Defects in hafnium-doped lutetium oxide and the corresponding electron traps: a meta-GGA study

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Supplementary information

Geometry optimization

Quantum Espresso 6.1 and 6.5 (QE, <u>https://www.quantum-espresso.org/</u>) module pw.x (total energy calculations and geometry optimization) was used with mostly default settings. Perdew-Zunger local density approximation (LDA) functional (<u>10.1103/PhysRevB.23.5048</u>) was used. Crucial settings are shown in Table S1. QE 6.1 was used for the initial part of the study, where various structures with empty traps were analyzed. The following part with the filled traps used QE 6.5. The results should be reproducible with either of codes.

Table 51: Selected Settings used in Quantum Espresso calculations.								
Section &	CONTROL	Section &ELE	CTRONS					
calculation	calculation 'vc-relax'		200					
etot_conv_thr	1E-5	conv_thr	1.0D-7					
forc_conv_thr	0.0001	diago_thr_init	1.0E-4					
nstep	nstep 700		'atomic'					
		mixing_mode	'plain'					
Section 8	SYSTEM	mixing_beta	0.5					
ecutwfc	40	mixing_ndim	8					
ecutrho	ecutrho 400		'david'					
occupations	occupations 'smearing'		Section &IONS					
smearing	'gaussian'	ion_dynamics	'bfgs'					
degauss	0.001							
nspin 1 or 2 *		Section &C	CELL					
tot_charge	2 / 1 / 0 / -1 / -2 *	cell_dynamics	'bfgs'					

Table S1. Selected settings used in Quantum Espresso calculations

* tot_charge is total charge on the system, while nspin controls spin polarization (1 for unpolarized and 2 for polarized); spinpolarization was used for systems with odd tot_charge.

Pseudopotentials

The pseudopotentials (PPs) used were ultrasoft (USPP), generated by the Vanderbilt code version 7.3.6. oxygen recipe (PP generation input file) from **GBRV** The PP group (10.1016/j.commatsci.2013.08.053), version 1.2 was used. The Lu USPP recipe was kindly provided by co-author of the GBRV set, Kevin F. Garrity. The potential had the 4f electrons in core; the valence electrons were effectively of a *d*-element, not an *f*-element.

Initial geometry of Lu₂O₃ cell

Initial geometry (in the from of fractional coordinates of atoms) was generated by Spacegroup code shipped with Elk code version 4.3.6 (*http://elk.sourceforge.net/*), using space group Ia-3, all cell angles of 90.0 degrees and the following fractional coordinates of atoms (*10.3390/ma7107059*):

Lu1: 0.25, 0.25, 0.25

Lu2: 0.46685, 0.0, 0.25

O: 0.39159, 0.15282, 0.38011

Positions of the rest of the atoms were generated by the symmetry operations respective to the space group. Note that Lu1 and Lu2 here are site labels, not to be confused with the atom labels used below. The geometry from Spacegroup code was optimized using QE and shown in Table S2. Cell dimension was 19.432845 bohr.

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Atom label	fc1	fc2	fc3	Atom label	fc1	fc2	fc3
Lu1	0.2499998	0.2499998	0.2499998	O41	0.3912785	0.8476405	0.1200032
Lu2	0.7500002	0.7500002	0.7500002	O42	0.8912793	0.3476402	0.6200032
Lu3	0.7500004	0.2500000	0.2499994	O43	0.6087215	0.1523595	0.8799968
Lu4	0.2499996	0.7500000	0.7500006	O44	0.1087207	0.6523598	0.3799968
Lu5	0.2499994	0.7500004	0.2500000	O45	0.6087213	0.6523598	0.1200033
Lu6	0.7500006	0.2499996	0.7500000	O46	0.1087210	0.1523596	0.6200034
Lu7	0.7500000	0.7500006	0.2499996	O47	0.3912787	0.3476402	0.8799967
Lu8	0.2500000	0.2499994	0.7500004	O48	0.8912790	0.8476404	0.3799966
Lu9	0.4664097	0.0000001	0.2499996	O49	0.3799966	0.3912785	0.1523596
Lu10	0.9664106	0.4999998	0.7500001	O50	0.8799967	0.8912790	0.6523597
Lu11	0.5335903	-0.0000001	0.7500004	O51	0.6200034	0.6087215	0.8476404
Lu12	0.0335894	0.5000002	0.2499999	O52	0.1200033	0.1087210	0.3476403
Lu13	0.5335896	0.5000000	0.2500000	O53	0.3799966	0.6087216	0.3476403
Lu14	0.0335890	0.0000003	0.7500004	O54	0.8799966	0.1087207	0.8476408
Lu15	0.4664104	0.5000000	0.7500000	O55	0.6200034	0.3912784	0.6523597
Lu16	0.9664110	-0.0000003	0.2499996	O56	0.1200034	0.8912793	0.1523592
Lu17	0.2499996	0.4664097	0.0000001	O57	0.1200032	0.3912785	0.8476405
Lu18	0.7500001	0.9664106	0.4999998	O58	0.6200032	0.8912793	0.3476402
Lu19	0.7500004	0.5335903	-0.0000001	O59	0.8799968	0.6087215	0.1523595
Lu20	0.2499999	0.0335894	0.5000002	O60	0.3799968	0.1087207	0.6523598
Lu21	0.2500000	0.5335896	0.5000000	O61	0.1200033	0.6087213	0.6523598
Lu22	0.7500004	0.0335890	0.0000003	O62	0.6200034	0.1087210	0.1523596
Lu23	0.7500000	0.4664104	0.5000000	O63	0.8799967	0.3912787	0.3476402
Lu24	0.2499996	0.9664110	-0.0000003	O64	0.3799966	0.8912790	0.8476404
Lu25	0.0000001	0.2499996	0.4664097	O65	0.1523596	0.3799966	0.3912785
Lu26	0.4999998	0.7500001	0.9664106	O66	0.6523597	0.8799967	0.8912790
Lu27	-0.0000001	0.7500004	0.5335903	O67	0.8476404	0.6200034	0.6087215
Lu28	0.5000002	0.2499999	0.0335894	O68	0.3476403	0.1200033	0.1087210
Lu29	0.5000000	0.2500000	0.5335896	O69	0.3476403	0.3799966	0.6087216
Lu30	0.0000003	0.7500004	0.0335890	O70	0.8476408	0.8799966	0.1087207
Lu31	0.5000000	0.7500000	0.4664104	O71	0.6523597	0.6200034	0.3912784
Lu32	-0.0000003	0.2499996	0.9664110	O72	0.1523592	0.1200034	0.8912793
O33	0.3912785	0.1523596	0.3799966	O73	0.8476405	0.1200032	0.3912785
O34	0.8912790	0.6523597	0.8799967	O74	0.3476402	0.6200032	0.8912793
O 35	0.6087215	0.8476404	0.6200034	O75	0.1523595	0.8799968	0.6087215
O36	0.1087210	0.3476403	0.1200033	O76	0.6523598	0.3799968	0.1087207
O37	0.6087216	0.3476403	0.3799966	077	0.6523598	0.1200033	0.6087213
O38	0.1087207	0.8476408	0.8799966	O78	0.1523596	0.6200034	0.1087210
O39	0.3912784	0.6523597	0.6200034	O79	0.3476402	0.8799967	0.3912787
O40	0.8912793	0.1523592	0.1200034	O80	0.8476404	0.3799966	0.8912790

Anionic and cationic voids

The crystal properties of the voids are similar to those of the anions and cations. There are namely 8 cationic voids of C_{3i} symmetry and 24 cationic voids of C_2 symmetry, generated by the cell symmetry operations from position fc. 0, 0, 0 and 0, 0.25, 0.25, respectively. The anionic voids were generated from a position fc. 0.375, 0.375, 0.375. The list is given below, in Table S3.

Site label	fc1	fc2	fc3	Site symmetry
Oi1	0.375	0.375	0.375	C ₁
Oi2	0.875	0.875	0.875	C_1
Oi3	0.625	0.625	0.625	C_1
Oi4	0.125	0.125	0.125	C_1
Oi5	0.625	0.125	0.375	C_1
Oi6	0.125	0.625	0.875	C_1
Oi7	0.375	0.875	0.625	C_1
Oi8	0.875	0.375	0.125	C_1
Oi9	0.375	0.625	0.125	C_1
Oi10	0.875	0.125	0.625	C_1
Oi11	0.625	0.375	0.875	C_1
Oi12	0.125	0.875	0.375	C_1
Oi13	0.625	0.875	0.125	C_1
Oi14	0.125	0.375	0.625	C_1
Oi15	0.375	0.125	0.875	C_1
Oi16	0.875	0.625	0.375	C_1
CV1	0	0	0	
CV1 CV2	05	0.5	05	C _{3i}
CV3	0.5	0.5	0.5	C _{3i}
CV4	05	0.5	05	C _{3i}
CV5	0.5	0	0.5	C _{3i}
CV6	0.5	0.5	0.5	C _{3i}
CV7	0.5	0.5	05	C _{3i}
CV8	0.5	0.5	0.5	C _{3i}
CV9	0.5	0.25	0.25	
CV10	0.5	0.25	0.25	
CV10 CV11	0.5	0.75	0.75	
CV11 CV12	0.5	0.75	0.75	
CV12 CV13	0.5	0.25	0.25	
CV15	0.5	0.75	0.25	
CV14 CV15	0.5	0.25	0.75	
CV16	05	0.25	0.75	C2
CV10 CV17	0.5	0.75	0.25	
CV18	0.25	0.5	0.25	
CV10	0.75	0	0.75	
CV20	0.75	0.5	0.75	G2 C2
CV20	0.25	0.5	0.25	
CV21 CV22	0.25	0.5	0.75	
CV22	0.75	0	0.25	C ₂
CV24	0.25	0.5	0.75	C2
CV25	0.25	0.25	0	
CV26	0.75	0.25	05	C2
CV27	0.75	0.75	0.5	C2
CV28	0.25	0.75	05	C2
CV29	0.25	0.25	0.5	C2
CV30	0.75	0.25	05	C-
CV31	0.25	0.75	0.5	C_2
CV32	0.75	0.25	0.5	C2
0,04	0.70	0.20	0.0	02

Table S3. Anionic void (interstitial oxygen) and cationic void sites in c-Lu2O3

FP-LAPW calculations

Calculations with Elk 4.3.6 (the initial part) and 4.6.8 (the filled traps part) used species files provided with the code. Only oxygen species file was modified – the local orbital with lorbl = 0and lorbord = 3 was removed, resulting in total of two local orbitals with fixed linearization energies for oxygen. The muffin-tin radius for Lu was 2.0 bohr (2.3 bohr in some of the latter cases), and 1.45 bohr for O. Other non-default options are specified in Table S4. Note that, due to the use of atomic units, electron charge in elk is +1, while proton charge is -1. Consequently, e.g. "chqexs -2" means two additional holes in the system, while "chqexs 1" means one additional electron. The value of *rqkmax* (defines maximum $|\mathbf{G}+\mathbf{k}|$ for APW functions) was 7.6. The value of *gmaxvr* (maximum |**G**| for potential and density) was 17. Smoothing operations to the exchangecorrelation potentials were applied using *msmooth* value 4. Fixed spin magnetization (FSM) was used via *fsmtype* 1 and *msmooth* 0. 0. *X*, where *X* was the total cell magnetization(i.e. the number of unpaired electrons), directed up along *z* axis. In the calculation without FSM, Broyden mixing (default) was used, but the mixing parameters set via *broydpm* were reduced. The k-point grid was 3×3×3. Convergence threshold was twofold: root mean square change from last three iterations in Kohn-Sham potential was required to be lower than $1 \cdot 10^{-6}$ a.u., change in total energy was required to be lower than $1 \cdot 10^{-4}$ a.u..

Table S4. Selected settings used in Elk code.								
Variable name	Value	Variable name	Value					
tasks	0, 10	chgexs	-2 / -1 / 0 / 1 / 2					
xctype	100 209 9	fsmtype	1					
gmaxvr	17	momfix	0. 0. 1. or 0. 0. 2.					
rgkmax	7.6	ngridk	333					
msmooth	4	spinpol	f / t					
isgkmax	-2	lradstp	2					
broydpm	0.2 0.075 (or 0.1 0.0375)	dosmsum	t					

The xctype option selects Räsänen, Pittalis and Proetto mGGA for exchange (209) and PZ correlation (9) from libxc (100).

Dopant, vacancy and interstitial sites

The sites for the impurities were selected so that different structures had something in common. E.g. the C₂ Hf and the O_i sites are the same in Lu₂O₃:Hf $_{C_3i}^{\bullet}$,Hf $_{C_2}^{\bullet}$,O'' and Lu₂O₃:Hf $_{C_2}^{\bullet}$,Hf $_{C_2}^{\bullet}$,O''. The list of the sites are listed in the tables below. The coordinates are given as in the initial Lu₂O₃ geometry from Table S2, or as the initial (crystal symmetry defined) O_i positions. Note that some values in Table S5 and Table S6 differ from those in Table S3. The changes were made to reduce the symmetry of the initial system (i.e. to avoid a possible meta-stable symmetric situation). In some cases, the geometries converged to the higher-symmetric states, as discussed in the main text.

Гable S	5. Positions	of th	e Hf and	10	i impurities	in t	he Lu ₂ (D₃:2Hí	anc	l Lu ₂ ()₃:2Hf,C	D _i structures
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	Us	ed in structures	s with Hf at the	e following site	es:			
Atom label	fc1	fc2	fc3	C_{3i}, C_{3i}	C _{3i} , C ₂	C ₂ , C ₂	i - C_{3i}	i-C ₂
Lu1 / Hf1	0.2499998	0.2499998	0.2499998	√				
Lu2 / Hf1	0.7500002	0.7500002	0.7500002	\checkmark	√			
Lu15 / Hf2	0.4664104	0.5000000	0.7500000		√	\checkmark		
Lu31 / Hf2	0.5000000	0.7500000	0.4664104			\checkmark		
Oi1	0.37	0.37	0.37				√	
Oi2	0.875	0.877	0.873	\checkmark				
Oi3	0.625	0.625	0.625		√	\checkmark		
Oi3	0.63	0.63	0.63				\checkmark	\checkmark
Oi7	0.37	0.89	0.63					\checkmark
CV2 / Hf3	0.5	0.5	0.5				\checkmark	
CV10 / Hf4	0.50001	0.750001	0.76677					\checkmark

Atom label	fc1	fc2	fc3	i - C_{3i}	i-C ₂	R(Hf-O _i), Å
CV2 / Hf3 CV10 / Hf4	0.5 0.50001	0.5 0.750001	0.5 0.76677	4	V	
Oi1	0.37	0.37	0.37	1^{st} , 1^{st}		2.315
Oi3	0.63	0.63	0.63	C_{3i}		2.315
Oi1	0.375	0.375	0.375	1 st , far,		2.226
Oi2	0.875	0.875	0.875	C ₃		6.679
Oi1	0.375	0.375	0.375	1 st , 2 nd ,		2.226
Oi11	0.625	0.375	0.875	C ₁		4.263
Oi9	0.375	0.625	0.125	2 nd , 2 nd ,		4.263
Oi11	0.625	0.375	0.875	S ₂		4.263
Oi2	0.875	0.875	0.875	far, far,		6.679
Oi4	0.125	0.125	0.125	C _{3i}		6.679
Oi3	0.63	0.63	0.63		1 st , 1 st ,	2.300
Oi7	0.37	0.89	0.63		C ₂	2.416
Oi7 Oi9	0.375 0.375	0.875 0.625	0.625 0.125		$1^{st}, 2^{nd}, C_1$	2.330 4.109
Oi7	0.375	0.875	0.625		1 st , far,	2.330
Oi8	0.875	0.375	0.125		C ₁	6.582
Oi9	0.375	0.625	0.125		2 nd , 2 nd ,	4.109
Oi11	0.625	0.375	0.875		C ₁	4.214
Oi4	0.125	0.125	0.125		far, far,	6.582
Oi8	0.875	0.375	0.125		C ₂	6.582

Table S6. Positions of the Hf and O_i impurities in the Lu₂O₃:Hf,2Oi structures, the corresponding O_i arrangements in respect to Hf, the Hf-O_i distances (in the input geometry) and the resulting (post-optimization) local symmetries of the Hf coordination surround.

Cell dimensions of the calculated strctures

The optimized pure Lu₂O₃ cell volume was 1087.5 Å³, while the experimental volume is 1122.7 Å³ (Zeler *et al.*, 2014). Such a difference corresponds to the linear dimensions of the cell (and bond lengths) being about 1% underestimated, which is an acceptable error, and even a good result for LDA. With Hf⁴⁺ dopant, the cell dimensions were 1.5% smaller with respect to the experimental geometry and 0.44-0.45% smaller with respect to the optimized Lu₂O₃ cell. With two Hf⁴⁺ ions, the values were about 1.9% and 0.88% respectively. With the 3+ dopant, the cell dimensions were about the same as that of the optimized dopant-free cell. For the structures with a cluster of two Hf⁴⁺ ions and an interstitial O²⁻ ion, the cell size was almost the same as that of the optimized Lu₂O₃ cell (differences smaller than 0.05%). Adding a single electron to the Lu₂O₃:2Hf,O_i systems resulted in the dimensions 0.61-0.64% smaller than the experimental one, and 0.42-0.45% larger than those of the optimized cell. The structures with an interstitial Hf⁴⁺ ion and two interstitial O²⁻ ions were 0.19-0.29% smaller than the experimental cell and 0.78-0.88% larger than the optimized defect-free cell. The same structures with Hf³⁺ dopant (i.e. with a trapped electron) were characterized by the cell

dimensions 0.1-0.56% larger than the experimental ones, and 1.1-1.6% larger than that of the optimized cell. Structures where Cl⁻ anion accompanied a Hf⁴⁺ cation had cell dimensions about 0.6% smaller than the experimental geometry and 0.45% larger than the optimized defect-free cell. Introduction of an additional electron to all of the Hf⁴⁺ structures thus resulted in a slight increase in the cell dimensions. The mentioned data is tabulated in the Supplementary_Tables.xls spreadsheet.

In order to get a more complete picture of the defects in question, some of the calculations were also performed using projector-augmented wave (PAW) method, with the respective pseudopotentials (Jollet *et al.*, 2014; Holzwarth, 2019) (which included Lu 4f electrons as a valence shell). While having the numerical cost of only up to several times larger than that of USPP, PAW method accounts for the nodal structure of the valence orbitals and ensures orthogonality between valence and core wave functions, resulting in geometries as good as those from all-electron FP-LAPW calculations (Hafner, 2008). With Hf⁴⁺ dopant, the cell dimensions were 1.1% smaller with respect to the experimental geometry and 0.65% smaller with respect to the PAW optimized Lu₂O₃ cell. With Hf³⁺ dopant, the cell dimensions were 0.55% and 0.1% smaller, respectively. The structures codoped with Hf⁴⁺ and Cl⁻ were 0.15% smaller compared to the experimental cell dimensions, and 0.3% larger compared to the PAW optimized cell.

The PAW calculations were made for control purposes. Thus, most of the data was collected using USPP geometries.

Bond lengths in the studied structures

In order to analyze bond length, the first step was to calculate average bond length within coordination surround of the analyzed ion. If there were many of the ions, the next step was to calculate cell-average of the individual average bond lengths. In the undoped optimized c-Lu₂O₃ cell, the cell-average Lu-O bond length is 2.215 Å.

Introduction of Hf dopant (with or without an interstitial oxygen) results in reduction of the cellaverage Lu-O bonds. With a single Hf⁴⁺ ion substituting single Lu³⁺ ion, the cell-average Lu-O bond length becomes 2.208 Å. With two Hf⁴⁺ ions in Lu³⁺ sites, the cell-average Lu-O bond length is 2.201 Å. With two Hf⁴⁺ ions in Lu³⁺ sites and a single interstitial oxygen, the bond length for the Lu ions with coordination number (CN) of 6 is 2.213-2.214 Å; in the case of CN=7, the length is 2.260-2.266 Å. Introduction of Hf⁴⁺ into a cationic void, with the two interstitial oxygens in the dopant coordination sphere, results in cell-average Lu-O bond lengths of 2.221 Å for CN=6; 2.287-2.291 Å for CN=7; 2.374 Å for CN=8. The larger cell-average bonds for higher CN result from the fact that the Lu-O_i bond length may be noticeably larger than that of the other Lu-O bonds, namely about 2.376- 2.461 Å.

Introduction of electrons into the Hf-based traps (populating Hf 5d orbitals and turning the dopant into a formally 3+ ion) resulted in increase in Hf bond length and increase in the cell dimensions. For the structures with one dopant ion and one additional electron, the cell-average Lu-O bond lengths are 2.215-2.217 Å. The same values characterize structures with two dopant ions and two additional electrons. In the "mixed valence" cases (two dopant ions and one additional electron) the values were 2.207-2.208 Å. For the structures with two dopant ions, single interstitial oxygen and one additional electron, the cell-average Lu-O bond lengths are 2.221-2.223 Å for CN=6 and 2.268-2.273 Å for CN=7. Yet again, O_i localizes further from Lu then the oxygens in regular positions. In the Lu₂O₃:Hf_i,2O_i structures with one additional electron, the cell-average Lu-O bond lengths are 2.237-2.247 Å for CN=6, 2.275-2.301 Å for CN=7 and 2.356-2.364 for CN=8.

Similarly to Lu-O bonds, Hf-O bonds depended on the dopant oxidation state and coordination number. In the structures with a single Hf⁴⁺ (CN=6), its average-per-site bond length is 2.128 Å in the C_{3i} site and 2.130 Å in the C₂ site. In the structures with two Hf⁴⁺ dopants (CN=6), the bond lengths are 2.121-2.125 Å. Adding O_i to the aforementioned pairs results in bond length of 2.184-2.191 Å for CN=7 and 2.134 Å for CN=6 (C_{3i} site).

In the Lu₂O₃:Hf,2O_i structures, putting the Hf⁴⁺ dopant in the C_{3i} cationic void results in average bond length of 2.224 Å (CN=8), while in C₂ cationic void it is 2.251 Å (CN=8). For Hf³⁺, average Hf-O bond were 2.150-2.174 Å (CN=6), 2.205-2.219 Å (CN=7) and 2.250-2.260 Å (CN=8).

For Hf^{3+} in the C_{3i} site and CN=6, its bond length is 2.179-2.182 Å, for the structures with either one or two of such dopants. In a mixed-valence $Lu_2O_3:Hf^{\times}_{C_{3i}}, Hf^{\bullet}_{C_{3i}}$ structure, the bond lengths were

2.127 Å for the 4+ dopant and 2.173 Å for the 3+ dopant (CN=6). In Lu₂O₃:Hf[×]_{C_{3i}}, Hf[×]_{C₂}, both sites exhibited bond length of 2.171 Å (CN=6). In Lu₂O₃:Hf[×]_{C_{3i}}, Hf[•]_{C₂</sup> the lengths were 2.165 and 2.150 Å (CN=6), respectively, indicating a mixed-valence character of both sites, with the C_{3i} site being more similar to other 3+ sites (this corresponds to magnetization density data discussed later in the text). In the (Lu₂O₃:Hf[•], Hf[•], O''_i)' structures, the bond lengths were 2.186-2.198 Å (CN=7). For Hf³⁺ in the C₂ site (CN=6), the bond length were 2.141 Å for Lu₂O₃:Hf[×]_{C₂</sup> and 2.166, 2.168 Å for Lu₂O₃:Hf[×]_{C₂</sup>, Hf[×]_{C₂</sup>. However, in these structures, the additional electrons were not localized at the dopant ions (as will be shown below), and hence it is unclear how to specify the charge states: 3+ or 4+. The intermediate 3+/4+ length of the bonds corresponds to the said character of the electron (de)localization.}}}}

Hf³⁺ bond length was larger than Hf⁴⁺ bond length, while for both of them the bond length increased with the increasing coordination number (CN). The average Lu-O bonds were also a bit longer in the structures with the additional electrons. The details are presented in the Supplementary_Tables.xls spreadsheet. These changes in bond lengths were utilized when creating $Lu_2O_3:Hf_{C_{3i}}^{\times}, Hf_{C_{3i}}^{\bullet}$ geometries. With two Hf atoms in the structure, there is a chance that only one of them has a +3 charge (that is, that only one trap of the two is occupied). Setting up the respective calculation with identical surrounds of the two dopant results in magnetization density equally spread between the two ions. The resulting bond lengths turn out to be somewhat in between the Hf³⁺ and Hf⁴⁺ lengths. The problem was not possible to solve using starting magnetization or constrained magnetization options of PW program. Alternatively, an optimized geometry of $Lu_2O_3:Hf_{C_{3i}}^{\times}$ was used, where one of the Lu atoms was replaced with Hf in order to create the second dopant site. Such a calculation yet again resulted in a mixed magnetization. As Lu bonds are longer than Hf³⁺ bonds, the second dopant in the (initially) Lu surround had a stronger tendency to become Hf³⁺, while the (initially) Hf³⁺ dopant becomes Hf⁴⁺. The successful attempt used optimized geometry of Lu_2O_3 :Hf[•]_{C₃}, where one more Lu had been substituted with Hf. In the resulting calculation with two Hf ions, the "old" Hf site had a Hf⁴⁺ surround (and kept it), while the newly added dopant had (initially) a Lu surround. As the geometry was being optimized, the "new" dopant became Hf³⁺ with most of the magnetization localized at itself.