Structural, Thermodynamic, Electronic and Elastic Properties of $Th_{1-x}U_xO_2$ and $Th_{1-x}Pu_xO_2$ Mixed Oxides

P.S. Ghosh, A. Arya

Glass & Advanced Materials Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

Supplementary Information Materials

Table 1: Pair and multisite correlation functions of SQS-96 structures for mimicking ideal random $A_{1-x}B_xO_2$ solid-solution (x = 1/6, 2/16, 3/16, 4/16, 5,16, 6/16, 7/16 and 8/16). Table also shows standard deviation (S.D.) of error in SQS structures at each concentration calculated as:

$$(f)=\sqrt{\frac{\sum_{m=1}^{6}\left(\overline{\Pi}_{2,m}-(2x-1)^2\right)}{m}+\frac{\sum_{m=1}^{3}\left(\overline{\Pi}_{3,m}-(2x-1)^3\right)}{m}+\frac{\sum_{m=1}^{3}\left(\overline{\Pi}_{4,m}-(2x-1)^4\right)}{m}}$$

$\Pi_{k,m}$	Composition $A_{1-X}B_xO_2$							
	x = 1/16 (0.0625)	x = 2/16 (0.125)	x = 3/16 (0.1875)	x = 4/16 (0.25)	x = 5/16 (0.3125)	x = 6/16 (0.375)	x = 7/16 (0.4375)	x = 8/16 (0.5)
$\Pi_{2,1}$	0.77083	0.56250	0.39583	0.25000	0.14583	0.08333	0.00000 -	0.00000
$\Pi_{2,2}$	0.75000	0.58333	0.41667	0.25000	0.08333	0.00000	0.16667	0.00000
$\Pi_{2,3}$	0.75000	0.54167	0.35417	0.22917	0.12500	0.04167	0.00000	0.00000 -
$\Pi_{2,4}$	0.75000	0.50000	0.33333	0.16667	0.08333	0.00000	0.00000	0.33333
$\Pi_{2,5}$	0.77083	0.56250	0.39583	0.25000	0.14583	0.08333 -	0.00000	0.00000
$\Pi_{2,6}$	0.75000	0.50000	0.25000	0.00000	-0.25000	0.50000	0.00000	0.00000
random	0.76562	0.56250	0.39062	0.25	0.14062	0.0625	0.015625	0.00000
$\Pi_{3,1}$	0.68750	0.4375	0.2500	0.1250	0.0625	0.03125	0.00000	0.0000
$\Pi_{3,2}$	0.66667	0.43750	0.27083	0.10417	0.02083	0.02083		0.00000
$\Pi_{3,3}$	0.66667	0.40625	0.23958	0.12500	0.06250	0.02083	-0.04167	0.00000
$\Pi_{3,3}$	0.64583	0.38542	0.18750	0.09375	0.03125	0.01042	0.00000	0.00000
$\Pi_{3,3}$	0.64583	0.41667	0.25000	0.12500	0.04167	0.00000 -	0.00000	0.00000
$\Pi_{3,3}$	0.62500	0.41667	0.22917	0.12500	0.04167	0.02083	0.00000 -	0.00000
$\Pi_{3,3}$	0.62500	0.37500	0.15625	0.09375	0.03125	0.00000	0.04167	0.00000
	0.66992	0.42188	0.24414	0.125	0.05273	0.015625	0.00000	0.00000

random							0.001953	
$\Pi_{4,1}$ $\Pi_{4,2}$ $\Pi_{4,3}$ random	0.62500 0.60417 0.58333 0.58618	0.37500 0.35417 0.33333 0.31641	0.12500 0.18750 0.16667 0.15259	0.00000 0.04167 -0.08333 0.0625	0.12500 0.02083 0.00000 0.01978	-0.12500 0.02083 - 0.08333 0.00391	0.00000 - 0.04167 0.00000 0.000244	0.00000 0.00000 0.33333 0.00000
S.D.of errors	0.039675 118	0.061464 689	0.081427 987	0.116527 426	0.085430 551	0.203338 132	0.070932 242	0.2357020 24

DFT optimised structures VASP POSCAR files

(a) $U_{0.25}Th_{0.75}O_2$ (AFM = antiferro-magnetic)

Generated by cif2cell 1.1.5 from ICSD re

1.00000000000000

11.2854037487247805 0.0163452702760634 -0.0018677539605601

0.0154872883660834 11.2866561489073138 -0.0000660903454404

-0.0029426708012730 0.0004332413927231 11.2941591336884670

U O Th

8 64 24

Direct

0.9992371163397840 0.0006839811716882 0.9995493608378695

0.5017054166768694 0.4991932254779639 0.9992737911276491

0.7481151289441197 0.2496944255805056 0.5009281714439899

0.9974016976187892 0.2488919099810555 0.7506690061779704

0.4987031155521552 0.2486405023419976 0.7495554011684957

0.2488301532184058 0.9995230894727670 0.2496766039903588

0.2480677523104546 0.0005180377268424 0.7510517814621436

0.7486495285158921 0.0020316261260671 0.7495203817141336

0.1284027319140340 0.1216705697305131 0.1289775250131015

0.1162263307824553 0.1290543531901743 0.6300325322728714

0.1272158501480926 0.6249632442061317 0.1247765875276158

0.1264039311270254 0.6269803997004230 0.6254896416640746

0.6264655458568550 0.1259272322987070 0.1237908412318634
0.6162112524503328 0.1290920661045943 0.6259726835980678
0.6265350625114875 0.6254165314135222 0.1235720339146501
0.6263846803699123 0.6253079800669005 0.6246398456364861
0.3707599178393028 0.1237717887076069 0.3721758892623125
0.3661207968006883 0.1194559112276801 0.8717959856302965
0.3765426990672554 0.6252776688514465 0.3750484098674970
0.3802447697413709 0.6199265823085808 0.8771422855375450
0.8707222762048796 0.1287506011762774 0.3762536910624844
0.8665440155475843 0.1204362545164168 0.8719142575251111
0.8761639565265823 0.6264583747568926 0.3751890401521562
0.8774810468778436 0.6235378843947069 0.8748223643036493
0.3761005959411373 0.3743840556176179 0.3759823146547140
0.3787724086932836 0.3688854999767370 0.8740377474831555
0.3712709780267180 0.8768048102281700 0.3711371849705239
0.3748905554988537 0.8727464743564252 0.8730506840550585
0.8753726438940973 0.3756711731722197 0.3764476727019420
0.8779335416786395 0.3704292624395334 0.8733458169360319
0.8741451178846034 0.8770107152997186 0.3739631000314789
0.876971941676132 0.8758796970771081 0.8741596538262453
0.1258781923445633 0.3744029146802648 0.3747959475980781
0.1259489280847599 0.3751404303061311 0.8743559673683106
0.1236783524262554 0.8758402748187739 0.3778593854961865
0.1258464881377636 0.8809223245130737 0.8786605942908720
0.6282453721247601 0.3710552472359947 0.3760032171189979
0.6235540883621659 0.3789579213302139 0.8750733451460132
0.6237863254565327 0.8742788311688492 0.3750854401274663
0.6281592002493455 0.8801199626832256 0.8728927982526499
0.1228057926869034 0.1242088433487687 0.3773292849166389
0.1132653481429523 0.1272290632022371 0.8780422152487841
0.1264688387479647 0.6247608610557988 0.3749650833949127
0.1280948545519421 0.6266478444139624 0.8751674838647098
0.6233540152253088 0.1240402321961652 0.3754933035908017

0.6167365892514235 0.1304662021172530 0.8724800197087305
0.6260962414747517 0.6234288695054346 0.3750368860887456
0.6274437896392117 0.6267737287428991 0.8750796444560457
0.3759214537965487 0.1236402976016137 0.1240154863976619
0.3662511242924505 0.1202217046745872 0.6267464043747336
0.3791496195775699 0.6216603076695196 0.1232165425822664
0.3767230341915955 0.6226206899200839 0.6256122284659003
0.8788695350959258 0.1239295892502534 0.1212658039212981
0.8636935197002750 0.1242194646146678 0.6246527145473595
0.8769581111874296 0.6258097521821699 0.1251113483196885
0.8760673212022537 0.6243332394879754 0.6255880780694987
0.1240686682081188 0.3739515433418498 0.1253053406368129
0.1272889402593584 0.3756985863765984 0.6260261749887999
0.1294616773833274 0.8766476222891134 0.1286293445369129
0.1286513193504469 0.8803879911810039 0.6291428548707848
0.6213918674989883 0.3778532528373481 0.1231038943942705
0.6299287063658354 0.3726579372852140 0.6239856301312298
0.6268992769028404 0.8758880724613874 0.1241110381081056
0.6286643215902289 0.8792884911030950 0.6262726216668123
0.3741888472552993 0.3743291484473379 0.1234233837039566
0.3802309093040837 0.3697745663735381 0.6264400815919535
0.3766083642589882 0.8744197773502386 0.1239774086918249
0.3763167434108221 0.8735908018709582 0.6248161903675976
0.8734312370595791 0.3746410091606313 0.1239294890998786
0.8792866718437516 0.3701929419029392 0.6262448820321120
0.8799425368347626 0.8776923410943385 0.1219714193665961
0.8764176325374797 0.8751733257562228 0.6253355032417768
0.0017112479123470 0.4995562804300314 0.9997410885672962
0.4982730320054186 0.0000690411035433 0.9986105332282760
0.7484672911151473 0.2498908449767679 0.9976943140172112
0.7519462659266197 0.7508711051158528 0.9988240295457339
0.2490131101977314 0.2485298184537853 0.9998189609284567
0.4980192234377419 0.0008265501178343 0.5004306709766361

0.9980400914840111 0.0015124178537845 0.5014611404415604
0.5020418927417974 0.4984026885216553 0.5002529058711676
0.0008922980298546 0.4991387567344573 0.5008418948728545
0.2479616467381816 0.2486497588357267 0.5012899481918859
0.2508037161649059 0.7507863979913938 0.5002924550473957
0.7512350375816912 0.7507897568915796 0.5002053622963764
0.2521514794894628 0.7504735110863769 0.0008021537992955
0.9997740853111312 0.2496046353676931 0.2507691189842349
0.7510041670932724 0.5001750235350927 0.2497045568281709
0.0022223329013100 0.7513149435612336 0.2503560946832744
0.4990092431953516 0.2493284519822909 0.2491974979386044
0.2517198463470637 0.4992844595833056 0.2497438370655635
0.0007795215864892 0.7520261727191021 0.7510829645085995
0.7509370500066254 0.4988851064874718 0.7496859591845689
0.5014326184043135 0.7500798810177066 0.7500641988673347
0.2517699465121547 0.4979624499485125 0.7508065210189955
0.7497136982776609 0.0009060376106157 0.2496271917530047
0.5010606089134110 0.7495298181945758 0.2487020284464231

(b) $U_{0.5}Th_{0.5}O_2$ (AFM = antiferro-magnetic)

Generated by cif2cell 1.1.5 from ICSD re

1.00000000000000

11.2073292820394972 -0.0019979989972927 -0.0015637166158337

0.0053815747812455 11.2160033400292427 -0.0014550400551832

-0.0034010096885002 -0.0037055329602777 11.2464385332697656

U O Th

16 64 16

Direct

0.2461998497924529 0.2513891681847250 0.4990005243138987

0.7501908893039466 0.2473863583809059 0.4999976287921966

0.0011549262272545 0.4989159792925144 0.4998093230682135

0.0002204988929296 0.0024727961112677 0.5008909215625861

0.5013008831595264 0.4990493976571828 0.0009495060167132

-0.0001582845120640 0.5001540979638263 0.0001997980070590

0.7485347237901323 0.2491498725087928 0.0000542167023213

0.7523177842080191 0.7475109318601457 0.9990819743546919

0.2490733821681883 0.4999494279990510 0.2500728323251115

0.2500474213681546 0.0034866843951131 0.2510197687508652

0.4973721049091271 0.2511254063354483 0.2499861417799258

0.9991340206979170 0.2501331657932305 0.2509734886745960

0.2486710916398995 0.0023575289438504 0.7489537472976194

0.7523836981349180 0.9984320981333628 0.7498766597096258

0.9973170187654018 0.2483167337180407 0.7489911549720324

0.0012828117324185 0.7501677694135132 0.7501484945793394

0.1196660612525060 0.1308825999993170 0.1276488366040692

0.1232036562924781 0.1350121591909342 0.6242905299354693

0.1279660956958070 0.6269067858665558 0.1246698460847487

0.1225990290614886 0.6323393501064102 0.6262964461902774

0.6224578877415796 0.1322800997790056 0.1258378891766451

0.6277570498958759 0.1274295112742350 0.6239665274033552

0.6303976012125349 0.6281556971388634 0.1224921814852390

0.6264254955010267 0.6245055985024477 0.6254270420721995

0.3711931363965716 0.1218970739695898 0.3737871129583083

0.3695840995916220 0.1229775907311774 0.8739339088552301

0.3722979996999491 0.6202852163760439 0.3725442913472584

0.3800015660763650 0.6225241852285320 0.8771108134111996

0.8779054119601928 0.1206507244310752 0.3775293908546292

0.8699727276943668 0.1177324772468384 0.8724918732353498

0.8788120060538247 0.6188748251833268 0.3760141284769971

0.8802220983133758 0.6174828624778532 0.8761600700117608

0.3733364814128441 0.3678754369464816 0.3741280069486179

0.3723549846393996 0.3750890993863207 0.8756645542793985

0.3748791406352801 0.8741292105055271 0.3740259047796516

0.3772972078396662 0.8753095530945944 0.8742653779818289

0.8752078591230882 0.3665283340790054 0.3756933398112114

0.8722819533169438 0.3647493674332871 0.8756095523825106

0.8767130885687372 0.8732036353729745 0.3756272493634112

0.8778603757698444 0.8653859915870747 0.8745528280282382

0.1243378507664173 0.3835549119176033 0.3745224380440694

0.1190165641412529 0.3801816035081465 0.8762824028249817

0.1253404714230213 0.8854813686987204 0.3754817981624379

0.1290066102153114 0.8805457827799931 0.8722611267458890

0.6245330298505546 0.3735610198008548 0.3741086056563104

0.6207769541211532 0.3793057313547884 0.8773321854492190

0.6257045127151163 0.8752329950394289 0.3759062617563672

0.6309086522209424 0.8796370711480024 0.8741604497853837

0.1242685944697656 0.1355047093750433 0.3754963101943175

0.1189858185025222 0.1306873126818477 0.8724540469362830

0.1257702218821952 0.6286442869637383 0.3757783287066729

0.1243665934619020 0.6303675172915674 0.8739985763404995

0.6246047944064405 0.1299016904547695 0.3745402170749597

0.6254637622274201 0.1296913001645337 0.8764134607389752

0.6259460888683163 0.6238131755397298 0.3745113947366095

0.6311344034097814 0.6291654312494025 0.8771902320937417

0.3699533840032916 0.1219683704483087 0.1268868107353082

0.3708223746052318 0.1230537131176494 0.6254851780391379

0.3775560648546037 0.6177736540256129 0.1248515849702124

0.3749278769223807 0.6249831700847231 0.6249297529481511

0.8724655682599025 0.1231091584742991 0.1245093842881775

0.8753346398906257 0.1153008843577216 0.6248796817818346

0.8801744263939125 0.6190277182388639 0.1232905705500847

0.8789709884708302 0.6173635910991632 0.6244627096293658

0.1242196419784470 0.3822851374603845 0.1266986977959377

0.1190336384733711 0.3815746399489685 0.6235214618479817

0.1277587462649248 0.8804055956642813 0.1266546706369315

0.1266793441150602 0.8856547627590990 0.6248788460328737

0.6219531507645480 0.3787912664498174 0.1229889105992100

0.6235603371951872 0.3740212721478544 0.6246612862724570

0.6258250234654175 0.8766726491365603 0.1237679976604021

0.6307591621471549 0.8782337818876560 0.6266027150012262

0.3765425543174581 0.3708075942290968 0.1275124585917678

0.3689072592837724 0.3717991264337943 0.6224940698192547

0.3755169591408099 0.8738343889934168 0.1257897416702803

0.3767376568957717 0.8758294157789689 0.6260023646390315

0.8745807688922527 0.3673075720864913 0.1242050043985477

0.8730540167931129 0.3641600103313732 0.6244275261189755

0.8732959286994133 0.8698627834355951 0.1226910443379872

0.8810293305933238 0.8684573049224226 0.6273280239526065

0.9985326014749066 0.0005524872029353 0.9989697387964636

0.5002035819526673 0.0004531776983542 0.0000802220064991

0.2498973921027868 0.7525934598386026 0.5001366178336845

0.4996489372300175 0.4976379150858546 0.4988344571690859

0.4991766405857673 0.0012823050812243 0.4999227959826578

0.2473440239571378 0.2524474324901512 0.0010991764223654

0.7536009676438771 0.7485289769951912 0.5010040636993622

0.2515970627993351 0.7509802214775562 0.9998927100772568

0.4984900863359730 0.2498717054396073 0.7499740552497741

0.5026349180384618 0.7512107187912600 0.7509737115504900

0.7514033874119805 0.4973839792684900 0.7508907340615245

0.2474982761777943 0.5015305089846190 0.7500381842377947

0.0024858159655661 0.7493141303564385 0.2499160856917239

0.5010670287908960 0.7495957469039891 0.2489364573670582

0.7503719383686764 0.4964127547772729 0.2489995622830626

0.7506759114864003 0.0001718572269938 0.2501560778402624

(c) $U_{0.75}Th_{0.25}O_2$ (AFM = antiferro-magnetic)

Generated by cif2cell 1.1.5 from ICSD re

1.00000000000000

11.1482235765931552 0.0490807842453200 -0.0054867206859241

0.0468922608675907 11.1481432289980482 -0.0047437253855465

-0.0048040756947582 -0.0053092523258161 11.1990337828580397

U O Th

24 64 8

Direct

0.0015467187737529 0.5006640856048792 0.0002537865125607

0.4996352870132971 0.9996516403992889 0.0014611479692123

0.7503191831819646 0.2503935533829769 0.0014177122065922

0.7507734593626558 0.7495160304749530 0.0007127485931568

0.2502516501409933 0.2510484150881447 0.0008110920429863

0.4981670679448506 0.9983039627783705 0.4993607454578206

0.9980866092349436 0.9985044991613705 0.4986397554083162

0.5005836638508806 0.5006146180910784 0.4996476932956726

0.0020705453443403 0.5014200907198549 0.4993648876977286

0.2495760619995753 0.2509094975099492 0.4989629397977591

0.2499749018772795 0.7487829888884997 0.5001145553274121

0.7495431986458563 0.7494070975976842 0.4994088772410601

0.2502473793768648 0.7489933864832110 0.0000698487210954

0.0006921076467620 0.2521496508979266 0.2492008451683710

0.7517662219574609 0.5008046386812000 0.2500037581481878

0.9986113387088651 0.7486972922752402 0.2503456122173993

0.4996011491939108 0.2492041998028238 0.2501932671389324

0.2503234595494603 0.4994155160080688 0.2505876896871625

-0.0000809924230233 0.7482822304530830 0.7495794302141008

0.7521982648221532 0.5023314687103203 0.7499732981282379

0.5007839694030023 0.7487659060481154 0.7501308814561971

0.2505243411600489 0.5008157810697014 0.7497460866675578

0.7483501052131912 0.9988386678697286 0.2498047455879647

0.5009255848077110 0.7497022057334689 0.2513763177704804

0.1193176602165766 0.1279461189930179 0.1268367345729959

0.1293255956541901 0.1294234006203783 0.6214585869703453

0.1148109610607991 0.6244801018432324 0.1253822207300536

0.1370054362883041 0.6272528104615889 0.6253794503397767

0.6186652016720016 0.1248573645932832 0.1257771730909237

0.6264092137087967 0.1253903557907415 0.6236392596323777

0.6179926011117414 0.6284338403213048 0.1275566054825827

0.6370127263559564 0.6262352283605449 0.6247792189179018

0.3767978771894329 0.1178301498173831 0.3763176718641800

0.3697436470101350 0.1311609607409519 0.8766884650943838

0.3753243521251783 0.6145939445998755 0.3753334206623025

0.3764686914542558 0.6339587612275148 0.8750000302292901

0.8744703958149012 0.1155544261858357 0.3718569763584499

0.8689266899426709 0.1316607294426686 0.8752443899733644

0.8753156072716944 0.6158949598217290 0.3747310479415072

0.8774132357174261 0.6334079438668905 0.8750592065590276

0.3760446427616748 0.3653343938876175 0.3758060531581105

0.3738604592161475 0.3824515515018035 0.8738203735885584

0.3716021196148260 0.8643079191482027 0.3749377201754356

0.3787503614842110 0.8808204435065944 0.8773386188467758

0.8791528415542996 0.3684562041730447 0.3729190456969526

0.8766682649174762 0.3848398368958985 0.8761497935538641

0.8699987522278091 0.8656131563042686 0.3732032999193959

0.8759816228041176 0.8777897212692665 0.8748688222052653

0.1268404252214496 0.3856431959935503 0.3744670798233289

0.1284273839290719 0.3699673565526931 0.8765890873855732

0.1190459503539297 0.8822980546743733 0.3762312395739634

0.1265364972421533 0.8649884322895740 0.8745831130800359

0.6261593775445106 0.3844008995724251 0.3736791728880837

0.6289879226857110 0.3686899990488486 0.8764367178733105

0.6200376467027543 0.8811274908863194 0.3768577756282762

0.6257455175340431 0.8654023796556316 0.8764824237781275

0.1243741645488947 0.1353220129148008 0.3750027044683908

0.1217157700609112 0.1211275589142218 0.8752522032789549

0.1253671627570616 0.6347995176812209 0.3749560534776377

0.1268606862101123 0.6162168800752229 0.8752921686701949

0.6226773012492774 0.1297272727438987 0.3721109694339957

0.6192196507372086 0.1179294517776806 0.8782509791591170

0.6252032297151527 0.6334598464731501 0.3754196600849807

0.6293503107366155 0.6185552256850149 0.8735685186528697

0.3698839260153874 0.1269923028286147 0.1238742221909183

0.3786648430814440 0.1201423819286388 0.6232327279992186

0.3648733668262719 0.6248460804394240 0.1256452133647505

0.3870283876146316 0.6223127139911229 0.6259443038214673

0.8683260306634230 0.1275464711108561 0.1239057666600945

0.8792605099343280 0.1211074578716730 0.6223994501825686

0.8654991570696809 0.6242428493891805 0.1249094464016208

0.8872226891171497 0.6243139012371910 0.6250766449613347

0.1352969346589102 0.3761888627766566 0.1258394108321938

0.1191225110627531 0.3806704674416835 0.6232444153534339

0.1314496081077669 0.8715935062622659 0.1233310681412335

0.1145156409238502 0.8762205908850578 0.6250349434665134

0.6359029193421664 0.3758749507900249 0.1263151679614460

0.6183134329726746 0.3792541271748940 0.6235902633575727

0.6337033806751742 0.8754180005406230 0.1267332854613726

0.6147372093720668 0.8743787913615825 0.6260554243915183

0.3833139117950481 0.3730220686578349 0.1274110386139848

0.3658818744613487 0.3736732198247791 0.6241789424299673

0.3844652939493800 0.8746710358850737 0.1258428646810759

0.3671935280871143 0.8686058160899711 0.6232616271908223

0.8857011994472926 0.3758562034054448 0.1241991762362690

0.8687877177734821 0.3777787527459287 0.6254893490657230

0.8804000207192032 0.8730804996092829 0.1282403974725632

0.8671458975835943 0.8703148442810205 0.6217897916045265

0.9983609462536243 0.9998773223571503 0.0009437614487681

0.5016194043029458 0.5003443870146187 0.0007920554024980

0.7492670982149010 0.2502988962241557 0.4980006090608828

0.0004790672943974 0.2523886521982890 0.7496322230060172

0.4986215306550881 0.2499831165530809 0.7500082873428371

0.2496244462456575 0.0004789093739512 0.2504617865155646

0.2493620119027114 0.9989490066771753 0.7495186391732451

0.7478673888016300 0.9975123333996360 0.7498581155516423

(d) $Pu_{0.25}Th_{0.75}O_2$ (AFM = antiferro-magnetic)

Generated by cif2cell 1.1.5 from ICSD re

1.00000000000000

11.2444845851264592 0.0031568131184450 0.0013654192575503

0.0028122786885132 11.2405907665250933 0.0015115334978897

0.0014646807721748 0.0024884225944383 11.2414587457832411

Pu O Th

8 64 24

Direct

0.0008238571881472 0.0012397688456951 0.9980223418638771

0.5001326932067024 0.4989411513940342 0.9990270945343065

0.7502655177116998 0.2486910704462425 0.5028555587245684

0.9990164322476904 0.2468905506613197 0.7503802807164928

0.5012468375309617 0.2491972540849445 0.7501241358549720

0.2491216094923226 0.9996833835967440 0.2493450255411510

0.2486651897129734 0.0017741999839473 0.7511252507355898

0.7510523331494446 0.0030322481782990 0.7496972203943694

0.1252093345581155 0.1197881524644204 0.1237194903703533

0.1238779284413931 0.1245606184986366 0.6315528597562151

0.1255842951089719 0.6257849337081935 0.1243317627915548

0.1250139980816486 0.6248616794615011 0.6255357391075013

0.6251092231450646 0.1254930529755359 0.1236089110611085

0.6277056225107056 0.1276382909774224 0.6279984785011560

0.6221558550014565 0.6224470026975815 0.1222220279442167

0.6249842830966871 0.6238750679951363 0.6253402801906655

0.3728293394453752 0.1227874133036107 0.3737678509908466

0.3732932529488970 0.1248561091041910 0.8711511809494946

0.3753901204648390 0.6250606195122100 0.3748373949846515

0.3772534949913949 0.6224789980238117 0.8778342846611686

0.8727218108283576 0.1271296257960141 0.3780510784550221

0.8778611570435596 0.1241546466207879 0.8710158661452829

0.8748729042778335 0.6245999539282950 0.3750108315545199

0.8749451525877532 0.6251678027967897 0.8746573789869884

0.3748075597969973 0.3738860275429943 0.3763651121779322

0.3808099979688471 0.3736873252051734 0.8749895153106123

0.3723307588678011 0.8780533784287132 0.3726609188001853

0.3723308208629508 0.8776722833951857 0.8720464610395131

0.8722352520702680 0.3713856485372479 0.3783331758000881

0.8772733306419532 0.3714878560423431 0.8717814872568783

0.8756973648284989 0.8759707513859720 0.3756104145665160

0.8749368292101639 0.8811947608325625 0.8749313307118540

0.1249910567003554 0.3738498868811750 0.3759730120960694

0.1241546526076069 0.3719526124510004 0.8735929405793588

0.1270141872463320 0.8782019346437561 0.3729762704054901

0.1238240997036280 0.8818457476351983 0.8748929815390343

0.6261381743925332 0.3728807666828056 0.3761470212972680

0.6207711300028995 0.3733910731389810 0.8739247173465089

0.6245156812312479 0.8758009026398360 0.3750869570189797

0.6273522743265407 0.8786878964957828 0.8724686102829449

0.1261832808693213 0.1231474731502245 0.3749674261808195

0.1221343686593904 0.1234460647254121 0.8731412310076773

0.1250401257051892 0.6254197971382118 0.3749161774219139

0.1256450765963710 0.6264765845206819 0.8751769229347757

0.6273564134500063 0.1275306196413742 0.3789098005521914

0.6253045152711555 0.1255901556348642 0.8689248223082956

0.6247795590882110 0.6248878739198286 0.3749494735915241

0.6236313628185309 0.6228999402416995 0.8761594021182466

0.3722348823880140 0.1225618284102209 0.1268658515130298

0.3759856246323510 0.1252044207083146 0.6306749064347007

0.3769736344455247 0.6231950915337595 0.1219409903429878

0.3754212029478203 0.6246137394637957 0.6255571150019190

0.8781548959920190 0.1224621398366182 0.1215523704890378

0.8723992224837233 0.1257803167673322 0.6278669582120837

0.8746794616080898 0.6254945054327605 0.1246240657002503

0.8746125073950430 0.6244416967340612 0.6256086187102684

0.1249798874673559 0.3735511189252856 0.1248909865419252

0.1225278110601089 0.3706579438038252 0.6285446559570731

0.1259959461459701 0.8796182106281947 0.1252787060655121

0.1267485494249848 0.8784121570011805 0.6276847460804247

0.6228359288335805 0.3767261346491961 0.1207572784570331

0.6268593714043810 0.3691589029749247 0.6249226027378163

0.6251054921327052 0.8752904674482502 0.1240700936546953

0.6261255233455414 0.8777251975100427 0.6270108188016690

0.3764820867568273 0.3756840434387306 0.1227983189741048

0.3779817956291943 0.3710266773666000 0.6285948813720725

0.3732696634898688 0.8768264758198472 0.1249742199012894

0.3721964856136588 0.8782604034665903 0.6274144460446179

0.8744056175554454 0.3736683632835456 0.1243475115019656

0.8747175313133975 0.3680411703310404 0.6254113534837524

0.8782720626564846 0.8779466327206583 0.1214153842128115

0.8727996602784506 0.8787271189577398 0.6281878821099203

0.0002273127460002 0.4991525358611206 0.9991578693121349

0.4988618147848896 0.0008976588571054 0.9976863316771944

0.7502739120884431 0.2490657633659126 0.9966927763159089

0.7501087113524451 0.7510719692076039 0.9987467366601250

0.2498233663368622 0.2477901145049876 0.9984454737282894

0.5000589890826945 0.0018658372122884 0.5021604546440962

0.9995859336911802 0.0019128143940481 0.5024083881050878

0.5011511333910874 0.4978225811500977 0.5006757122340028

0.9990353772825200 0.4977730367809428 0.5011181476400833

0.2498537886705864 0.2479149621752517 0.5025646358026533

0.2499005489738365 0.7518100848461813 0.5000286368341493

0.7497635289521832 0.7506637327246749 0.5007067889071400

0.2501020950757550 0.7519803371643076 0.0000889494607140

0.0000782914994751 0.2479248095858941 0.2503138764360665

0.7488521645097482 0.4989916711977071 0.2496915102465192

0.0011559263357186 0.7519272718916487 0.2491268346782710

0.4996542263344005 0.2499593518968084 0.2499508611364060

0.2508700620194845 0.4997791057741851 0.2492482879325119

0.9999023782058610 0.7529856948703942 0.7509459267531928

0.7493023602668576 0.4969962491954972 0.7496878006970028

0.5000744516904883 0.7507216431638923 0.7505719971856147

0.2512497690272887 0.4980746541751450 0.7514075808811641

0.7508886115960103 0.0008805940451131 0.2499307488743107

0.4990414015121884 0.7499876551494237 0.2487025990159232

(e) $Pu_{0.5}Th_{0.5}O_2$ (AFM = antiferro-magnetic)

Generated by cif2cell 1.1.5 from ICSD re

1.00000000000000

11.1348197469980494 0.0019675673534503 -0.0034582071646574

-0.0011940289308022 11.1358651677425815 -0.0051413185599627

-0.0052765026906354 -0.0065626422137791 11.1384069354696251

Pu O Th

16 64 16

Direct

0.2493589980160429 0.4971758672621678 0.2505418141941601

0.2492718448890853 0.0031010049779965 0.2520092065100984

0.4991570418208420 0.2507808876327761 0.2500220535697905

0.0017111668697268 0.2508300863232989 0.2521597413144228

0.2472450133121605 0.2492565266499419 0.4980259637685257

0.7530456139181274 0.2487116646863588 0.5000774113538615

0.0010318183917548 0.4970052131672193 0.5001550753378192

0.0008994696740613 0.0031009529874560 0.5015127023953425

0.5013517305261367 0.4991697390832581 0.0018124417830808

0.9995386532170066 0.4990605396342935 0.0008502157617509

0.2468385559296049 0.0013276931246284 0.7477556567813818

0.7523781632918916 0.0006830146831973 0.7493788358680501

0.9987097643982412 0.2486869751421447 0.7477357992272968

0.9987129458333783 0.7512568899119043 0.7502346979612010

0.7507670862532050 0.2509358563019755 0.9996206805218485

0.7509631763255401 0.7490145561579237 0.9981635578355315

0.1242036628883934 0.1261100873862433 0.1298262242583310

0.1232971549195648 0.1257819426911708 0.6235432933342292

0.1255493352226927 0.6204142636433544 0.1256834743795926

0.1198783434695846 0.6266704188498352 0.6261859963867298

0.6248342923405819 0.1303883035662205 0.1256883619925805

0.6312221007291480 0.1249438416275706 0.6248469603169335

0.6264895124358215 0.6235303438433053 0.1202047856488592

0.6259876464984421 0.6246087852329129 0.6258728204592505

0.3721179634285791 0.1276803364730392 0.3732017885938630

0.3717011186654830 0.1232504965882463 0.8726930786852131

0.3711113183503009 0.6219274775174148 0.3714661587371087

0.3772997292645768 0.6226312050695749 0.8775707261965058

0.8799970135162706 0.1272077431711854 0.3773228401383321

0.8736712784625980 0.1271623949099090 0.8716916107290117

0.8783825760846420 0.6215069941631212 0.3778231649670679

0.8779939147826397 0.6271905312603123 0.8779394028651812

0.3721689018973618 0.3705817530772427 0.3723377625979980

0.3766437053313198 0.3769248922328902 0.8781130093879851

0.3716085646708016 0.8775955252285607 0.3726485338881754

0.3718662542463929 0.8776464823475414 0.8730107020280303

0.8781037504094770 0.3705488542119292 0.3772212877895237

0.8762092412157875 0.3712767396503179 0.8761378994744659

0.8785943103953012 0.8783413622721631 0.3780073231201330

0.8723079636220189 0.8730952338690632 0.8718627974526750

0.1252370411394632 0.3747314073363607 0.3758419934369758

0.1195830508083548 0.3747953195483447 0.8768805210768955

0.1246140294668489 0.8820621918242433 0.3757558425947941

0.1227100527024597 0.8736001663627688 0.8698125737514584

0.6254529579135172 0.3694877497469190 0.3735530613041501

0.6261348831515501 0.3758317398025483 0.8802742227190686

0.6250689045893861 0.8760767450800316 0.3748220501228537

0.6303286108569198 0.8761927810684494 0.8743148569514804

0.1255343081417603 0.1278967907672257 0.3758473581285459

0.1237864748672633 0.1253665156645143 0.8686874241966748

0.1247311392782999 0.6190549141946665 0.3758188860211478

0.1196259555515263 0.6236399003660307 0.8758711068269910

0.6255368713055902 0.1305614865114475 0.3753516610635073

0.6292056241719708 0.1260335832979333 0.8752068630757728

0.6255761287692616 0.6235810616039656 0.3739423889080246

0.6267959876531747 0.6254757345423614 0.8799518710542634

0.3749860084086563 0.1261668833828319 0.1295120775580290

0.3695330579479876 0.1264619257627730 0.6234038003933020

0.3752318210753103 0.6185359607380359 0.1243335235712976

0.3737127664855424 0.6249014552372535 0.6246715153439200

0.8747128569317094 0.1299212960349997 0.1240997655864461

0.8757735335508754 0.1249693508864515 0.6239145018039775

0.8758583044134599 0.6228945301610674 0.1206379901947335

0.8801480187832748 0.6243056499426727 0.6267893866120356

0.1235046273330648 0.3762012230410358 0.1296385587208805

0.1205587311051571 0.3716891518231110 0.6221695897286460

0.1261364893238630 0.8770596890165319 0.1263995923716147

0.1211184556212343 0.8795630742323346 0.6263477307971805

0.6244651424635566 0.3727058408856886 0.1219474352742016

0.6274254273944239 0.3720468862466758 0.6231583939710275

0.6274270408408105 0.8726939663460183 0.1215252315989190

0.6275713513004403 0.8788482211816333 0.6278208534721635

0.3773633457024193 0.3765020932938036 0.1284636469465198

0.3702933789421634 0.3719022936803203 0.6220581660154214

0.3726505182017045 0.8776340488360338 0.1269697968823733

0.3712539044021441 0.8783528563310887 0.6271216577308928

0.8798088748422128 0.3727511873561077 0.1233913220610632

0.8781061676321456 0.3716238139105755 0.6227494555044394

0.8729644539679241 0.8723664584308466 0.1218164430210065

0.8782034670790516 0.8779577885494737 0.6279437721936969

0.9986400750248726 0.0006954918787834 0.9976902971244070

0.5005328429927410 0.2493944915906190 0.7500914142327443

0.5008060116481294 0.7509967134567223 0.7517823228449364

0.7530063058864763 0.4990782784376536 0.7520833514240288

0.2466165148677918 0.4992385069006303 0.7503116408794203

0.5007307320183938 0.0011501673499887 0.9998074942172411

0.2468536323100356 0.7513555570729773 0.5003763635400835

0.4988925584884424 0.4970151036353333 0.4980742195869109

0.4987922753790646 0.0030539318848491 0.4995919088906315

0.2489302581285743 0.2511866274733904 0.0022226361578750

0.7529649402127535 0.7509012819642230 0.5020502549807697

0.2487522393678836 0.7488594678083682 0.9999440608560379

0.0010901911412657 0.7489715018154156 0.2498501088076709

0.4994215298560117 0.7487992339030539 0.2479331986759133

0.7515738404539480 0.4965800109621591 0.2480600692728532

0.7513337620413318 0.0028920739283375 0.2499147727280707

(f) $Pu_{0.75}Th_{0.25}O_2$ (AFM = antiferro-magnetic)

Generated by cif2cell 1.1.5 from ICSD re

1.00000000000000

11.0302085508776102 -0.0040952418089438 0.0019856835744161

-0.0045331633381538 11.0320849692448704 -0.0015152553112686

0.0019867145028449 0.0024258816260339 11.0326030039112695

Pu O Th

24 64 8

Direct

0.9998804773789808 0.5009532804307034 0.0010248535837979

0.5011476055316433 0.9989625141337481 0.0020377368119712

0.7498357618681331 0.2509560132094815 0.0029405510492840

0.7502151238576718 0.7488050808759702 0.0010336519722204

0.2499051051802265 0.2520238403099446 0.0021012480946115

0.5001917204850098 0.9982282003808531 0.4981581863050177

0.9996629306878639 0.9979042894213684 0.4978961373880421

0.4990068712980308 0.5021402490190315 0.4988539930155987

0.0010137279810154 0.5017982257919724 0.4990495764082444

0.2498586978135821 0.2518861126357577 0.4980493289223034

0.2500870005198071 0.7475871475692286 0.5000147325151362

0.7500756364069657 0.7490125586678245 0.4989045685508122

0.2500662500295475 0.7478888720082080 0.0000946981127724

0.0002291394065125 0.2520800932636832 0.2499903378905440

0.7511670616711511 0.5011831519306735 0.2499825558004671

0.9988992416070621 0.7475692140477437 0.2513191321995002

0.4996569481707110 0.2501213709909656 0.2498493883340911

0.2489133457577958 0.4999794020691011 0.2512557873883139

0.9997298570829034 0.7469327903280106 0.7484194527911059

0.7510364867655464 0.5029409859075316 0.7494991939499380

0.5000065635000912 0.7487354853515454 0.7491474215137298

0.2488847527799697 0.5019223736320865 0.7492086057755758

0.7489683914845104 0.9990405896246142 0.2500635996783194

0.5011247905775268 0.7500141109191751 0.2512387467093289

0.1251863654110071 0.1298490725166640 0.1264269685869396

0.1259635508220236 0.1245646056543195 0.6193595227966239

0.1235070730627457 0.6237838228548566 0.1268274386680982

0.1255013709575705 0.6250543255729482 0.6244602656012553

0.6249201864889019 0.1240824612377113 0.1261908498648381

0.6220623698504136 0.1222645019770819 0.6215999512646981

0.6284037871336975 0.6283923672949526 0.1289601818865968

0.6244501095669991 0.6259218130246184 0.6242188495739394

0.3764648139648877 0.1269900367446505 0.3759987110709979

0.3762010900097049 0.1233089961170599 0.8793429547827776

0.3749724037895042 0.6248509727646470 0.3747428524325729

0.3719304960181338 0.6271021181815620 0.8736027270098343

0.8772356517096896 0.1218437523499790 0.3711687997533674

0.8735212291583309 0.1264376142631302 0.8771747238685187

0.8749367112390367 0.6251443917034425 0.3745053194429033

0.8752685472106707 0.6246654156192820 0.8758328855126647

0.3747515985217609 0.3763313213618280 0.3744711900155790

0.3700697651935344 0.3763105852023707 0.8752764587800592

0.3778027838676898 0.8716697442351893 0.3774641544125012

0.3776430943625172 0.8714060773690421 0.8773418999340313

0.8775056984351821 0.3775765030836815 0.3714215209661826

0.8735702626574045 0.3791836642275284 0.8770417717473266

0.8743380643851623 0.8741600654304461 0.3746249289145804

0.8738890503539049 0.8683937684082896 0.8741711868856772

0.1253066492036324 0.3760823011389679 0.3754677387010967

0.1274476958874755 0.3790722889468753 0.8784916308502034

0.1230916463793518 0.8704532648498938 0.3768273916800350

0.1246449298698460 0.8696401290799847 0.8749716746522394

0.6220143881639785 0.3788263043580399 0.3721866312498434

0.6292032808503921 0.3757030703432498 0.8765465953931731

0.6264106733732702 0.8749691763182608 0.3752022457193861

0.6219705561405955 0.8711270977220520 0.8788336863243532

0.1222635342085529 0.1280448235233579 0.3763797833607507

0.1276798947884317 0.1278697763683642 0.8778687030624440

0.1253680273299692 0.6242670479142309 0.3757081659678228

0.1237884563143111 0.6238203782799309 0.8733166493820521

0.6222521538765872 0.1232796487583144 0.3716561323099475

0.6255351675385795 0.1253788354072165 0.8805838871907576

0.6253743934168857 0.6254667655542392 0.3752284332116830

0.6274543401540191 0.6273325488222435 0.8714479099244344

0.3781179037161267 0.1280999109616479 0.1236221966172484

0.3748147340239940 0.1247305871385453 0.6200716990209624

0.3730421266660058 0.6262047729941963 0.1275675689570215

0.3746427784277951 0.6248368038303412 0.6247638355076718

0.8708587898066203 0.1270394490282927 0.1277473374600326

0.8769453568731568 0.1230646138586618 0.6218812800587334

0.8750241795361441 0.6239456896076708 0.1243678496785587

0.8753434668328619 0.6250746818557114 0.6229876477909724

0.1240714769499572 0.3769829537639832 0.1262011810762336

0.1273794144371410 0.3787354845786056 0.6228701898984892

0.1263365026363399 0.8698572606783119 0.1255465779238826

0.1215175303224066 0.8713229955187514 0.6227039033430395

0.6271239842773537 0.3739249181990218 0.1274488487909421

0.6260463872362411 0.3808209602934018 0.6248417884070658

0.6250220992145704 0.8752762473621672 0.1262978823215756

0.6228604263627905 0.8712988526895997 0.6227258487141091

0.3722234195402888 0.3729833403172544 0.1285595858170465

0.3729547219839959 0.3786877085589059 0.6215834187265716

0.3781334733452156 0.8720964503541959 0.1241362475756210

0.3766320136293788 0.8709151537597539 0.6221350140609345

0.8761245823669945 0.3759202911267133 0.1265197519824487

0.8757920954555876 0.3814022082674824 0.6234868823040497

0.8728640761688076 0.8705694242862797 0.1286418083717428

0.8763922513649565 0.8703313178240905 0.6214494254734160

0.9990348938179905 0.9986284948446046 0.0018867873475487

0.4999435947677378 0.5010814454242405 0.0013351230248618

0.7499065916365435 0.2511560015797831 0.4967057023863992

0.0011108483902474 0.2530182997716252 0.7499088242459480

0.4992659220265456 0.2510338012615305 0.7501781496466418

0.2512026965250680 0.9997377132250752 0.2510810128620175

0.2508441200134702 0.9976315931404663 0.7490835267987836

0.7489333082543758 0.9968090091685263 0.7497784409161981

Choices of U/J parameters for PuO_2

The GGA+*U* formalism requires knowledge of strong onsite Coulomb interaction *U* and exchange *J* parameters applied to the 5*f* electrons of the Pu^{4+} cations. For Pu^{4+}, these parameters have been adjusted from previous electronic structure calculations **[1]** and there is no unique choice of *U/J* parameters for LDA+*U*/GGA+*U* formalism in the literature. This is in contrast to UO_2 where *U* and *J* values are extracted from experiment and further validated by many electronic structure calculations **[2-5]**. The evaluation of structural and electronic properties of (U, Pu)O_2 using LDA+*U* has been performed with different *U* values for Pu^{4+} cations by Dorado *et al.* (*U* = 4.0 eV and *J* = 0.70 eV) **[6]** and Yang *et al.* (*U* = 4.7 eV and *J* = 0.70 eV) **[4]**. Zhang *et al.* **[11]** used U_{eff} = 4 eV to study ground state and high pressure structural, electronic and elastic properties of PuO_2. Similarly, no unique choice of *U* parameter has been found in the literature to study structural and electronic properties of α-Pu_2O_3 **[7-11]**. It is therefore important to assess the effect of *U* parameter for Pu^{4+} cation on the structural and electronic properties of PuO_2 and α-Pu_2O_3. In this section, we present the effect of small variations of the onsite Coulomb interaction parameter *U* on the lattice parameter and the band gap of PuO_2 and α-Pu_2O_3. The value of the *J* parameter is kept constant at 0.7 eV throughout the study. The results are shown in **Figure S2** and compared with available experimental data.

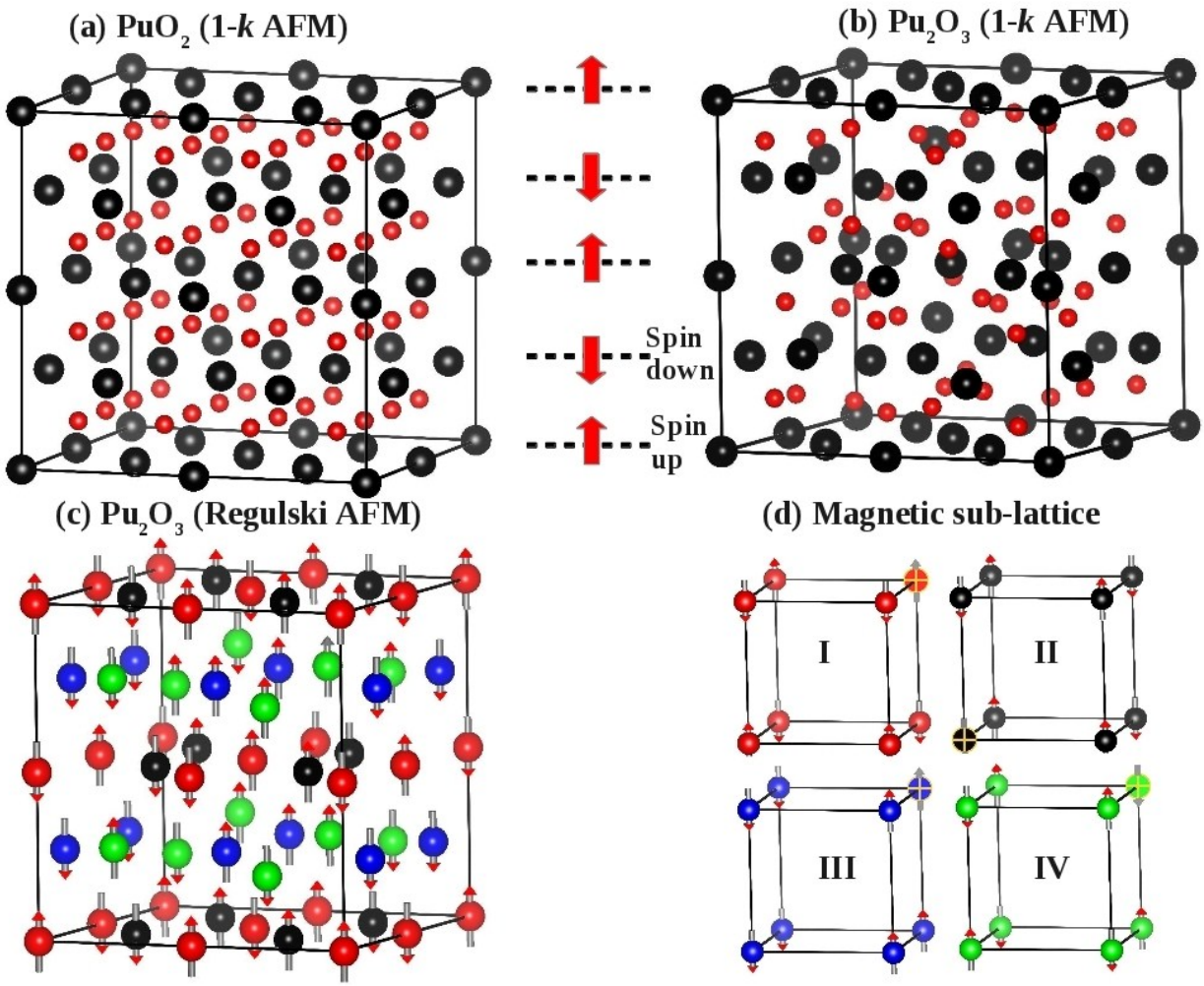

Figure S1: Magnetic configurations of PuO_2 and Pu_2O_3. (a) 1-*k* AFM PuO_2 with the magnetic order along (0 0 1) lattice direction; (b) 1-*k* AFM Pu_2O_3 with the magnetic order along (0 0 1) lattice direction; (c) Regulski AFM Pu_2O_3 with four magnetic sublattices I, II, III and IV (d). In Fig. (a) and (b), the black and red balls designate Pu and O atoms, respectively. In Fig. (c), O atoms are removed for the sake of a clear indication of Pu magnetic order.

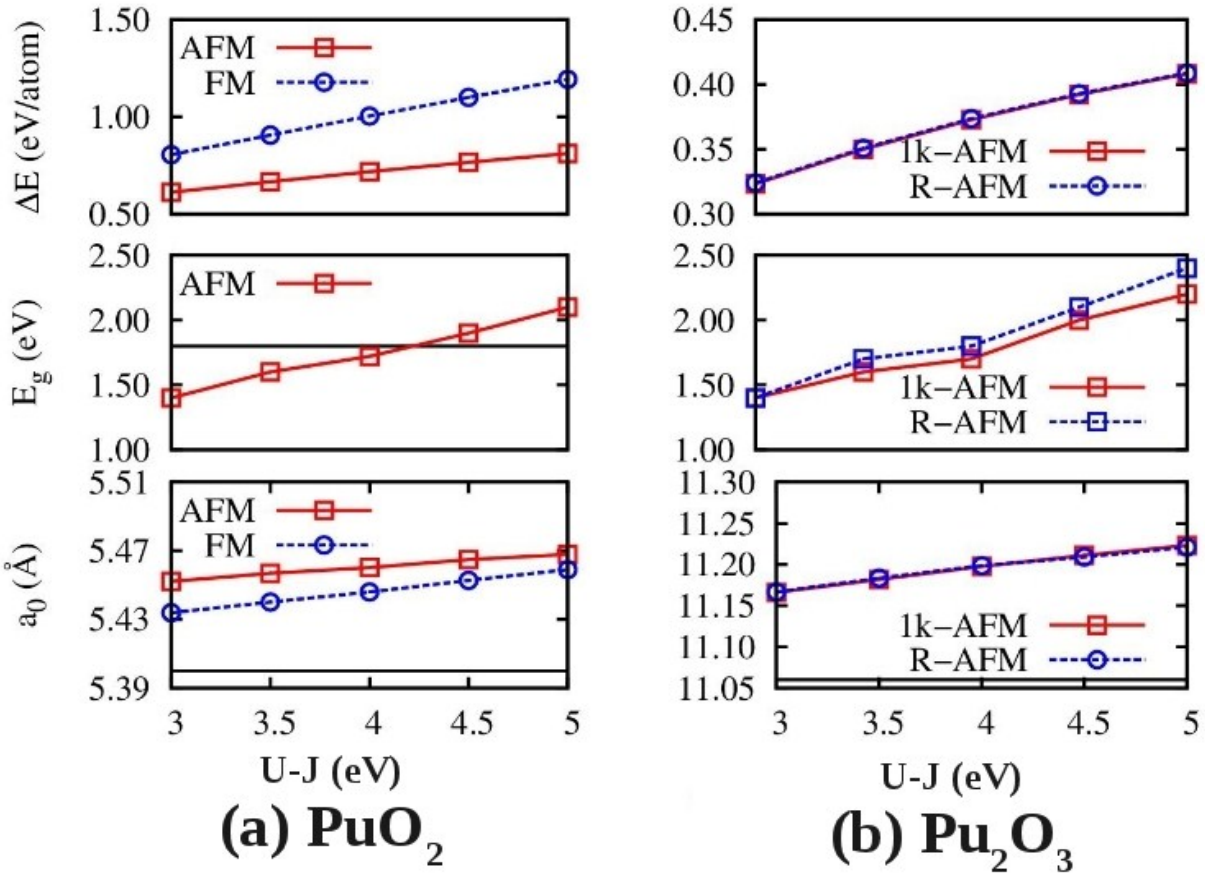

Figure S2: Variation of lattice constant (a_0), electronic band gap (E_g) and and cohesive energies (with respect to the most stable structure at *U*-*J* = 0 eV) in ferromagnetic (FM) and 1*k*-antiferromagnetic (AFM) configuration of (a) PuO_2 and (b) Pu_2O_3 as a function of the onsite Coulomb interaction parameter. For Pu_2O_3 a comparison of FM, 1*k*-AFM and R-AFM configuration (shown in Figure S1) is also shown.

The structural and electronic properties of PuO_2 and Pu_2O_3 in FM/AFM configuration presented in **Figure S2** show a very small variation as a function of the *U* parameter. For *U* = 3 eV, an overestimation of 1% is observed in the lattice parameter of PuO_2 and Pu_2O_3 compared to their respective experimental values. Further, when U increases from 3 to 5 eV, the lattice constant of PuO_2 and Pu_2O_3 increases by 0.5% and 0.3%, respectively. These are the order of magnitude of the usual PBE overestimation in interatomic distances. In this context it is important to note that *U*-ramping method was used throughout the study and atomic configurations were relaxed without symmetry

constraints. Although the optimized structures are all non cubic, the lattice parameters shown on the **Figure S2** are calculated from the equilibrium volumes assuming structures to be cubic. In most of the cases the optimized structure is tetragonal/orthorhombic with b_0/a_0 and c_0/a_0 less than 1.005. We can therefore conclude that a small variation of *U* parameter of Pu^{4+} has a negligible impact on structural properties of PuO_2 and Pu_2O_3. **Figure S2** also shows lattice parameters of PuO_2 and Pu_2O_3 in FM configuration which is lower compared to the AFM configuration. When *U* is increased from 3 to 5 eV, the electronic band gap (E_g) increases from 1.4 to 2.1 eV for PuO_2 and from 1.4 to 2.4 eV for Pu_2O_3 in 1-*k* AFM configuration. The values calculated for PuO_2 compare well with the available experimental value by McNeilly *et al.* **[12]** for the optimal value of $U = 4$ eV adopted in this study. The E_g values are almost identical in 1-*k* and Regulski AFM configuration of Pu_2O_3. **Figure S2** also shows the variation of cohesive energies (with respect to the most stable structures at $U\text{-}J = 0$ eV (ΔE)) as a function of effective Hubbard parameter for PuO_2 and Pu_2O_3 in FM and AFM configurations. We find that the total energies of 1*k*-AFM and R-AFM of Pu_2O_3 are almost degenerate (as shown in **Figure S2(b)**).

Table 2 compares PBE and PBE+*U* calculated equilibrium lattice parameters (a_0), band-gap energy (E_g), spin moments (μ_B) and cohesive energy differences between FM and AFM (E_{FM}-E_{AFM}) of PuO_2 with previous experiments and DFT calculated results. The PBE and PBE+*U* calculated a_0 is underestimation by 0.2% and overestimation by 1.1% of the experimental value **[13]**, respectively, for 1k AFM. The difference between a_0 calculated for FM and AFM configuration is less than 0.3%. The lattice parameters predicted by DFT+*U* are larger than those from pure DFT. This is because DFT+*U* scheme favours the delocalization of Pu 5*f* electrons, consequently, Pu 5*f* electrons exhibit less participation to the bonding which leads to an increase of lattice parameter. Moreover, our a_0 values are in agreement with previous DFT calculated values. Our PBE+*U* calculated E_g value of 1.6 eV is underestimates experimental value of 1.8 eV and PBE predicts null band-gap for FM/AFM PuO_2. The PBE predicted band-gap for FM configuration is 25% lower compared to AFM configuration. Although our PBE+*U* predicted band-gap underestimates the previous PBE0 predicted band-gap, but matches well with previous PBE+*U*+SOC calculated value **[10]**. In our study the spin-orbit coupling (SOC) effect is neglected since taking it into account is computationally demanding and prevents the use of supercells sufficiently large (between 80 and 96 atoms) for the description of PuO_{2-x} oxides. Moreover, our test calculations and in many previous studies it has been shown to have negligible impact on the ground state properties of bulk PuO_2 and Pu_2O_3 **[7-11]**. The PBE predicts FM to be ground state and conversely PBE+*U* predicts AFM to be ground state (E_{FM}-E_{AFM} positive in **Table 2**). This is in agreement with previous PBE and PBE0 calculated values. **Figure S2** also shows the variation of cohesive energies (with respect to the most stable structure at $U\text{-}J = 0$ eV) in FM and 1*k*-

AFM configuration of PuO_2 and AFM configuration is stable compared to FM in the range of *U-J* shown in figure. Therefore, PBE+*U* formalism lead to an AFM ground state with a net magnetic moment on plutonium atoms of around 4.1 μ_B which is not so far from the complete ionic limit of 4 μ_B.

Table 2: Equilibrium structural parameter (a_0), band-gap energy (E_g), spin moments (μ_B) and total-energy differences (E_{FM}-E_{AFM}) are reported for PBE and PBE+*U* approximations of the exchange and correlation functional of PuO_2 and Pu_2O_3. In addition, we also show experimental values and DFT calculated results obtained by Prodan *et al.* **[13]**. All our results are obtained performing a complete relaxation of the geometry with U=4.7 eV and J=0.7 eV.

	Method	**Lattice Constant (Å)**		**Band gap (eV)**		**E_{FM}-E_{AFM} (eV/formula unit)**	**Magnetic Moment (μ_B)**	
		FM	**AFM**	**FM**	**AFM**		**FM**	**AFM**
PuO_2	**This study**							
	PBE	5.382	5.386	0.0	0.0	-0.236	4.20	4.05
	PBE+*U*	5.446	5.460	1.0	1.6	+0.858	4.06	4.12
	Previous DFT							
	LSDA **[13]**	5.278	5.285	0.0	0.0	-0.310		
	PBE **[13]**	5.399	5.412	0.0	0.0	-0.259		
	PBE0 **[13]**	5.387	5.385	2.4	3.4	+0.014		
	PBE+SOC+U(=4)+QA **[10]**	-	5.466	-	1.6		-	3.82
	Experiment	5.398 **[14]**		1.8 **[12]**		≥ 0		
Pu_2O_3	This study							
	PBE	10.85	10.94	0.0	1.7			
	PBE+*U*	11.18	11.20		1.7			5.02
	Previous DFT							
	PBE **[9]**	10.91	10.92					
	PBE+U **[9]**	11.18	11.20					
	PBE+SOC+U(=4)+QA **[10]**	-	11.204	-	1.6		-	4.72
	Experiment	11.05 **[15,16]**		> 0		> 0		

The PBE and PBE+*U* calculated a_0 is underestimatied by 0.1% and overestimated by 1.4% of the experimental value **[15,16]**, respectively, for 1k-AFM Pu_2O_3. The difference between a_0 calculated for FM and AFM configurations is less than 0.3%. Moreover our a_0 values are in excellent agreement with previous DFT calculated values.

The PBE predicts FM to be ground state for Pu_2O_3, similar to PuO_2, and conversely PBE+*U* predicts

AFM to be ground state (E_{FM}-E_{AFM} is positive in **Table 2**). This is in agreement with previous PBE and PBE+*U* calculated values **[9,10]**. The magnetic moment on plutonium atoms of Pu_2O_3 is around 5.0 μ_B, larger than that of PuO_2.

[1] G. Jomard, B. Amadon, F. Bottin, M. Torrent, Phys. Rev. B: Condens. Matter Mater. Phys. 78 (2008) 075125.

[2] B. Dorado, B. Amadon, M. Freyss, M. Bertolus, Phys. Rev. B: Condens. Matter Mater. Phys. 79 (2009) 235125.

[3] S.L. Dudarev, G.A. Botton, S.Y. Savrasov, Z. Szotek, W.M. Temmerman, A.P. Sutton, Phys. Status Solidi A 1998, 166, 429−443.

[4] Y. Yang, B. Wang, P. Zhang, J. Nucl. Mater. 433 (2013) 345-350.

[5] E. Vathonne, J. Wiktor, M. Freyss, G. Jomard, M. Bertolus, J. Phys.: Condens. Matter 26 (2014) 325501.

[6] B. Dorado, P. Garcia, Phys. Rev. B: Condens. Matter Mater. Phys. 87 (2013) 195139.

[7] A. Svane, L. Petit, Z. Szotek, and W. M. Temmerman, Phys. Rev. B 76 (2007) 115116.

[8] I. D. Prodan, G. E. Scuseria, and R. L. Martin, Phys. Rev. B 76 (2007) 033101.

[9] I. Prodan, G. Scuseria, J. Sordo, K. Kudin, and R. Martin, J. Chem. Phys. 123 (2005) 014703.

[10] Gérald Jomard, Bernard Amadon, François Bottin, and Marc Torrent, Phys. Rev. B 78 (2008) 075125.

[11] Yu Yang, Yong Lu, Ping Zhang, Journal of Nuclear Materials 452 (2014) 414-418.

[12] C.E. McNeilly, The electrical properties of plutonium oxides. J. Nucl. Mater. 11 (1964) 53-58.

[13] I. Prodan, G. Scuseria, J. Sordo, K. Kudin, and R. Martin, J. Chem. Phys. 123 (2005) 014703.

[14] J. M. Haschke, T. H. Allen, and L. A. Morales, Science 287, 285 (2000).

[15] IAEA Technical Reports Series, No. 79, International Atomic Energy Agency, Vienna, 1967.

[16] O. Wick, Plutonium Handbook: A Guide to the Technology (Lagrange Park, Illinois, 1980).