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Intrinsic radioactivity of a $Li_6Eu(BO_3)_3$ crystal and α decays of Eu

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Abstract

A small $Li_6Eu(BO_3)_3$ crystal (2.72 g) was measured deep underground at the Gran Sasso National Laboratories with a HP Ge detector of 408 cm^3 during 1500 h. While the crystal is not polluted by usual radioactive contaminants (only limits on the activity of U/Th chains, ^{40}K, ^{60}Co, ^{137}Cs were set on the level of 0.01–1 Bq/kg), the presence of radioactive ^{152}Eu and ^{154}Eu is evident; these are created in capture of neutrons by naturally abundant ^{151}Eu and ^{153}Eu. The measured activities correspond to 0.95 and 0.21 Bq/kg for ^{152}Eu and ^{154}Eu, respectively, with a ratio far from the standard expectation. As by-products, limits on half lives for the α decays $^{151}Eu \rightarrow {}^{147}Pm$ ($E_{exc} =$ 91.1 keV) and $^{153}Eu \rightarrow {}^{149}Pm$ are determined as $T_{1/2} > 2.4 \times 10^{16}$ yr and $T_{1/2} > 1.1 \times 10^{16}$ yr, respectively.

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Keywords: Alpha decay; ^{151}Eu; ^{152}Eu; ^{153}Eu; ^{154}Eu; Neutron capture; $Li_6Eu(BO_3)_3$ crystal

1. Introduction

While alpha decay is an old phenomenon with a history more than 100 years old, it continues to attract interest—which has even increased in the last years—of both theoreticians [1] and experimentalists. Developments of experimental techniques recently lead to two interesting observations of α decays of very long-lived isotopes. The alpha decay of ^{209}Bi was registered in Ref. [2] with a $Bi_4Ge_3O_{12}$ scintillating bolometer; the half life is $T_{1/2} = (1.9 \pm 0.2) \times 10^{19}$ yr. The alpha decay of the ^{180}W isotope with $T_{1/2} = 1.2^{+0.8}_{-0.4}(stat) \pm 0.3(syst) \times 10^{18}$ yr was observed in an experiment with $^{116}CdWO_4$ crystal scintillators [3]. This result was later confirmed with $CaWO_4$ bolometers [4] and $CaWO_4$ crystal scintillators [5]. ^{209}Bi and ^{180}W nuclides are in competition for the most rarely observed α decay: while the half life of ^{209}Bi is one order of magnitude longer than that of ^{180}W, the specific activity of ^{209}Bi (105 disintegrations per year per gram of Bi) is much more convenient for experimental observation than the one of ^{180}W (only 2.3 disintegrations per year per gram of W of natural composition[1]), which is the lowest natural α activity ever observed.

The ^{151}Eu nucleus is also potentially unstable to α decay; the energy release would be $Q_\alpha = 1.964$ MeV [7]. While ^{151}Eu decay was not experimentally detected to-date, it is another candidate for observation of the α decay with the current techniques. Its half life was calculated as $\sim 3 \times 10^{18}$ yr [8], and measurements with a relatively large $CaF_2(Eu)$ crystal scintillator have been carried out in the

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[1]Natural abundance of ^{209}Bi is 100%, while abundance of ^{180}W is only 0.12% [6].

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Laboratori Nazionali del Gran Sasso (LNGS); the results will appear soon [8]. It is worth to note that, although Eu is present in CaF_2(Eu) crystals only as a dopant with mass fraction of $\simeq 0.5\%$, the use of CaF_2(Eu) crystals offers many advantages because of the possibility to obtain detectors of good radiopurity and of large mass and because of the exploitation of the active source approach. Nevertheless, future experiments may be considered using materials with greater content of Eu as $Li_6Eu(BO_3)_3$ crystals; their scintillation properties are quite poor, but they might be used as bolometers.

We report here on an investigation of the intrinsic radioactive purity of a small (2.72 g) $Li_6Eu(BO_3)_3$ crystal which is important for low-background measurements. In addition, it should be also mentioned that $Li_6Eu(BO_3)_3$, as well as borates with Eu as dopant, are used as red phosphor in plasma display panels and cathodoluminescent screens (see e.g. Refs. [9,10]). Thus radioactivity of these materials is important also from the safety point of view.

2. Measurements and data treatment

$Li_6Eu(BO_3)_3$ monocrystals with diameter up to 20 mm and length up to 25 mm were grown by the Czochralsky method in air atmosphere with Platinum crucibles in accordance with Ref. [11]. A small crystal was used in the present measurements: its dimensions were $\oslash 14.5 \times 5.6$ mm, and the mass of the crystal was 2.72 g. Radioactive contamination of the crystal, as an external source with respect to the HP Ge detector of 408 cm^3 volume, was measured in the low-background set-up. The measurements were performed deep underground in the Laboratori Nazionali del Gran Sasso (3800 m w.e.). The $Li_6Eu(BO_3)_3$ sample was measured over 1500 h; the background of the HP Ge detector was measured over 689 h. As an example, part of the experimental spectrum in the energy region up to 450 keV together with the background for comparison is presented in Fig. 1.

There are quite a lot of peaks in the spectrum of the $Li_6Eu(BO_3)_3$ crystal. Analysis showed that all of them belong either to (1) usual contaminants such as chains of ^{232}Th, ^{238}U, and also ^{40}K, ^{60}Co, ^{137}Cs or to (2) radioactive decays of ^{152}Eu and ^{154}Eu.

Comparing the rates of the peaks of "usual" contaminants in the $Li_6Eu(BO_3)_3$ spectrum with those in the background, no evidence was found for an additional pollution of the $Li_6Eu(BO_3)_3$ crystal by these nuclides: rates were equal inside statistical uncertainties. Thus only limits on their activities were calculated at 90% C.L. as summarized in Table 1.

Activities were calculated with the formula

$$A = (S_{\mathrm{sample}}/t_{\mathrm{sample}} - S_{\mathrm{bg}}/t_{\mathrm{bg}})/(y \cdot \varepsilon \cdot m)$$

where S_{sample} (S_{bg}) is the area of a peak in the sample (background) spectrum; t_{sample} (t_{bg}) is the time of the sample (background) measurement; y is the yield of the corresponding γ line [12]; ε is the efficiency of the full peak detection; m is the mass of the sample. Efficiencies were calculated with the GEANT4 package [13].

Measured rates of ^{152}Eu and ^{154}Eu peaks correspond to activities in the crystal of 949 ± 48 mBq/kg for ^{152}Eu and 212 ± 35 mBq/kg for ^{154}Eu, respectively.

3. ^{152}Eu and ^{154}Eu contamination

Natural Europium consists of only two stable isotopes: ^{151}Eu (47.81%) and ^{153}Eu (52.19%) [6]. Radioactive ^{152}Eu and ^{154}Eu nuclei were produced by neutron capture by ^{151}Eu and ^{153}Eu, respectively. These nuclei have quite long half lives: ^{152}Eu—13.537 yr, and ^{154}Eu—8.593 yr [12]. Cross-sections for capture of thermal neutrons are equal to $\sigma_{151} = 5900 \pm 200$ b (^{151}Eu) and $\sigma_{153} = 312 \pm 7$ b (^{153}Eu) [12]. The $Li_6Eu(BO_3)_3$ crystal with a mass of 2.72 g contains $N_{151} = 7.78 \times 10^{20}$ nuclei of ^{151}Eu and $N_{153} = 8.49 \times 10^{20}$ nuclei of ^{153}Eu.

The dynamics of unstable daughter nuclides in a flux of neutrons is given by two terms; the first describes the creation of daughter nuclei, and the second their decay:

$$\mathrm{d}N_{\mathrm{d}}/\mathrm{d}t = \phi \cdot \sigma_{\mathrm{m}} \cdot N_{\mathrm{m}} - \lambda_{\mathrm{d}} \cdot N_{\mathrm{d}}$$

where N_{d} (N_{m}) is the number of daughter (mother) nuclei; ϕ the flux of neutrons; σ_{m} the cross-section of neutron capture by mother nuclei; and $\lambda_{\mathrm{d}} = \ln 2/T_{1/2\mathrm{d}}$ is the decay constant of the daughter isotope.

A solution of this equation is $N_{\mathrm{d}}(t) = R_{\mathrm{m}} \cdot (1 - \mathrm{e}^{-\lambda_{\mathrm{d}} t})/\lambda_{\mathrm{d}}$, where $R_{\mathrm{m}} = \phi \cdot \sigma_{\mathrm{m}} \cdot N_{\mathrm{m}}$. The corresponding activity of the daughter is

$$A_{\mathrm{d}}(t) = \lambda_{\mathrm{d}} \cdot N_{\mathrm{d}}(t) = R_{\mathrm{m}} \cdot (1 - \mathrm{e}^{-\lambda_{\mathrm{d}} t}).$$

Thus, the maximal activity of the daughter is equal to the rate of its creation, as could be expected.

The ratio of ^{152}Eu and ^{154}Eu activities should be equal to

$$A_{152}/A_{154} = (R_{151}/R_{153}) \cdot X,$$

where $R_{151}/R_{153} = (\sigma_{151} N_{151})/(\sigma_{153} N_{153}) = 17.33$, and $X = (1 - \mathrm{e}^{-\lambda_{152} t})/(1 - \mathrm{e}^{-\lambda_{154} t})$. For $t \to \infty$, $X = 1$, and for $t \to 0$, $X = \lambda_{152}/\lambda_{154} = 0.635$. Thus, for given N_i and σ_i, the value of $A_{152}/A_{154} = (R_{151}/R_{153}) \cdot X$ should be in the range of 11.00–17.33, which is inconsistent with the measured ratio $A_{152}/A_{154} = 4.48 \pm 0.77$.

Two solutions were considered to solve this contradiction:

(1) The isotopic composition of natural Eu in the crystal was, for some reason, heavily distorted. To see the observed ratio of activities, we should have 19.1% of ^{151}Eu and 80.9% of ^{153}Eu, instead of 47.81% for ^{151}Eu and 52.19% for ^{153}Eu in natural isotopic composition [6]. However, mass-spectrometric measurements showed that the Eu in the crystal was of normal composition: 47.9(3)% of ^{151}Eu and 52.1(3)% of ^{153}Eu. The measurements of the Eu isotope ratio have been carried out with the help of the secondary ion-mass spectroscopy method with an IMS-4f system (CAMECA, France).

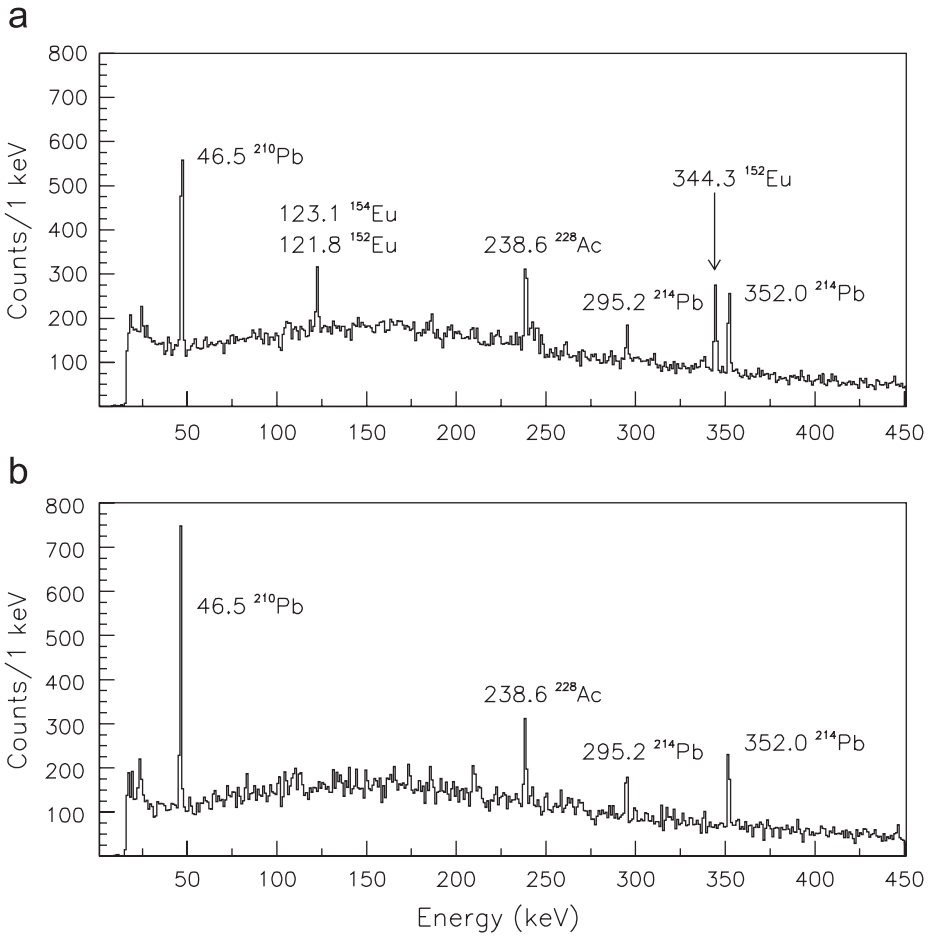

Fig. 1. Spectra measured underground in the LNGS with a low-background HP Ge detector of 408 cm^3: (a) $Li_6Eu(BO_3)_3$ sample during 1500 h; (b) background of the HP Ge detector during 689 h (normalized to 1500 h). Peaks of 122 and 344 keV of ^{152}Eu radioactive decay are evident in the $Li_6Eu(BO_3)_3$ spectrum.

Table 1
Radioactive contaminations in $Li_6Eu(BO_3)_3$ crystal

Chain	Nuclide	Activity (Bq/kg)
^{232}Th	^{228}Ac	<0.20
	^{212}Pb	<0.25
	^{208}Tl	<0.13
^{238}U	^{214}Pb	<0.17
	^{214}Bi	<0.07
	^{40}K	<1.5
	^{60}Co	<0.026
	^{137}Cs	<0.081
	^{207}Bi	<0.009
	^{152}Eu	= 0.949(48)
	^{154}Eu	= 0.212(35)

Limits are given at 90% C.L.

(2) The $Li_6Eu(BO_3)_3$ crystal was, for some time, exposed to a flux of non-thermal neutrons, and the used values of cross-sections are not valid. We consider this hypothesis as correct: as we found later, Eu is recovered commercially from the minerals bastnasite and monazite. At the same time, monazite ore is the main source of Thorium. Usually it contains from 3% to 9% of ThO_2 and up to 1% of UO_2 [14]; however, sometimes species with much higher content (11% of ThO_2 and 16% of UO_2 [15]) are found too. Thus, non-thermal neutrons from spontaneous fission of Th and U, and from (α, n) reactions in ore caused by α decays in the U/Th chains, could be the real reason for the observed distortion of the ^{152}Eu and ^{154}Eu activities.

4. Alpha decay of ^{151}Eu to the first excited level of ^{147}Pm

^{151}Eu can decay with the emission of an α particle not only to the ground state of ^{147}Pm, but also to its first excited level with an energy of $E_{exc} = 91.1$ keV.[2] In this

[2]The energy of the α decay $^{151}\text{Eu} \rightarrow {}^{147}\text{Pm}$, $Q_\alpha = 1964$ keV, gives the possibility to populate also other excited levels of ^{147}Pm, however the corresponding probabilities are very small because of the exponential dependence on energy release.

latter case the Q_α value is equal to 1873 keV. In the subsequent deexcitation process, a γ quantum with $E_\gamma = 91.1$ keV will be emitted, and we can search for this γ in the spectrum of the $Li_6Eu(BO_3)_3$ crystal.

No evidence for this peak has been found in the spectrum (see Fig. 1), and we can give only a limit on the half life

$$\lim T_{1/2} = \ln 2 \cdot \varepsilon \cdot y \cdot N_{151} \cdot t / \lim S$$

where the efficiency to detect a γ quantum with an energy of 91.1 keV is $\varepsilon = 2.8\%$; the γ yield is $y = 0.327$ (because of a big conversion coefficient to electrons for this transition: $\alpha = 2.06$ [16]); the number of ^{151}Eu nuclei $N_{151} = 7.78 \times 10^{20}$; time of measurement $t = 1500$ h.

The value of $\lim S$ was determined in two ways. First, by using the so-called "one σ approach", in which the excluded number of real events that could be invisible in the spectrum is estimated simply as square root of the number of background counts in a suitably chosen energy window ΔE. Notwithstanding its simplicity, this method gives the right scale of the sensitivity of the experiment. For instance, the counting rate in the measured spectrum within the energy interval 80–100 keV is $\simeq 151$ counts/keV. Taking into account that the whole peak is not wider than 3 keV (FWHM value is equal $\simeq 1.2$ keV), the square root estimate gives $\lim S = 21$ events. Using this value of $\lim S$, we obtain the half-life limit: $T_{1/2} \geqslant 4.0 \times 10^{16}$ yr (68% C.L.). Further, the value of $\lim S$ was determined by using the standard least squares procedure, where the experimental energy distribution in the vicinity of the peak searched for was fitted by the sum of the background model (here the straight line) and the peak being sought. As a result of the fitting procedure in the energy region 80–100 keV, the obtained area for the peak is 12 ± 14 counts thus giving no evidence for the effect. The maximum number of real events, which can be excluded with 90%(68%) C.L. was calculated with the Feldman–Cousins procedure [17], recommended by the Particle Data Group [18], as 35(26). It yields the half-life limit: $\lim T_{1/2} = 2.4 \times 10^{16}$ yr at 90% C.L.

The ground state of ^{151}Eu and the first excited level of ^{147}Pm have both spin and parity of $5/2^+$; thus, an α particle is emitted preferably with 0 angular momentum. A theoretical half life value for this decay was calculated with the cluster model of Ref. [19] and a few semiempirical formulae [20–23]; predictions obtained in these approaches are known to be in good agreement with $T_{1/2}$ values measured for α decays (mainly inside the factor of 2–3). Estimated half life values were in the range of 7.7×10^{18} yr to 1.0×10^{20} yr. While the experimental $T_{1/2}$ limit established here is still far from the calculated $T_{1/2}$'s, improvement in the sensitivity is expected in future measurements.

5. Alpha decay ^{153}Eu→^{149}Pm

It is interesting to note that the other naturally occurring Eu isotope, ^{153}Eu, is also potentially α unstable. However, its low energy release ($Q_\alpha = 274$ keV [7]) results in a very big estimated half life of $\simeq 10^{144}$ yr, and, so, there is no perspective to experimentally observe this process, unless some unpredictable exotics.

Nevertheless, the collected data can be used to set an experimental limit on this decay too. For this, we can use the fact that the daughter nucleus ^{149}Pm is unstable and decays further to ^{149}Sm [12]: $^{153}_{63}$Eu ($Q_\alpha = 274$ keV) $\xrightarrow{\alpha}$ $^{149}_{61}$Pm ($Q_\beta = 1071$ keV, $T_{1/2} = 53.08$ h) $\xrightarrow{\beta}$ $^{149}_{62}$Sm.

In the β decay of ^{149}Pm, the most intense γ line has an energy of $E_\gamma = 286.0$ keV and a yield $y = 3.1\%$ [12] (other lines are practically absent). The peak with an energy of 286 keV is absent in the experimental spectrum (Fig. 1). The background rate at this energy is $\simeq 115$ counts/1 keV. With a number of ^{153}Eu nuclei in the crystal, $N_{153} = 8.49 \times 10^{20}$, and an efficiency for the 286 keV γ ray of $\varepsilon = 11.0\%$, we will have a limit on the α decay of the ^{153}Eu: $\lim T_{1/2} = 1.1 \times 10^{16}$ yr at 90% C.L.

For both kinds of α decay discussed above, limits are absent from the literature.

6. Conclusions

Measurements of a small $Li_6Eu(BO_3)_3$ crystal with a low-background HP Ge detector of 408 cm^3 were used to determine its internal radioactive contamination. Only limits (90% C.L.) were set for the usual radioactive pollutions: ^{232}Th chain <0.2 Bq/kg, ^{238}U chain <0.1 Bq/kg, ^{40}K <1.5 Bq/kg, ^{60}Co <26 mBq/kg, ^{137}Cs <81 mBq/kg, ^{207}Bi <9 mBq/kg. At the same time, the radioactive isotopes ^{152}Eu and ^{154}Eu were found with activities of 949 ± 48 mBq/kg and 212 ± 35 mBq/kg, respectively. The ratio of ^{152}Eu/^{154}Eu activities is equal to 4.5 and is far from the expected value of 17.3 calculated for thermal neutrons. This can be explained by the presence of Th and some amount of U in the monazite ores (which is a commercial source for both Eu and Th elements), and a consequent flux of non-thermal neutrons from spontaneous fission and (α, n) reactions.

Half life limits on α decay of natural Eu isotopes were derived for the first time as $T_{1/2} > 2.4 \times 10^{16}$ yr for ^{151}Eu → ^{147}Pm ($E_{exc} = 91.1$ keV), and $T_{1/2} > 1.1 \times 10^{16}$ yr for ^{153}Eu → ^{149}Pm, both at 90% C.L. Higher sensitivities are expected in future measurements. One of the possibilities could be the use of a $Li_6Eu(BO_3)_3$ crystal as a cryogenic bolometer with energy resolution for alpha particles at the level of a few keV.

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