Effects of the atomic environment on the electron binding energies in samarium

A.Kh. Inoyatov [a,b,*], A. Kovalík [a,c], D.V. Filosofov [a], M. Ryšavý [c], D. Vénos [c], Yu.V. Yushkevich [a], L.L. Perevoshchikov [a], V.S. Zhdanov [d]

[a] Laboratory of Nuclear Problems, JINR, Dubna, Moscow Region, Russian Federation
[b] Institute of Applied Physics, National University, Tashkent, Republic of Uzbekistan
[c] Nuclear Physics Institute of the ASCR, CZ-25068 Řež near Prague, Czech Republic
[d] Nuclear Physics Institute, Almaty, Republic of Kazakhstan

ARTICLE INFO

ABSTRACT

Effects of the atomic environment on the L_1, L_2, L_3, M_1, M_2, M_3, and N_1 electron binding energies in samarium generated in the electron capture decay of radioactive ^{149}Eu were investigated by means of the internal conversion electron spectroscopy using the conversion electron spectrum of the 22.5 keV M1 + E2 nuclear transition in the daughter ^{149}Sm. In this investigation, four pairs of ^{149}Eu sources prepared by vacuum evaporation deposition and by ion implantation at 30 keV with the use of four different source backing materials, namely polycrystalline carbon, aluminium, gadolinium and platinum foils, were employed. The greatest average difference of (3.1 ± 0.1) eV in the L_1, L_2, L_3, and M_1 subshell electron binding energies was observed between the ^{149}Eu sources prepared by ion implantation into the aluminium and platinum substrates. On the other hand, minimal differences in the electron binding energies were generally found between samarium generated in the evaporated layer and in the bulk for the individual investigated source backings with the exception of the gadolinium foil. A doublet structure of all investigated conversion electron lines with the average values of 8.1 ± 0.2 eV and 1.5 ± 0.1 for the separation energy and the intensity ratio of the low-energy to high-energy components, respectively, was observed for the ^{149}Eu sources prepared by ion implantation into the aluminium and carbon foils. This structure was presumably caused by the presence of both the trivalent and divalent Sm ions in the sources. No significant differences in natural widths of the L_1, L_2, L_3, M_1, M_2, and M_3 samarium atomic levels among the investigated matrices were observed with the exception of the source prepared by the implantation of the ^{149}Eu ions into the platinum foil for which the determined values for all investigated subshells were apparently higher.

1. Introduction

The need for precise electron energy standards for low-energy electron spectroscopy (the energy region from units to a few tens of keV) increased in the last period also in connection with the neutrino mass experiments. For example, in the international neutrino project KATRIN [1], the intended sensitivity of 0.2 eV in searching for the electron antineutrino mass in tritium beta spectrum is stated. In order to achieve such a sensitivity, a long-term stability of the energy scale of an electrostatic retardation β-ray spectrometer on the ±3 ppm level (i.e., ±60 meV at 18.6 keV) for at least two months of continuous measurements is required. This extremely high stability will be checked by two independent ways, namely: (i) by electronic control of the spectrometer retarding voltage around the tritium β-spectrum endpoint (18.6 keV), (ii) by energy monitoring of the electrons of a very narrow energy distribution close to the tritium β-spectrum endpoint emitted by a natural source in a parallel (so called monitoring) spectrometer. It is, however, known that there are not available any precise internal-conversion or Auger electron energy standards in the keV region at all at present time. This state is due to the fact that the energy of these electrons depends on both the chemical state and environment of radioactive atoms which can, moreover, change with time. (To avoid this very serious problem, feasibility of calibration photoelectron sources with sharp lines (the natural width from 1.0 to 4.5 eV) in the energy region 20–80 keV was studied in Ref. [2] as

* Corresponding author at: Joint Institute for Nuclear Research, Laboratory of Nuclear Problems, Joliot-Curie 6, Moscow Region, 141980 Dubna, Russian Federation. Tel.: +7 4962163956; fax: +7 4962165805.
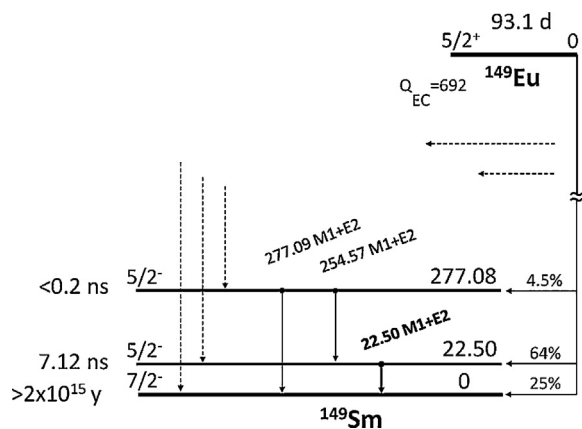 *E-mail address:* inoyatov@jinr.ru (A.Kh. Inoyatov).

Fig. 1. The relevant part of the decay scheme of the ^{149}Eu radioisotope [8]. The energies are given in keV.

photoelectrons ejected by γ-rays from metallic convertors might exhibit lines of constant energy.) In the works [3,4], applicability of the K conversion electron line (kinetic energy of 17.8 keV, natural width of 2.7 eV) of the 32.2 keV E3 nuclear transition in ^{83m}Kr ($T_{1/2}$ = 1.83 h) generated in the electron capture decay of ^{83}Rb ($T_{1/2}$ = 86.2 d) was extensively investigated. The electron sources prepared by ion implantation of ^{83}Rb into metallic substrates were found to be most suitable. Optimization with respect to the substrate material and implantation conditions requires additional extensive experimental investigations of the influence of local physicochemical environment of ^{83}Rb atoms on the electron binding energies like those performed in Ref. [5] for thulium or in Refs. [6,7] for the KLL Auger electrons of Kr and Rb, respectively.

In this paper, we present results of our investigation of the effects of the physicochemical environment of radioactive atoms on the electron binding energies in samarium via the investigation of the conversion electron spectrum of the 22.5 keV M1 + E2 nuclear transition in the ^{149}Sm isotope generated in the electron capture (EC) decay of ^{149}Eu ($T_{1/2}$ = 93.1 d), see Fig. 1. (It is worth noting that the electron capture in ^{149}Eu is followed by extremely fast reorganization of the originally Eu inner electron orbitals to Sm ones. Then the ^{149}Sm nucleus stays in 70% of decays in the first excited state with energy of 22.5 keV and a half-life of 7.12 ns. Only after that this nucleus either emits γ-ray or interacts electromagnetically with the Sm atomic electrons that results in emission of an atomic electron–so called conversion electron.) In the investigation, four pairs of ^{149}Eu sources were used. In each pair, one source was prepared by vacuum evaporation deposition and the other one by ion implantation (i.e., the bulk source) with the use of the same type of source backing. Four different source backing materials were chosen, namely: (i) a polycrystalline carbon foil (150 μm thickness, 99.9% purity); (ii) a standard industrial polycrystalline aluminium foil of 200 μm thickness (an oxidized layer of about 4 nm thickness is known to cover the surface of such a foil); (iii) a common polycrystalline gadolinium foil of 100 μm thickness; (iv) a high purity polycrystalline platinum foil (50 μm thickness, 99.95% purity). The investigation method applied (Internal Conversion Electron Spectroscopy—ICES [9]) exhibits some considerable advantages in comparison with the standard ESCA method [10] (Electron Spectroscopy for Chemical Analysis) such as: (i) natural line widths Γ_γ of the "exiting gammas" are extremely small (typically 10^{-8} to 10^{-4} eV); (ii) choosing a nuclear transition of suitable energy and multipolarity, the outermost or deep-lying core electrons with a preferable orbital angular momentum can be investigated; (iii) one can investigate physicochemical atomic environment (and also a dynamics of its change) at the surface or in the bulk by incorporation there suitable radioactive atoms

(radioisotopic labelling, "marker"); (iv) very high sensitivity (relative—in the ppm range, absolute—in the nanogram range); (v) electrons are emitted only by atoms of a chosen radioactive isotope etc. Thus the ICES method seems to be also a capable competitor of high energy photoelectron spectroscopy or (as often denoted) hard X-ray photoelectron spectroscopy providing simultaneous access to deep core levels and to the valence band. This and the aforelisted characteristics open a possibility to apply the ICES method for investigation, for instance, interface properties of the multilayer systems and some phenomena, such as diffusion and reactions at interfaces (see, e.g., [11]).

The present work is one of the results of our research activities devoted to the development of the aforementioned ultra-stable electron calibration source for the KATRIN neutrino mass project. It should be noted, however, that information on the influence of local environment on the low energy electron spectra (obtained also in our measurements) can be helpful in other fields too, e.g., in another neutrino project "Electron Capture ^{163}Ho experiment" (ECHo) [12] based on microcalorimetric measurements.

2. Experimental

2.1. Source preparation

The ^{149}Eu isotope was obtained by spallation of metallic tantalum by 660 MeV protons from the internal beam of the synchrocyclotron particle accelerator at the JINR, Dubna, Russia. After "cooling" for ten days, the irradiated target (6.6 g weight) was dissolved in the concentrated fluoric acid with the addition of nitric acid. The fraction of europium together with other radioactive lanthanides was separated from the rest target material by the co-precipitation with lanthanum fluoride (1 mg). The subsequent separation of the lanthanides was carried out on a cation-exchange chromatography column (100 mm length, 2 mm diameter, A5 resin in the NH$_4$ form). A preparation obtained was put on the column with a solution of the chloric acid saturated by the boric acid. Afterwards the column was washed with 0.5 M NH$_4$Cl solution and water. The separation was performed by elution using a water solution of ammonium alpha-hydroxyisobutyrate (alpha-HIB) with consequent increasing of its concentration. The europium fraction gained (consisting of several drops of 0.16 M alpha-HIB) was then used for the two aforementioned methods of electron source preparation, namely mass separation and thermal vacuum evaporation deposition.

In addition, the ^{149}Eu isotope was also obtained by chemical separation of the gadolinium and europium fractions performed 100 days after the above-mentioned irradiation of the tantalum target. During this period, ^{149}Eu was accumulated from the electron capture decay of ^{149}Gd ($T_{1/2}$ = 9.28 d). The europium fraction gained consisted of several drops of 0.17 M of alpha-HIB. This fraction was used for the preparation of the ^{149}Eu sources by vacuum evaporation deposition on the C and Gd source backings.

2.1.1. Thermal vacuum evaporation deposition

As mentioned in Section 1, four different source backing materials were used for preparation of ^{149}Eu sources by vacuum evaporation deposition, namely polycrystalline carbon, aluminium, gadolinium, and platinum foils. Prior to use, surfaces of the foils were only mechanically cleansed with application of high purity alcohol.

In all cases, the evaporation procedure started by transferring of several drops (from 40 to 100 μl) of europium fraction to a Ta evaporation boat (annealed at about 1300 °C) and their drying up. Afterwards the Ta evaporation boat with the deposited activity was preheated at 600 °C for about 60 s to remove possible