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Thorium Doped CsI: Implications for the Thorium Nuclear Clock Transition

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For ^{229m}Th isomer nucleus with an anomalously low nuclear excitation energy, E^* (currently accepted value of 7.8 ± 0.5 eV), the bound internal conversion (BIC) decay process is caused by the excitation of a valence electron that is sensitive to the electronic structure of the atomic-sized neighborhood. We analyze an experiment where an impacting Th-ion is neutralized by a negatively charged ion-receiving Cesium Iodide (CsI) surface, to obtain the minimal nuclear excitation energy E_{\min}^* necessary for BIC-promotion of a Th-impurity valence electron in a CsI matrix. We analyze two cases: CsI with Th deposited into the bulk and with Th deposited on the CsI surface. In the bulk we consider band gap effects while on the surface we consider the work-function. The energy to pull the electron to the surface is $1.5 - 2.2$ eV depending on the surface plane, while to promote to the conduction band in the bulk is 1.5 eV. Therefore we conclude that the Th-surface interaction can significantly reduce the lower E^* -bound of 6.3 eV, as estimated from the direct observation of the Th-clock transition (von der Wense et al., *Nature* **533**, 47-51, 2016). We suggest coating the multi-channel plate with differing materials leading to different Th-impurity gaps and work-functions can further narrow the E^* uncertainty interval.

Introduction: The prospects for ultra-precise time keeping at the 10^{-16} to 10^{-17} level of stability (accuracies of 1 s in 10^{16} to 10^{17} s) are fervently being pursued by atomic clock researchers using optical ion clocks [1, 2] and optical lattice clocks [3–5]. These endeavors can push the bounds on fundamental physics searches including dark matter [6], variations of the fine-structure constant α [7–9], and quark mass variation and other fundamental constants [10]. In addition, optical atomic clocks can be used to eventually realize a new standard by which to define the S.I. second [11]. But on the horizon is a new technology that requires precise knowledge of the inner workings of the thorium nucleus, ^{229}Th . A nuclear clock made from Th is expected to have a high transition frequency and narrow linewidth [12–16] capable of reaching an expected remarkable stability as small as 10^{-20} .

A nuclear clock made from ^{229}Th is expected to be free from some of the systematic uncertainties that plague modern atomic clocks. For instance, the black body radiation (BBR) shift in modern atomic clocks is a source of uncertainty that must be controlled and calculated at the same level as the stability, or 10^{-15} as is the case in the current Cs standard [17, 18]. Due to the shielding of electrons around the Th nucleus, Th has been identified as an optical nuclear clock that has a suppressed BBR shift [16, 19].

A recent experiment [15] measured directly the isomer transition energy. To get the lower bound of the transition energy, the authors used the ionization potential of the neutral, free thorium atom. However, the thorium were embedded into a micro-channel plate (MCP) coated with a CsI layer [23] which leads to surface physics effects. Instead of being a neutral, free atom, the thorium atom experiences the solid state neighborhood of the CsI coating and therefore an ejected electron due to a bound internal conversion process would have to overcome the

work function Φ , which is the energy between the Fermi energy E_F of the doped system and the vacuum energy of the surface E_{vac} . If deeply embedded, as in the case of solid state Th-nuclear clock experiments, the band gap is the minimum energy for promoting an electron, therefore E_{\min}^* must be less than the band gap energy E_{bg} . At the surface, for the electron to be accelerated by the MCP, the electron must overcome Φ , so $E_{\min}^* > \Phi$. We show below that these energies are less than the 6.3 eV of a neutral, free thorium atom and therefore a smaller lower bound for the energy of the process is required to interpret the experimental results of Ref. [15].

Background: The recent experiment of von der Wense et al. [15] observed the decay of the excited nuclear or isomer state, ^{229m}Th , by directly detecting the initially bound valence electron that is expelled from the Th-atom in a bound internal conversion (BIC) process [20–22]. The $^{229m}\text{Th}^{2+}$ -ion was observed to live longer than a minute in the gas-phase, indicating that the nuclear excitation energy E^* is insufficient for ionizing the $^{229m}\text{Th}^{2+}$ -particle and hence $E^* < 18.3$ eV. However, after Th^{2+} and Th^{3+} were deposited onto the charged micro channel plate (MCP) (initially coated with CsI but also done with no coating [23]) surface with a kinetic energy of 50 and 75 eV respectively, the implanted Th impurities were observed to expel electrons. These electrons were accelerated towards the positively charged MCP-surface, causing electron cascades that were detected with a CCD camera. Several dependencies ruled out other electron generation mechanisms and the BIC energy E^* would have been sufficient for the Th nucleus to expel a BIC electron. The authors concluded that E^* was greater than the first ionization potential of Th, $E^* > 6.3$ eV. However, the BIC process is expected to happen on the μs time scale [16], which leaves ample time for the neutralized Th to become embedded as an impurity in the

MCP matrix.

Impinging Th can situate within the CsI matrix in many ways, but we follow the interpretation of von Wense et al. that the Th-impurity neutralizes as it impinges on the MCP and embeds in the CsI matrix. This would imply that the Th-atom will find itself in interstitial sites in the B2 structure of CsI in the μs time scales before decay due to BIC. A 50-75 eV Th-atom is travelling at $\approx 1 \times 10^7 \text{ \AA}/\mu\text{s}$, which is enough to traverse multiple lattice constants in CsI and undergo many collisions before coming to a halt within the matrix. A simple stopping range calculation [24] gives a value of $R_p \sim 400 \text{ \AA}$ using an ion-atom interaction potential. However this ignores effects due to crystal structure. Low-energy ion deposition is likely to leave the impinging ion only a few atomic layers deep, but if the energy exceeds the displacement energy E_d of the Cs or I atoms then the Th can also embed at a Cs/I site with defects forming further down the crystal structure [25].

To answer the question of whether the Th-atom embeds interstitially or at an ionic site of Cs or I requires an experimental determination due to the short time scales involved before BIC occurs. Probing the spectroscopic nature of the embedded impurities will help distinguish between these lattice positions. This can be done shortly after implantation (order 1 second if using ^{232}Th), the neutral, interstitial spectrum should be distinguishable from the ionic spectrum associated with lattice site substitutions.

Channelling effects have been ignored, which are of concern in heavy ion deposition onto metal surfaces at low energies [25] which could allow the Th to impact deep into the CsI matrix. Channeling can be avoided by tilting the CsI surface with respect to the incident ion beam. Here we assume that the incident, neutralized Th-particle is deposited within a CsI-matrix, and we calculate the minimal energy needed to either expel an electron from the surface (work-function) or to excite an electron onto the lowest CsI conduction band. Ion-displacement configurations, which require charge balancing from defect formations and thus happen on longer timescales, are not considered in this work. We find the lowest energy state of the interstitial geometry, yielding results consistent with the short lifetime of the excited isomer due to BIC processes.

In the low-doped limit the electron generation process must overcome the work function Φ for CsI. This value is as low as 2.6 eV [26] but has been measured as high as 6.5 eV [?] in photo-electron spectroscopic experiments. Therefore, the BIC energy needs to be at least larger than a work-function of the Th-doped CsI surface. If the Th impurity embeds deep in the crystal, the energy release will produce no photon provided the band gap E_{bg} is smaller than the energy release from BIC and thus ionization and excited phonon modes will occur.

Methods: To study the electronic properties of CsI and ^{229}Th :CsI, we use the Vienna *ab initio* Simulation Package (VASP) [29–32]. We employ the general-

ized gradient approximation (GGA) in the formulation of Perdew, Burke, and Ernzerhof [33] to make an initial guess of the spin-polarized wave function with plane-wave projector augmented pseudo-potentials [34, 35]. These wave functions are the basis for the more sophisticated Green’s function perturbation theory approach G_0W_0 [36–39] that we apply to the ground state structures in the bulk. The G_0W_0 approach has been shown to better represent insulators and other large gap materials, even though the computational overhead is larger than either the local density approximation [40] or GGA respectively.

We represent CsI using the B2, or CsCl, structure from Wyckoff [41] and optimize both a unit cell (1 CsI molecule) and a 2x2x2 supercell (with periodic boundary conditions) of 8 CsI molecules. We found a lattice constant of 4.66 \AA and 4.67 \AA in the unit cell and 2x2x2 system respectively, to be compared with the experimental value of 4.56 \AA [41]. We then increase the bands a factor of four and perform a G_0W_0 calculation. We get a direct electronic band gap at Γ of 5.9 eV and 5.2 eV in the two systems in good agreement with the experimental value of 6.1 eV [27].

In the case of CsI:Th, we model ^{229}Th with concentrations of 50%, 33%, 25%, and 12.5% by taking the unit cell of CsI and expanding in multiples of two in each Cartesian direction. A single Th atom is placed at an interstitial site. There are three distinct interstitial sites: two octahedral and one tetrahedral. Each octahedral site gives Th four planar neighbors of either Cs or I while the tetrahedral site gives two of each neighbor in a rhombohedral shape. At higher doping the Th atoms are close enough together that the *d*-electrons can metallize. Only at 12.5% do they become sufficiently separate for a gap to open at the GGA level. In the experiment, the doping level was far below this 12.5%, which would further isolate the *d*-electrons on Th. However, due to the intense computational requirements to model 12.5% at the G_0W_0 level, smaller concentrations were not studied. The lowest energy state in the 12.5% doped system is the octahedral with 4 planar I atoms, though in optimization Cs atoms become planar along a different plane breaking the overall local octahedral symmetry. This helps to maintain lattice stability as well as electrons localized on Th atom. See Fig. 1 for reference. We checked the stability of this configuration by calculating the phonon spectrum. We find no evidence of imaginary phonon frequencies at the Γ -point. Further decreasing the doping percentage will flatten out the bands associated with the Th-atom embedded at the interstitial site. This can affect the overall gap between valence electrons in Th and the conduction band by the amount that these bands currently span in *k*-space, which is about a few tenths of an eV. Additionally, the location within the CsI band gap that the Th-electrons situate can also shift, but in either direction, as the doping percentage is dropped.

A spin-polarized G_0W_0 calculation is performed next on the resulting 12.5%-doped geometry, and we present

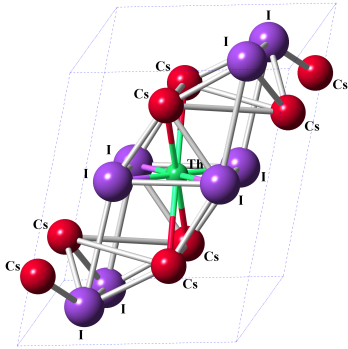


FIG. 1. (Color Online) Th:CsI optimized at GGA level of theory for 12.5% doping. The planar iodine atoms (purple, large spheres labeled I) form quasi-molecular ThI_4 , which helps with the stability, but the planar cesium atoms (red, slightly smaller spheres labeled Cs) form four balancing positive charges which helps to keep thorium atom (green, small sphere labeled Th) in the neutral state which has 4 electrons.

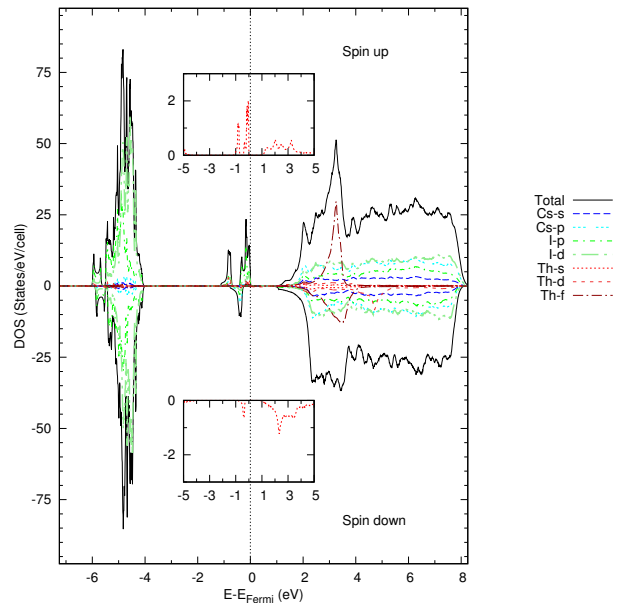


FIG. 2. (Color Online) Th:CsI electronic density of states at the G_0W_0 level of theory for the bulk. The gap has a magnitude of $\Delta = 1.2$ eV. The gap from the Th s -band (light red, short-dash lines) is $E^* = 2.0$ eV in the spin-up channel and $E^* = 1.5$ eV in the spin-down channel. The upper (lower) panel is for spin up (down). The insets show the localization of the Th- s -orbital below the Fermi-level which is set to 0 eV. Th d -orbitals are medium-dash, brown lines. Th f -orbitals are long-short dashed, dark brown lines. Cs s -orbitals are labeled with medium-dashed, blue lines. Cs p -orbitals are labeled with a short-gap dashed, cyan line. I p -orbitals are labeled with a medium-short dashed, bright-green line. I d -orbitals have a short-long dashed, thicker dark-green line. Finally, the total density of states is given by a solid, black, no-dash line.

209 the electronic density of states (DOS) in Fig. 2. The DOS
 210 is split into spin up and down components in the upper
 211 and lower panels and the Fermi-energy is subtracted to
 212 set the highest occupied state at zero energy. The high-
 213 est unpaired electrons are of Th- d character, similar to
 214 the neutral, vacuum state Th atom, as well as two Th- s
 215 electrons. These electrons are fairly-localized just below
 216 the Fermi-energy as indicated in the density of states.
 217 The gap from the highest occupied orbital to the lowest
 218 unoccupied orbital is $\Delta = 1.2$ eV and is of an indirect
 219 nature along $M \rightarrow X$ path.

220 Traditional matrix elements for BIC involve dipole ma-
 221 trix elements of an s -orbital so it is imperative that there
 222 be a DOS corresponding to Th s -states and that it be lo-
 223 calized around Th, i.e., flat in k -space. Whether it is
 224 singly or doubly occupied is not as important so much as
 225 that it be occupied to begin with. In the insets of Fig. 2
 226 we see two localized s -orbitals below the Fermi-energy,
 227 one of each spin, that can each contribute to the BIC
 228 process. The energies are 2.0 and 1.5 eV in the up and
 229 down channel respectively and both are of an indirect na-
 230 ture. Since it is indirect, and BIC involves dipole matrix
 231 elements, at this energy we would expect the excitation
 232 of phonons to carry away the extra momentum of light
 233 needed to change the k -path. Otherwise, the lowest di-
 234 rect transition is of order 2.2 eV and 1.8 eV, respectively.
 235 These values are below the 6.3 eV experimental require-
 236 ment set by Ref. [15]. However, the surface environment
 237 is closer to the experimental conditions and we now en-
 238 deavor to model that system. 259

239 We construct the two most stable CsI surfaces: the
 240 (100) and (111) face, with a 16 (8 Cs and 8 I) atom su-
 241 261

percell. Using at least 10 \AA of vacuum in the z -direction,
 we optimize the top CsI ionic layer (a CsI layer consists
 of a Cs bonded to a I) and freeze the bottom CsI ionic
 layers. The optimized atoms are allowed to move in all di-
 rections but the unit cell is fixed. Because of the vacuum,
 the number of k -points is reduced in the z -direction. We
 find the (111) surface is more stable by 0.23 eV per CsI
 molecule. We calculate the vacuum energy and Fermi en-
 ergy at the GGA level of theory and find that $\Phi = 4.9$ eV,
 in the middle of the reported experimental values [26?].

To study the doped system, we take the (100) and
 (111) slice through the optimized 12.5% bulk structure
 and have the Th-atom site just below the surface. We use
 10 \AA of vacuum in the z -direction for a 17 atom system
 with one Th dopant. The top CsI layer containing the
 dopant Th is spatially-optimized (atoms allowed to move
 in x -, y -, and z - directions) while the bottom CsI layer
 is frozen. The value of the work-function at the GGA-
 level of theory is 1.5 eV and 2.2 eV for (100) and (111)
 surfaces, far below that of the isolated Th atom at 6.3 eV.

Additional Considerations: While the electronic DOS

studies so far capture the main transport physics, Rydberg series of a long-lived bound particle-hole excitation, such as an exciton, can be populated at energy differences less than the band gap E_{bg} in the bulk. If the bound particle-hole state of quantum number n (where n is a positive integer) exists, its energy lies approximately an amount [42]

$$E_n = \frac{\mu e^4}{2\hbar^2 n^2 \epsilon^2}, \quad (1)$$

below the conduction band, where e is the electron charge, ϵ is the dielectric constant of the doped system and accounts for screening, and μ is the particle-hole reduced mass $m_e^{-1} + m_h^{-1}$ with m_e the conduction band mass and m_h the mass of the hole band. In the Th-doped CsI system, the BIC process creates a particle-hole excitation where the hole is in the Th- s -band and the particle is in the conduction band. In general, an exciton is free to move through the lattice with an effective total mass $M = m_e + m_h$. Yet, here we expect, in the limit of a low-doped Th-impurities, that the Th- s -band becomes flat and $m_h \rightarrow \infty$ such that $\mu \rightarrow m_e$ and $M \rightarrow \infty$ which corresponds to a pinned exciton state. Such excitons trapped at impurity centers have been observed in ionic crystals [43]. In this limit, though, the Th-exciton becomes a localized entity and its excitation in BIC corresponds to a nuclear decay process that is made possible by the excitation of the s -electron state to the p -level. This state has a finite width Ξ and such bound-bound processes can contribute to the nuclear decay rate if $|E^* - (E_{\text{bg}} - E_n)|$ is of order Ξ . This process will affect bulk physics studies of Th-impurities, and therefore the band gap physics.

At the surface, an exciton polariton may be created between an outside dielectric medium and a crystal with bulk excitons as described above [?]. These effects may need to be incorporated in future studies to fully understand the physics coupling Th-impurities at the surface of ionic crystals.

Outlook: Using different materials such as CsBr and

CsCl could lead to a better restriction on the value of E_{min}^* . These materials have larger band-gaps in the bulk – 7 and 8 eV [27] – as well as larger work functions – 7.5 and 7.1 eV [?]. This could, in principle, be used to narrow down the isomer transition energy.

Further, engineered Cs-halide systems may offer finer restriction ability. One may dope Na atoms into a Cs-halide structure to tune E_{bg} or Φ to a larger value. For instance, the band gap of NaCl is 9 eV [28], while CsCl is 8 eV and tuning the mixing ratio x in $\text{Na}_x\text{Cs}_{1-x}\text{Cl}$ will in principle tune the gap between these two values, though complex interactions could lead to values not in the range 8-9 eV. We note that the work function will also change, and this must be understood concurrently in order to narrow down the isomer energy.

Summary: We have shown that one needs to consider the environment that Th is experiencing when determining a lower bound on the nuclear transition energy E^* . Without considering the material being used, too high of a constraint can be assessed and a window of possibly observable transition energies will be excluded from future searches. Using *ab initio* density functional theory methods we have produced the first calculations of Th doped in CsI both in the bulk and at the surface. The surface calculations show that the nuclear transition energy window should be adjusted downward from 6.3 eV to 2.2 eV. Theoretical uncertainty due to doping percentage as well as computational ability leads to an error bar of roughly 0.5 eV. At the surface, the embedded Th-atom yields a work-function at 2.2 eV, thereby diminishing the minimum energy found in Ref. [15, 22].

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