(\Phi 50 \text{ mm} \times 5 \text{ mm} \) and \(\Phi 30 \text{ mm} \times 3 \text{ mm} \) size coupled to a calibrated Photonis XP5200 photomultiplier were tested. A response of \(^6\)LiI(Eu) to neutrons emitted from a paraffin moderated Pu-Be source has been investigated and the thermal neutron peak has been found to be located at Gamma Equivalent Energy (GEE) of about 3.5 MeV. High sensitivity of the \(^6\)LiI(Eu) crystal is demonstrated as the neutron peak is observed at the rate as low as \(10^{-2}\) counts per second. Apart from neutron spectra a light output, energy resolution and non-proportionality of the \(^6\)LiI(Eu) response versus \(\gamma\)-ray energy have been measured for the two crystals. The light yield of \(1.5 \times 10^4\) ph/MeV (about 40% of NaI(Tl)) was obtained and the energy resolution at 662 keV (Cs-137) of \(7.5 \times 10^{-3}\) was found for the large crystal. The non-proportionality has been measured to have more proportional character as compared to NaI(Tl). Due to the high sensitivity to thermal neutrons and good proportionality against \(\gamma\)-ray energy, the \(^6\)LiI(Eu) crystal was brought under testing with few samples of fissile nuclear materials. Shielded fissile samples can be recognized via detection of neutrons followed spontaneous fission.

I. INTRODUCTION

Europium doped \(^6\)LiI crystal was investigated in late fiftieths by Murray [1]. Emission spectrum upon X-rays excitation was found to be centered at 475 nm. The absorption spectrum showed that \(^6\)LiI(Eu) absorbed strongly below a sharp cut-off at about 450 nm. Since the maximum of the emission spectrum is located just above the self-absorption edge, large crystal dimensions can reduce total light output of the scintillator and, in turn, degrade energy resolution. Pulse decay time constant of 1.2 \(\mu\)s was measured. The work by Murray [1] was focused on detection of fast neutrons in the energy range of 1-14 MeV, and demonstrated poorly defined and broad peaks of monoenergetic fast neutrons. Moreover, the peaks were measured to be sensitive to the ambient temperature. The peak resolution was improved for the crystal kept in very low temperatures down to about -140°C.

In later studies Sakai [2] obtained scintillation efficiency of LiI(Eu) about \(1.1 \times 10^5\) phons/MeV which was 3.4-4.2 times lower than those of three NaI(Tl) samples examined in his work.

The big interest to highly enriched \(^6\)LiI(Eu) crystal (96% \(^6\)Li) as a neutron detector is due to a high detection efficiency to thermal neutrons. \(^6\)Li nuclei have a large cross section of 940 b for thermal neutron capture. This principal feature of the crystal as an efficient neutron detector makes the scintillator very competitive in application to border monitoring. Detection of illicit nuclear weapons or components is based on observing neutrons or gamma rays produced by the radioactive decay of the \(^{235}\)U or \(^{239}\)Pu shielded or concealed in containers with natural nuclear materials. The aim of this work was to study the properties of \(^6\)LiI(Eu) in neutron and \(\gamma\)-ray spectrometry. Two samples of different size were investigated. At first, a performance of the \(^6\)LiI(Eu) crystal in detection of \(\gamma\)-ray spectrometry is evaluated. As of now, non-proportionality as well as energy resolution vs. \(\gamma\)-ray energy has not yet been measured for the crystal. Moreover, the \(^6\)LiI(Eu) crystal was tested with strong gamma sources to inspect a neutron response of the crystal disturbed by a pileup effect. Lastly, the feasibility of using \(^6\)LiI(Eu) in detection of fissile nuclear materials is assessed.

II. EXPERIMENTAL DETAILS

The LiI(Eu) scintillator is a very hygroscopic material and has to be used in hermetically sealed assembly. Its density is equal to 4.08 g/cm\(^3\) [3].

Two \(^6\)LiI(Eu) scintillators were examined. The large crystal (\(\Phi 50 \text{ mm} \times 5 \text{ mm}\), hereafter marked as L) from the Scientific Engineering Center in St. Petersburg, Russia and the smaller one (\(\Phi 30 \text{ mm} \times 3 \text{ mm}\), hereafter marked as S) from SCIONIX Holland B.V. were assembled in the aluminum case with transparent glass window.

Both \(^6\)LiI(Eu) scintillators were tested, each of them coupled to a calibrated Photonis XP5200 photomultiplier.
(PMT) with silicon grease. A light guide (Ø50 mm × 5 mm) was placed between the protective window of the large crystal and PMT to mix light produced in a planar-type crystal. The light guide was coated with a Teflon tape. In case of \(^{6}\)LiI(Eu) (S) a collimator was placed between a source and the scintillator.

An anode signal from photomultiplier was processed by a modified Canberra 2005E preamplifier and a Tenelec TC244 amplifier. The 6 µs shaping time used in an amplifier was long enough to integrate scintillation light produced by the crystals. However, measurements at very high rate of γ-rays require shorter time constants. For \(^{6}\)LiI(Eu) crystal with light pulse decay time of 1.2 µs the shorter 1 µs shaping time integrates a part of the scintillation light.

The PC-based multichannel analyzer TUKAN8K [4] was used to record the energy spectra. Positions and FWHMs of full-energy peaks were obtained from fitted Gaussian distributions. More advanced fitting procedure was applied to resolve double peaks characteristic of K X-rays.

Measurements of fissile nuclear materials were carried out in the Safeguards Instrumentation Laboratory (SIL) in Seibersdorf, Austria. The same PMT-preamplifier-amplifier system was used at 6 µs shaping time and the energy spectra were recorded with the miniature multi-channel analyzer MCA-166.

III. RESULTS
A. \(^{6}\)LiI(Eu) Crystal in γ-ray Spectrometry

Scintillation characteristics of the two \(^{6}\)LiI(Eu) detectors were examined with calibration sources emitting γ radiation in the range from 16 keV to 1770 keV. The shaping time constant of 6 µs was selected in the measurements except for the case where γ radiation at very high rate was detected.

1) Energy Resolution

Fig. 1 shows the energy spectrum of 662 keV γ-rays from a \(^{137}\)Cs source as measured with \(^{6}\)LiI(Eu) (L). The energy resolution of 7.5±0.1% was measured to be much better than a value of 8.8±0.1% obtained for the small one. However, both values are inferior to that obtained for NaI(Tl).

The energy resolution, \(\Delta E/E\), of the full energy peak measured with a scintillator coupled to a photomultiplier can be expressed as [5]-[6]:

\[
(\Delta E/E)^2 = (\delta_{sc})^2 + (\delta_{st})^2 + (\delta_t)^2
\]

(3)

where \(\delta_{sc}\) is the intrinsic resolution of the crystal, \(\delta_{st}\) is the statistical contribution and \(\delta_t\) is the transfer resolution associated with the variation of light and photoelectron collection [6]-[7]. In case of \(^{6}\)LiI(Eu) (L) the \(\delta_t\) term was substantially reduced by the light guide. Since its contribution to the energy resolution was not estimated in this work, the \(\delta_t\) term was not taken into account in calculations of the intrinsic resolution.

![Fig. 1. The γ-ray spectrum from a \(^{137}\)Cs source measured with \(^{6}\)LiI(Eu) (L) with a light guide placed between the crystal and the PMT window.](image)

The intrinsic resolution of a crystal, \(\delta_{sc}\), is mainly associated with the non-proportional response of the scintillator [6]-[8] as well as with various effects such as inhomogeneities in the scintillator that cause local variations of the light production. The intrinsic resolution also includes a non-uniform reflectivity of the crystal covering.

The statistical uncertainty of the signal from the PMT is described as:

\[
\delta_{st} = 2.35 \times 1/N^{1/2} \times (1 + \varepsilon)^{1/2}
\]

(4)

where \(N\) is the number of photoelectrons and \(\varepsilon\) is the variance of the electron multiplier gain that equals to 0.2 for XP5200.

![Fig. 2. Total and intrinsic energy resolution measured with \(^{6}\)LiI(Eu) (L).](image)

Total and intrinsic energy resolution of the \(^{6}\)LiI(Eu) (L) crystal is presented in Fig. 2. Since the crystal produces small amount of light per energy unit (1 MeV) deposited in the volume, the statistical contribution becomes dominant, especially in the low energy region.

2) Light Yield and Non-proportionality Curve

The photoelectron number per 1 MeV-γ, defined as a ratio between the position of the γ-ray peak and the position of the
single photoelectron peak, was found to be as low as 3000±150 phe/MeV at 662 keV γ-rays for both the crystals. At the quantum efficiency of the photocathode of about 20% at 475 nm wavelength, the light output was obtained of the order of 15000±1500 ph/MeV (~40% of NaI(Tl)), significantly higher than that reported by Sakai [2].

Fig. 3 presents the non-proportionality characteristic of $^6$LiI(Eu) in comparison to that of a small NaI(Tl) [6]. The non-proportionality is defined here as the ratio of photoelectron yield measured for photopeaks at specific γ-ray energy relative to the yield at 662 keV γ-peak [7]. The non-proportionality of $^6$LiI(Eu) shows a characteristic shape for other halide crystals with an excess of light at low energies [7]. It points out that this shape is independent of a doping agent and correlates with the structure of the halide crystal. Light yield non-proportionality obtained in our measurements, presented in Fig. 3, has much better proportional character of the curve as compared to the NaI(Tl) crystal. On the other hand, more proportional scintillators have the downward bending of proportionality curve at few tens of keV [9]. Due to strong statistical variation in the light collection in $^6$LiI(Eu) that influences the energy resolution mainly in the region below 100 keV, the inspection of the non-proportional response of the crystal cannot be easily referred to the intrinsic resolution in this energy region.

The linearity and stability of $^6$LiI(Eu) (L) were simultaneously inspected with a multi-line $^{226}$Ra source emitting γ radiation from 186 to 2448 keV. The measurement lasted more than 10 hours. The 5% stability was observed for a marked full energy peak that is a typical value for most of scintillators. Positions of photopeaks were normalized to the 609 keV line. Deviations from the slope of the linear response of $^6$LiI(Eu) (L) were found up to 2.5 MeV, (see Fig. 4), and agree with the non-proportionality results presented in Fig. 3.

B. Neutron Detection with Pu-Be Source

Neutron detection in $^6$LiI(Eu) undergoes a thermal neutron capture through the reaction:

$$\begin{align*}
^6\text{Li} + ^1\text{n} &\rightarrow ^4\text{He} + ^3\text{H} + Q
\end{align*}$$

Since no γ-rays are emitted in the reaction (1) resulting spectra correspond to neutrons registered in the detector. For interaction with thermal neutrons, the energy released in the reaction (Q = 4.78 MeV) is uniquely specified and is divided
between the $\alpha$-particle and the triton, so the observed neutron peak appears as a sharp Gaussian. Fast neutrons are registered in $^6\text{LiI(Eu)}$ as a broad peak of irregular shape as observed in [1] due to a difference in the scintillation efficiency to the alpha and triton.

An intrinsic efficiency of the $^6\text{LiI(Eu)}$ crystal for the neutron capture can be expressed by the formula:

$$\varepsilon = 1 - \exp(-n \sigma x)$$  \hspace{1cm} (2)

where $n$ – number of $^6\text{Li}$ atoms per volume unit, $\sigma$ - neutron capture cross section, $x$ – thickness of the detector. According to the formula (2) the calculated intrinsic efficiency amounts to 99.98% assuming $n = 1.85\times10^{22}/\text{cm}^3$, $\sigma = 940$ barns, $x = 5$ mm and $^6\text{LiI(Eu)}$ enriched to 100% $^6\text{Li}$.

A Pu-Be neutron source was used to measure neutron spectra. The source emitted neutrons up to about 11 MeV with an intensity maximum in the 3-5 MeV range [10]. In principle, it is possible to measure energy spectrum of fast neutrons in $^6\text{LiI(Eu)}$ crystal [2] due to their kinetic energy added to that of the response to triton-alpha pairs. However, because of a strong neutron scattering on any materials surrounding the source and detector, the resulting fast neutron spectra, measured in this work, have been dominated by a continuous background and no neutron peak could be resolved.

Therefore, we focused on the thermal neutron detection. A neutron monitor Nuclear Enterprises NM2B\(^1\) was used to control a dose equivalent (DE) expressed in both $\mu$Sv/h units and counts of neutrons per second registered in the monitor. Since the $^6\text{Li}$ nuclei have a large cross-section for thermal neutron capture, the Pu-Be source was surrounded with paraffin blocks to slow down the fast neutrons and, therefore, increase total detection efficiency.

\(^1\) NMB2 monitor based on boron trifluoride proportional counter surrounded by a combined modulator/attenuator assembly to produce the correct dose corresponding to the human.
In contrast, a further test was done to show neutron detection with overloading of $^6$LiI(Eu) (L) crystal by a strong gamma background. The $^6$LiI(Eu) (L) has been irradiated with a very strong Co-60 source of several MBq activity and with the Pu-Be neutron source in a moderator at the same time. The number of events, registered in $^6$LiI(Eu) (L), was controlled by an additional counter connected to the TC244 amplifier. The shaping time of 1 µs was set in two successive measurements: the first one with the strong Co source and the second one measured with Co moved far away (see Fig. 9). The very high rate of gammas (about 100 k per second registered in $^6$LiI(Eu) (L)) caused the neutron peak shift about 140 channels to the right (see Fig. 9(a)). Nevertheless, the peak can be easily recognized even though the background increased due to pileup effects. The peak shift can be explained as due to a possible overload of the amplifier and/or too low current of the divider in the PMT base.

C. Neutron Detection of Fissile Materials

Due to the very high sensitivity of $^6$LiI(Eu) to neutrons, samples of fissile materials were measured. Three fissile samples were used: an enriched (4.46%) uranium, a low burnup plutonium-239 (93%) and a high burnup plutonium-239 (61%). The first sample contained 7.6 g of $^{235}$U, the second one consisted of 6.2 g of $^{239}$Pu, 0.4 g of $^{240}$Pu, and other small impurities. The high burnup plutonium-239 (61%) contained 4.2 g of $^{239}$Pu and 1.7 g of $^{240}$Pu. Each of the plutonium sample weighted about 6.6 g with all impurities included. Pure $^{239}$Pu produces fast neutrons at a rate about 20 neutrons per second per kilogram (n/s/kg) and simultaneously emits abundant gamma radiation at energies in the range of 300-770 keV. $^{240}$Pu is produced artificially, and every time it is produced, it is mixed with varying amounts of other isotopes, notably $^{240}$Pu, $^{241}$Pu and $^{242}$Pu. Since all the isotopes have the same chemical characteristics, it is not possible to separate isotopes from each other by chemical techniques.

$^{240}$Pu produces neutrons at a rate about $10^5$ times higher than $^{239}$Pu. Fig. 10 shows radiation of the low and high burnup samples of Pu shielded with a 30 mm thick Pb brick, registered in the $^6$LiI(Eu) crystal. The brick was placed between the sample and the detector. In both cases, the peak of neutrons which were thermalized by surrounding materials, is distinct from the $\gamma$-rays registered by the detector at the same time. The neutron count rates were measured as 45 n/s/kg and 240 n/s/kg for the low and high burnup $^{239}$Pu samples, respectively.

![Fig. 9. Spectrum measured with the Pu-Be source and (a) with a strong $^{60}$Co source (b) with the $^{60}$Co source moved away.](image)

As for $^{235}$U, it produces neutrons by spontaneous fission at a rate of only 0.01 neutrons per second per kilogram. Its $\gamma$-ray emission is limited to a few lines below 210 keV substantially attenuated by several mm thick Pb shielding. Hence, the enriched uranium is difficult to detect reliably when shielded or concealed by intentionally placed shielding. Unfortunately, in our measurements the detection of neutrons from $^{235}$U was obscured by the much stronger background neutron radiation in the laboratory.

IV. SUMMARY

Two samples of $^6$LiI(Eu), enriched to 96% of $^6$Li, were studied in $\gamma$- and neutron spectrometry. A very high sensitivity to thermal and slow neutrons was demonstrated as well as a high selectivity against $\gamma$-ray background was observed as the neutron peak was distinct from the highest energy background peaks. Due to the high neutron detection efficiency of $^6$LiI(Eu), the crystal can detect fast neutrons following spontaneous fission of plutonium isotopes, slowed down by surrounding materials. The high sensitivity and efficiency in detection of thermal and slow neutrons are major merits of the $^6$LiI(Eu) scintillator and can play an important role in the selection of the best crystal for border monitoring equipment.
The large $^6\text{LiI(Eu)}$ crystal showed an energy resolution of 7.5% at 662 keV that was achieved as a light guide between the crystal and PMT window was used. The smaller crystal was measured to have a poorer energy resolution (8.8%) than the large one even if a collimator was placed between a source and the crystal to assure better mixing of the light produced in the volume. Low light output was measured to be about $1.5 \times 10^4$ ph/MeV-$\gamma$. In spite of the superior non-proportionality characteristics of $^6\text{LiI(Eu)}$ as compared to NaI(Tl), the lower light yield and the poorer energy resolution of $^6\text{LiI(Eu)}$ than those of NaI(Tl) make the latter one vastly superior detector to $^6\text{LiI(Eu)}$ in $\gamma$-ray spectrometry.

V. REFERENCES