Surface physicochemical properties and decay of the low-lying isomer in the ^{229}Th nucleus

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Abstract. **The effect of the ^{229}Th nucleus proximity to the CsI surface on the decay probability of its anomalously low lying isomeric level is studied. Results of experimental and theoretical studies show that the CsI surface does not produce chemical bonding with Th and does not noticeably change its valence shells. Hence, it is an optimal substrate for measuring the probability of the ^{229}Th isomer state decay via internal electron conversion. The half-life of the ^{229}Th^m isomer in the thorium atom is calculated for neutral chemical environment.**

1. Introduction

In the last two years, direct evidence was obtained for existence of anomalously low lying levels with an energy $E_{is} \leq 10$ eV in the ^{229}Th nucleus [1–3]. In addition, a life-time of the isomer state was measured in [2, 3]. In the experimental conditions of [2] it was $(7 \pm 1) \times 10^{-6}$ s, and in [3] it was about 23 min. Such a difference is explained by different decay channels for the isometric nucleus: in [2] it was the internal electron conversion, and in [3] it was γ-radiation in the VUV range with the photon energy of about 7.1 eV. The internal conversion is the dominating channel for the ^{229}Th^m decay in atomic thorium [4], whereas γ-radiation can be observed in Th ions and in decay of isomeric nuclei in a dielectric possessing a wide forbidden band [5, 6].

Study of the unusual isomeric state in the ^{229}Th nucleus is important for various reasons. These are the possibility of refining fundamental properties of nature [7, 8], study of specific features of nucleus interaction with shell and chemical environment [4, 5, 9], and, finally, physicochemical problems, which, having being solved, would result in creation of a new

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nuclear time reference [10] and optical-range laser on a nuclear transition [11].

Realisation of this investigation programme requires exact knowledge of the main parameters of isomeric transition from the excited state $3/2^+$ (E_{is}) of the ^{229}Th nucleus to its ground state $5/2^+$ (0.0). Such parameters are decay channels and the energy and value of a nucleus matrix element of this transition. The latter is usually taken in the form of the reduced probability of nucleus transition in Weisskopf units $B_{W.u.}$ (M1; $3/2^+ \rightarrow 5/2^+$), namely, the square modulus of the transition nucleus matrix element averaged over initial and summed over finite quantum numbers (for details concerning $B_{W.u.}$, see [12]).

In the present work, we show that a comparison of the isomer lifetime with respect to the internal electron conversion channel measured in [2] with that, calculated by using the nucleus matrix element from [3] makes it possible to discuss physicochemical properties of the interaction of the Th atom with a substrate surface. In addition, we performed a series of special experiments on determining the chemical state of thorium on a CsI substrate and made some quantum-mechanical calculations modelling the behaviour of the thorium atom near the CsI surface. Issuing from the data obtained, we calculated the probability of internal electron conversion W_{1C} for isomeric nuclei ^{229}Th^m on the surface of CsI and have shown that it weakly depends on the isomer energy E_{is} in the range of 7–17 eV and corresponds to isomer decay in isolated Th atoms. Results of the present work may be useful in planning further experiments on studying the anomalously low lying level in the ^{229}Th nucleus and in development of a nuclear clock and a new nuclear frequency reference.

2. Chemical state of thorium on the CsI substrate

The chemical state of thorium atoms deposited on the CsI substrate was studied by X-ray photoelectron spectroscopy (XPS). XPS measurements were performed in situ on an ultra-high vacuum (5×10^{-9} Torr) complex for surface analysis based on an electron spectrometer XSAM-800 (Kratos). Photoelectrons were excited by the X-ray Al emission line $K_{\alpha 1, \alpha 2}$ at an energy of 1486.6 eV. The experimental error of bond energy measurement was 0.05 eV. The spectrometer was calibrated by the line Au $4f_{7/2}$ with the bond energy $E_b = 8.4$ eV. Since thorium is a chemically active element, it oxidises during the measurement time in the conditions of depositing small quantities on the CsI surface in residual vacuum (5×10^{-9} Torr).

In experiment [2] on measuring the decay time of the excited state for softly deposited thorium atoms onto a micro-

channel plate coated with CsI, this circumstance is not sufficient. Indeed, in the decay time scale, thorium atoms have no time to interact with oxygen of the residual gas in the measurement installation because the rate of atom delivery to the surface does not exceed $\sim 10^{15}$ atom cm^{-2} s^{-1} even at the residual gas pressure of $\sim 10^{-6}$ Torr. Probable thorium oxidation by oxygen atoms that may be situated on the initial surface of the microchannel plate is also excluded. To this end, the surface is preliminarily exposed to a high-energy helium beam, which results in its actually perfect cleaning of light carbon-hydrogen impurities and adsorbed oxygen. Our preliminary XPS measurements of the initial CsI surface and the surface of CsI subjected to treatment by helium atoms with the energy of above 3 keV for several minutes confirm this circumstance. Hence, the chemical state in a short time interval after deposition is only determined by thorium interaction with the CsI substrate.

For determining this state by XPS excluding oxidation during the spectrum measurement cycle, thorium was implanted into a subsurface layer. Thorium was deposited to a surface by the pulsed laser deposition technique (PLD), in which case the ion component of laser plasma was accelerated in the electric field produced by the potential difference (15 kV) between the evaporated metallic thorium target and CsI sample. A neutral component was also deposited onto the surface and, oxidising, produced a thin ThO_2 layer. For studying Th implanted into a subsurface domain, the upper oxidised layer was removed by surface etching with Ar^+ ions at the energy of 3 keV; the etching rate was ~ 10 Å min^{-1}. The pulsed laser implantation was performed by using the radiation of a Q-switched YAG : Nd^{3+} laser ($\lambda = 1.06$ µm, the pulse duration is $\tau = 15$ ns, and pulse energy is 100 mJ).

Spectra of lines Th $4f_{7/2}$, Cs $3d_{5/2}$, and I $3d_{5/2}$ after deposition [curve (1)] and after the ion etching [curves (2) and (3)] are shown in Fig. 1. Also is shown the spectrum of the line Th $4f_{7/2}$ obtained in metal thorium with natural oxide ThO_2 [curve (4)]. After deposition, the line Th $4f_{7/2}$ looks like a single peak at $E_b = 335.8$ eV which corresponds to ThO_2. Lines Cs $3d_{5/2}$ and I $3d_{5/2}$ have the bond energies of 725.8 and

620.2 eV, respectively, which corresponds to the line positions of the initial CsI surface. After the ion etching, which partially removes the oxide layer, the line Th $4f_{7/2}$ broadens and a shoulder arises from the low-bond-energy side. The line is described by two peaks, one of them corresponds to oxide and the second refers to thorium with lower bond ionicity and has the chemical shift relative to the first peak of 2.3 eV. Further etching leads to total removal of the oxide layer, and the line Th $4f_{7/2}$ is described by a single peak at $E_b = 333.4$ eV. Positions of lines Cs $3d_{5/2}$ and I $3d_{5/2}$ do not change, which confirms that ion etching does not lead to CsI degradation and does not affect the chemical composition of its atoms. The position of the Th $4f_{7/2}$ line after etching becomes close to that in the metal state at $E_b = 333.2$ eV [Fig. 1, curve (4)]. Thus, we may conclude that thorium implanted into a subsurface domain of CsI does not produce a strong chemical bond with high ionicity.

Undoubtedly, the system of thorium atoms implanted into a CsI matrix differs from the system of thorium atoms adsorbed on the surface. However, taking into account the fact that even implanted thorium atoms do not interact with the substrate, one may assert that softly deposited thorium a fortiori will not interact with substrate atoms. Hence, thorium atoms on the CsI substrate can be considered as a system of physically retained and chemically unbound atoms.

3. Quantum-chemical study of Th-CsI system

In addition to the experimental results obtained, thorium adsorption on the CsI surface was numerically simulated in the frameworks of the density functional theory (DFT) in the pseudopotential approximation by using the periodical Quantum Espresso code [13]. The surface of CsI was modelled in the approximation of a periodical plate CsI [110] 2×2. The periodical cell in this model includes a plate of thickness equal to two atomic layers cut in the direction [110] of a face-centred lattice CsI and the vacuum layer of thickness ~ 25 Å over the surface, which guarantees absence of interaction with neighbouring cells. In the XY plane the cell comprises two elementary CsI cells [110] (Fig. 2).

First, geometrical optimisation (relaxation) of the clean CsI surface with fixed lower layer was performed by the DFT method; then, the thorium atom was placed over the relaxed CsI surface and relaxation was repeated. Convergence parameters were optimised with respect to the total energy of less than 10^{-4} eV and to forces acting on the atom of less than 10^{-2} eV/Å. Self-consistent DFT-calculations for the clean surface were performed in the generalised-gradient approximation of exchange-correlation energy in the Perdew–Burke–Ernzerhof form [14] and with scalar-relativistic pseudopotentials for CsI and I from [15], obtained by the PAW method for reconstructing the complete electron wavefunctions that are needed for calculating the complete electron density [16]. The surface with thorium was optimised in the Perdew–Wang generalised-gradient DFT approximation (GGA PW91) [17] with scalar-relativistic PAW–PW91 pseudopotential for Th. The structure at the beginning and at end of optimisation is schematically shown in Fig. 2 in two projections; arrows give the directions of forces acting on atom.

For studying the charge state of thorium on the surface, the complete electron density of the system was calculated and the Bader charge analysis [18] was performed by using the programme [19]. Table 1 presents the number of valence electrons, prescribed in the pseudopotential model for neutral
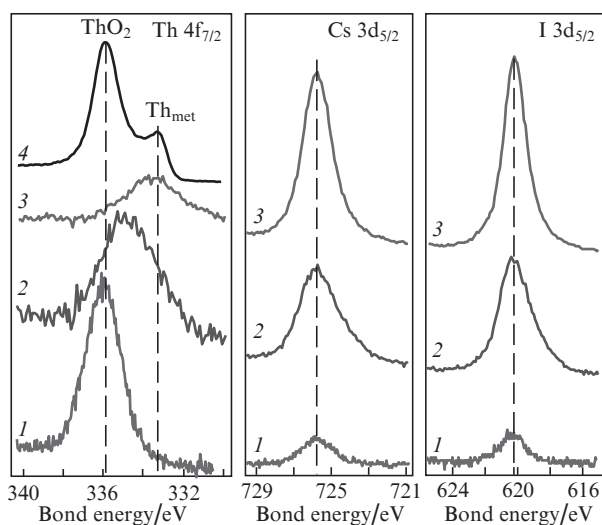

Figure 1. XPS-spectra of lines Th 4f, Cs 3d, and I 3d after (1) pulsed laser implantation, (2) 1-min ion etching, and (3) 3-min ion etching; 4f-line of metal Th with natural oxide ThO_2 is shown for comparison (4).
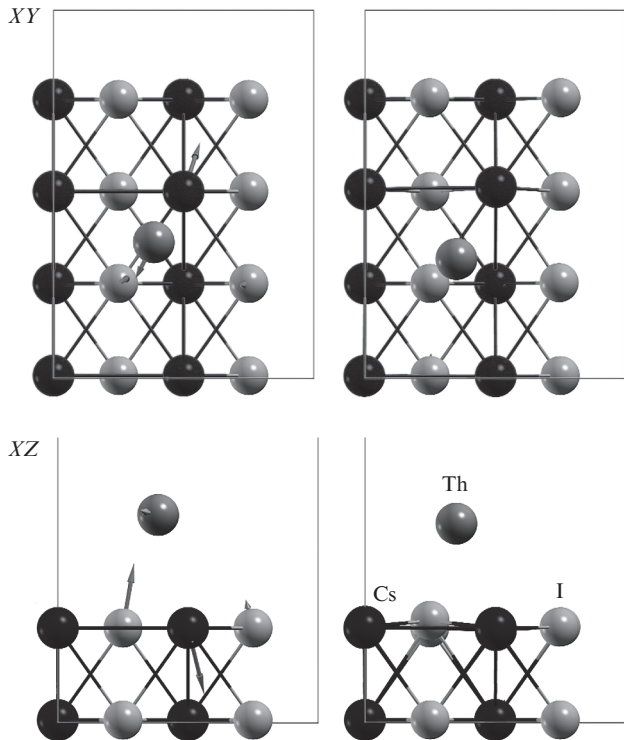
Figure 2. Periodical cell of the model surface CsI [110] with a deposited atom Th prior to and after optimisation in XY and XZ projections.

atoms and calculated according to Bader. Average differences of these values, that is, the effective charges of Cs, I, and Th are $-0.812e$, $+0.814e$, and $-0.009e$, respectively; here, the absolute error of calculated numbers for all valence electrons in the cell ($N_e = 138$) was $+0.006e$. Differences in the effective charges for internal and surface atoms Cs and I are $+0.002e$ and 0, respectively, that is, negligible.

Table 1. Effective atomic charges in the CsI–Th system (average values over internal and surface layers).

Atom	N_e (Val)	N_e (Bader)	N_e (Val)–N_e (Bader)
Cs (inside)	9	8.187	-0.813
Cs (on the surface)	9	8.189	-0.811
I (inside)	7	7.814	0.814
I (on the surface)	7	7.814	0.814
Th	10	9.991	-0.009
N_e (Val)		138	
N_e (Bader)		138.006	

Thus, from the results of numerical simulation one may conclude that exchange by approximately one electron occurs between Cs and I with no Th charge leakage within the calculation accuracy, which means the absence of a chemical bond between thorium and surface atoms.

4. Probability of internal conversion

Internal conversion is the main decay channel for the low-lying state in the Th atom [4]. We have calculated the probability of internal conversion by using the code developed by I.M. Band [20]. The result is shown in Fig. 3 in the form of dependences of the conversion probability for M1 and E2 transitions on the isomer level energy E_{is} in the frameworks of

the single-particle Weisskopf model at $B_{W.u.}(M1; 3/2^+ \rightarrow 5/2^+)$ $= 1$. From Fig. 3 one can see that $W_{1C}(M1;W)$ and $W_{1C}(E2;W)$ weakly depend on the transition energy in the range 7 eV $\leqslant$ $E_{is} \leqslant$ 17 eV. It is an important property of the internal conversion in ^{229}Th, because presently there is a large spread of data concerning the value of E_{is}: 7.1 ± 0.2 eV [3], 7.8 ± 0.5 eV [21], and 6.3 – 18 eV [1].
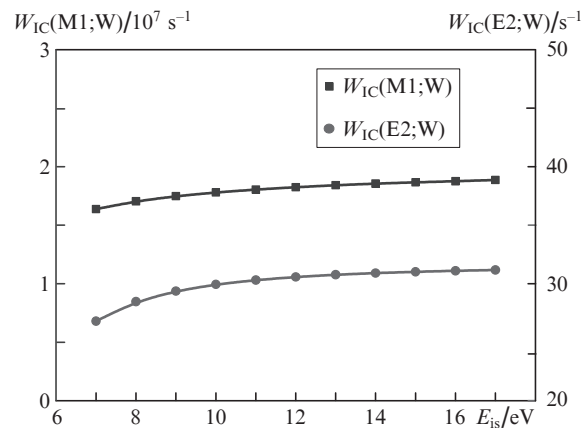

Figure 3. Internal conversion probabilities for M1 and E2 transitions in the Th atom in the frameworks of the single-particle Weisskopf model as a function of isomer state energy E_{is}.

By using data of Fig. 3, one can easily show that in calculations of the decay probability for the low-lying isomer in the isolated Th atom or in ^{229}Th on the CsI surface one may neglect the contribution of both the radiation channel and the E2 component into the process of internal electron conversion. The first assertion is valid because the coefficients of the internal conversion are very large. For example, $\alpha_{M1} = 5.6 \times 10^8$ and $\alpha_{E2} = 2.9 \times 10^{15}$ for the energy $E_{is} = 10$ eV. As for contribution of the E2-component, one can see from Fig. 3 that $W_{1C}(M1; W)/W_{1C}(E2; W) \approx 10^6$. Thus, if for $B_{W.u.}(M1; 3/2^+ \rightarrow 5/2^+)$ we take the value at the lower limit of expected values $0.28 \times 10^{-2} \leqslant B_{W.u.}(M1; 3/2^+ \rightarrow 5/2^+) \leqslant 5.0 \times 10^{-2}$ [12], and the maximal possible value for the reduced probability of the interband E2 transition $B_{W.u.}(M1; 3/2^+ \rightarrow 5/2^+) \approx 30$ then even in this case the contribution of the E2 component is at most 2%. This is substantially less than the measurement accuracy of the half-life period $T_{1/2}$ in [2, 3].

Now we can predict the half-life of the isomer ^{229}Th^m in the thorium atom in neutral chemical environment. In [13], for the reduced probability of the isomer transition at $E_{is} = 7.1$ eV the value of $B_{W.u.}(M1; 3/2^+ \rightarrow 5/2^+)$ was found.

Thus, we have

$$T_{1/2} = \frac{\ln 2}{B_{W.u.}(E2; 3/2^+ \rightarrow 5/2^+)\, W_{1C}(M1, W)} \approx 0.9 \text{ μs}.$$

The half-life obtained is almost by an order of magnitude less than that measured in [2]. This is easily explained. In [2], isomers ^{229}Th^m were deposited and decayed on a substrate made of a nickel alloy with no preliminary surface cleaning. Actually, such substrates are totally covered by organic matter and, importantly, by water molecules. Since Th is a chemically active element, it immediately combines with oxygen, oxidising and loosing valence electrons. (Duration of such chemical reactions is far shorter than several microseconds,

which is the characteristic time of isomer conversion decay.) Since $^{229}\text{Th}^m$ decay through the internal electron conversion occurs just on valence $7s_{1/2}$- and $6d_{3/2}$-electrons and no other, the probability of this process should fall in the case of thorium compounds with oxygen. This, seemingly, is the case of the experiment [2].

5. Conclusions

Thorough experimental and theoretical investigations of the present work show that the anomalously low lying isomer $^{229}\text{Th}^m$ through the channel of internal electron conversion on the surface of the CsI substrate decays at the same rate as in the neutral Th atom, because thorium does not produce chemical bonds with the CsI surface. In this sense, the CsI surface is convenient for taking such measurements because it does not affect the parameters of valence states of the thorium atom. The half-life of $^{229}\text{Th}^m$ calculated in the present work in the neutral thorium atom and in the atom on the CsI substrate is approximately 0.9 ms at the isomer level energy E_{is} = 7.1 eV. It is by an order of magnitude less than the half-life of $^{229}\text{Th}^m$ measured on a nickel substrate. The difference is explained by a substantial change in the properties of Th valence orbitals after thorium makes a chemical bond with oxygen.

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