Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Hidden Magnetic Order in Plutonium Dioxide Nuclear Fuel

James T. Pegg,[1,2*] Ashley E. Shields,[3] Mark T. Storr[2], Andrew S. Wills,[1] David O. Scanlon[1,4,5] and Nora H. de Leeuw[1,6]

[1] Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, United Kingdom.

[2] Atomic Weapons Establishment (AWE) Plc, Aldermaston, Reading, RG7 4PR, UK.

[3] Oak Ridge National Laboratory, One Bethel Valley Road, Oak Ridge, Tennessee 37831, USA

[4] Diamond Light Source Ltd., Diamond House, Harwell Science and Innovation Campus, Didcot, Oxfordshire OX11 0DE, United Kingdom.

[5] Thomas Young Centre, University College London, Gower Street, London WC1E 6BT, UK

[6] Cardiff University, School of Chemistry, Main Building, Park Place, Cardiff, CF1D 3AT, United Kingdom.

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Additional Information

To highlight the importance of SOI, HSE06 finds a FM (011) ground-state in its absence (**Table A1**). In addition, the initial DM state is unstable; the result is a highly-energetic AFM metastable configuration. In comparison, SOI HSE06 finds a longitudinal 3k AFM ground-state.

Table A1: The Relative Energy (eV.F.U), Band Gap (eV), Magnetic Moment (μ_B/Pu^{4+} ion), Lattice Volume (Å^3) and Space Group (number) for each PuO_2 Magnetic Configuration (no spin-orbit interaction included). Calculated by the HSE06 Functional. The Energetics of the Magnetic Configurations are Calculated Relative to the Longitudinal 3k Antiferromagnetic Ground-state.

Initial Configuration		Relative Energy (eV/F.U)	Band Gap (eV)	Magnetic Moment (μ_B/Pu^{4+} ion)	Lattice Volume (Å^3)	Space Group (Number)
Diamagnetic*						
		5.740	1.96	3.77	154.69	$Fm\bar{3}m$ (No. 225)
Ferromagnetic						
	(001)	0.202	1.84	4.07	155.41	I4/mmm (No. 139)
	(011)	0.000	2.94	4.05	155.29	C2/m (No. 12)
	(111)	0.000	2.95	4.05	155.15	$R\bar{3}m$ (No. 166)
Antiferromagnetic						
Longitudinal	1k	0.066	2.61	4.00	155.38	I4/mmm (No. 139)
	2k	0.138	2.81	4.01	155.23	I4/mmm (No. 139)
	3k	0.308	2.74	4.02	155.27	$Fm\bar{3}m$ (No. 225)
Transverse	1k	0.068	2.60	4.00	155.37	Fmmm (No. 69)
	2k	0.084	2.29	4.01	155.34	Pbca (No. 61)
	3k	0.080	2.80	4.00	155.45	$Pa\bar{3}$ (No. 205)
Experimental						
		-	2.80[1]	0.00[2-6]	157.25[7]	$Fm\bar{3}m$ (225)[7]

* The initial DM state is unstable; a highly-energetic AFM metastable configuration results.

The final relaxed ionic structures (calculated by the HSE06 functional, where SOI has been included) are reported in **Table A2-A11**.

Table A2: The final relaxed crystal structure for the DM configuration (calculated by HSE06). The dimensions of the unit cell are given in angstroms (Å); whereas, the ionic positions are given in terms of fractional coordinates.

	Coordinates		
	X	Y	Z
Unit Cell	5.37590	0.00000	0.00000
	0.00000	5.37590	0.00000
	0.00000	0.00000	5.37590
Ionic Positions	0.00000	0.00000	0.00000
	0.50000	0.50000	0.00000
	0.50000	0.00000	0.50000
	0.00000	0.50000	0.50000
	0.25000	0.25000	0.25000
	0.25000	0.25000	0.75000
	0.25000	0.75000	0.25000
	0.25000	0.75000	0.75000
	0.75000	0.75000	0.75000
	0.75000	0.75000	0.25000
	0.75000	0.25000	0.75000
	0.75000	0.25000	0.25000

Table A3: The final relaxed crystal structure for the FM (001) configuration (calculated by HSE06). The dimensions of the unit cell are given in angstroms (Å); whereas, the ionic positions are given in terms of fractional coordinates.

	Coordinates		
	X	Y	Z
Unit Cell	5.36330	0.00000	0.00000
	0.00000	5.36330	0.00000
	0.00000	0.00000	5.41911
Ionic Positions	0.00000	0.00000	0.00000
	0.50000	0.50000	0.00000
	0.50000	0.00000	0.50000
	0.00000	0.50000	0.50000
	0.25000	0.25000	0.25000
	0.25000	0.25000	0.75000
	0.25000	0.75000	0.25000
	0.25000	0.75000	0.75000
	0.75000	0.75000	0.75000
	0.75000	0.75000	0.25000
	0.75000	0.25000	0.75000
	0.75000	0.25000	0.25000

Table A4: The final relaxed crystal structure for the FM (011) configuration (calculated by HSE06). The dimensions of the unit cell are given in angstroms (Å); whereas, the ionic positions are given in terms of fractional coordinates.

	Coordinates		
	X	Y	Z
Unit Cell	5.38443	0.00000	0.00000
	0.00000	5.38321	-0.02091
	0.00000	-0.02091	5.38321
Ionic Positions	0.00000	0.00000	0.00000
	0.50000	0.50000	0.00000
	0.50000	0.00000	0.50000
	0.00000	0.50000	0.50000
	0.24912	0.25000	0.25000
	0.25088	0.25000	0.75000
	0.25088	0.75000	0.25000
	0.24912	0.75000	0.75000
	0.75088	0.75000	0.75000
	0.74912	0.75000	0.25000
	0.74912	0.25000	0.75000
	0.75088	0.25000	0.25000

Table A5: The final relaxed crystal structure for the FM (111) configuration (calculated by HSE06). The dimensions of the unit cell are given in angstroms (Å); whereas, the ionic positions are given in terms of fractional coordinates.

	Coordinates		
	X	Y	Z
Unit Cell	5.38313	-0.01184	-0.01183
	-0.01183	5.38313	-0.01184
	-0.01184	-0.01183	5.38313
Ionic Positions	0.00000	0.00000	0.00000
	0.50000	0.50000	0.00000
	0.50000	0.00000	0.50000
	0.00000	0.50000	0.50000
	0.24950	0.24950	0.24950
	0.25050	0.25050	0.75050
	0.25050	0.75050	0.25050
	0.24950	0.74950	0.74950
	0.75050	0.75050	0.75050
	0.74950	0.74950	0.24950
	0.74950	0.24950	0.74950
	0.75050	0.25050	0.25050

Table A6: The final relaxed crystal structure for the longitudinal 1k AFM configuration (calculated by HSE06). The dimensions of the unit cell are given in angstroms (Å); whereas, the ionic positions are given in terms of fractional coordinates.

	Coordinates		
	X	Y	Z
Unit Cell	5.36474	0.00000	0.00000
	0.00000	5.36474	0.00000
	0.00000	0.00000	5.40952
Ionic Positions	0.00000	0.00000	0.00000
	0.50000	0.50000	0.00000
	0.50000	0.00000	0.50000
	0.00000	0.50000	0.50000
	0.25000	0.25000	0.25000
	0.25000	0.25000	0.75000
	0.25000	0.75000	0.25000
	0.25000	0.75000	0.75000
	0.75000	0.75000	0.75000
	0.75000	0.75000	0.25000
	0.75000	0.25000	0.75000
	0.75000	0.25000	0.25000

Table A7: The final relaxed crystal structure for the longitudinal 2k AFM configuration (calculated by HSE06). The dimensions of the unit cell are given in angstroms (Å); whereas, the ionic positions are given in terms of fractional coordinates.

	Coordinates		
	X	Y	Z
Unit Cell	5.37964	0.00000	0.00000
	0.00000	5.37892	0.00000
	0.00000	0.00000	5.37892
Ionic Positions	0.00000	0.00000	0.00000
	0.50000	0.50000	0.00000
	0.50000	0.00000	0.50000
	0.00000	0.50000	0.50000
	0.25000	0.25000	0.25000
	0.25000	0.25000	0.75000
	0.25000	0.75000	0.25000
	0.25000	0.75000	0.75000
	0.75000	0.75000	0.75000
	0.75000	0.75000	0.25000
	0.75000	0.25000	0.75000
	0.75000	0.25000	0.25000

Table A8: The final relaxed crystal structure for the longitudinal 3k AFM configuration (calculated by HSE06). The dimensions of the unit cell are given in angstroms (Å); whereas, the ionic positions are given in terms of fractional coordinates.

	Coordinates		
	X	Y	Z
Unit Cell	5.37921	0.00000	0.00000
	0.00000	5.37921	0.00000
	0.00000	0.00000	5.37921
Ionic Positions	0.00000	0.00000	0.00000
	0.50000	0.50000	0.00000
	0.50000	0.00000	0.50000
	0.00000	0.50000	0.50000
	0.25000	0.25000	0.25000
	0.25000	0.25000	0.75000
	0.25000	0.75000	0.25000
	0.25000	0.75000	0.75000
	0.75000	0.75000	0.75000
	0.75000	0.75000	0.25000
	0.75000	0.25000	0.75000
	0.75000	0.25000	0.25000

Table A9: The final relaxed crystal structure for the transverse 1k AFM configuration (calculated by HSE06). The dimensions of the unit cell are given in angstroms (Å); whereas, the ionic positions are given in terms of fractional coordinates.

	Coordinates		
	X	Y	Z
Unit Cell	5.36794	0.00000	0.00000
	0.00000	5.36194	0.00000
	0.00000	0.00000	5.40738
Ionic Positions	0.00000	0.00000	0.00000
	0.50000	0.50000	0.00000
	0.50000	0.00000	0.50000
	0.00000	0.50000	0.50000
	0.25000	0.25000	0.25000
	0.25000	0.25000	0.75000
	0.25000	0.75000	0.25000
	0.25000	0.75000	0.75000
	0.75000	0.75000	0.75000
	0.75000	0.75000	0.25000
	0.75000	0.25000	0.75000
	0.75000	0.25000	0.25000

Table A10: The final relaxed crystal structure for the transverse 2k AFM configuration (calculated by HSE06). The dimensions of the unit cell are given in angstroms (Å); whereas, the ionic positions are given in terms of fractional coordinates.

	Coordinates		
	X	Y	Z
Unit Cell	5.38070	0.00000	0.00000
	0.00000	5.38103	0.00000
	0.00000	0.00000	5.37872
Ionic Positions	0.00000	0.00000	0.00000
	0.50000	0.50000	0.00000
	0.50000	0.00000	0.50000
	0.00000	0.50000	0.50000
	0.25000	0.24680	0.25000
	0.25000	0.25320	0.75000
	0.25000	0.74680	0.25000
	0.25000	0.75320	0.75000
	0.75000	0.75320	0.75000
	0.75000	0.74680	0.25000
	0.75000	0.25320	0.75000
	0.75000	0.24680	0.25000

Table A11: The final relaxed crystal structure for the transverse 3k AFM configuration (calculated by HSE06). The dimensions of the unit cell are given in angstroms (Å); whereas, the ionic positions are given in terms of fractional coordinates.

	Coordinates		
	X	Y	Z
Unit Cell	5.37998	0.00000	0.00000
	0.00000	5.37998	0.00000
	0.00000	0.00000	5.37998
Ionic Positions	0.00000	0.00000	0.00000
	0.50000	0.50000	0.00000
	0.50000	0.00000	0.50000
	0.00000	0.50000	0.50000
	0.24812	0.24812	0.24812
	0.24812	0.25188	0.74812
	0.25188	0.74812	0.24812
	0.25188	0.75188	0.74812
	0.75188	0.75188	0.75188
	0.75188	0.74812	0.25188
	0.74812	0.25188	0.75188
	0.74812	0.24812	0.25188

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