Magnetic Structure of UO$_2$ and NpO$_2$ by First-Principle Methods

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The magnetic structure of the actinide dioxides (AnO$_2$) remains a subject of intense research and is key to the development of high-accuracy computational models. A low-temperature experimental investigation of the magnetic ground-state is complicated by thermal energy released from the radioactive decay of the actinide nuclei. To establish the magnetic ground-state, we have employed high-accuracy computational methods to systematically probe different magnetic structures. A transverse 1k antiferromagnetic ground-state with Fmmm (No. 69) crystal symmetry has been established for UO$_2$, whereas a ferromagnetic (111) ground-state with R3m (No. 166) has been established for NpO$_2$. This has a profound impact on future computational investigations. Band structure calculations have been performed to analyse these results.
1 Introduction

The magnetic ground-state of the actinide dioxides (AnO$_2$) is a critical starting point for a theoretical description of experimental properties. The major actinides (An = U, Np, Pu) are difficult to study for a number of reasons. From a health and safety perspective, concerns arise from the radiogenic nature and toxicity of the actinide metals.\cite{1-3} Experimental measurements of the AnO$_2$ are therefore complicated not only by their radiogenic nature,\cite{1-3} but also due to the inhomogeneity of samples.\cite{4-9} Computational techniques, however, offer a complementary method to circumvent many of these problems and obtain detailed insight into AnO$_2$ structures and properties.

Under standard conditions, the AnO$_2$ are thought to crystallize in the calcium fluorite (CaF$_2$) structure with Fm$\overline{3}$m (No. 225) cubic symmetry.\cite{10,11} In this structure, the An$^{4+}$ cations occupy octahedral (4a) sites, whereas the O$^{2-}$ anions occupy tetrahedral (8c) sites. However, low-temperature measurements of UO$_2$ have indicated the Pa$\overline{3}$ (No. 205) crystal symmetry. In this structure, there is no distortion of the An$^{4+}$ ions or of the overall cubic environment, but there is an internal distortion of the O$^{2-}$ ions within the cubic lattice.

The magnetic structure of the AnO$_2$ is often inferred by the one-electron crystal electric field (Fig. 1). In crystal-field (CF) theory, the 5f electrons are highly localized due to the insulating nature of these materials. Thus, the orbitals do not hybridize and the crystal field is influenced by the electrostatic potential. Therefore, low-spin coupling is initially considered, with the crystal field as a perturbation. The spin-orbit interaction (SOI)\cite{12} generates $j = 7/2$ and $j = 5/2$ electronic levels, whereby the degeneracy of the levels is further broken by the crystal field. The interpretation of the magnetic structure by CF theory is only valid for the one-electron case,\cite{13,14} whereas the magnetic structure of the AnO$_2$ involves the complex interplay of spin-lattice, magneto-elastic, super-exchange, multipolar and cooperative Jahn-Teller interactions.\cite{15-19} The type of magnetism can be classified into paramagnetic (PM); diamagnetic (DM); ferromagnetic (FM); anti-ferromagnetic (AFM); and ferrimagnetic (FI) behaviour.

![Illustration of magnetic configurations in the calcium fluorite (CaF$_2$) crystal structure.](image-url)
In DM materials, as all electrons are paired, no magnetic moments are associated with the individual ions and as a result the net magnetic moment of the crystal is zero. The only magnetic response is a weak repulsion in an applied magnetic field.

In ordered FM, AFM or FI materials, an odd number of electrons generates a magnetic moment. These magnetic moments may couple resulting in a periodic arrangement. If the magnetic moments are aligned in one dimension, the material is FM and has a net crystal moment. The direction of the magnetic moment may vary, resulting in FM (111), (011) or (001) states in the Fm$\bar{3}$m crystal. If the magnetic moments are opposed, the material is AFM and no net magnetic moment exists. In the propagation vector formulism, contributions can be combined from a number of symmetry-related wavevectors. These are termed multi-$k$ structures. In the following, single (1$k$), double (2$k$), and triple (3$k$) structures will be considered.

If the opposing magnetic moments on the ions are unequal, the material is FI and the crystal has a net magnetic moment. If the magnetic moments are decoupled, the material is PM and there is no ordered distribution. The net magnetic moment of the crystal will average to zero. In addition, an isolated ion is said to be PM if it has a magnetic moment. As the magnetic moment of the An$^{4+}$ ions (in stoichiometric AnO$_2$) are equal (due to the occupation of chemically equivalent sites) the FI state cannot exist. In addition, significant exchange interactions are expected to be present and cause magnetic order. As a result, neither FI or PM is considered in this study.

The manifestation of metastable states and the juxtaposition of energy levels makes the determination of the magnetic ground-state challenging. In this paper, the magnetic structures of the AnO$_2$ are calculated for multiple configurations (Table 1).

Table 1 The wave vectors for the ordered magnetic states.

<table>
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<tr>
<th>Ion</th>
<th>Ferromagnetic</th>
<th>Antiferromagnetic (Transverse Domain)</th>
<th>Antiferromagnetic (Longitudinal Domain)</th>
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</thead>
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<tr>
<td></td>
<td>(001)</td>
<td>(011)</td>
<td>(111)</td>
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<td>(0, 0, 1)</td>
<td>(0, 1, 1)</td>
<td>(1, 1, 1)</td>
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<tr>
<td>($\frac{1}{2}$, $\frac{1}{2}$, 0)</td>
<td>(0, 0, 1)</td>
<td>(0, 1, 1)</td>
<td>(1, 1, 1)</td>
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<tr>
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<tr>
<td>($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$)</td>
<td>(0, 0, 1)</td>
<td>(0, 1, 1)</td>
<td>(1, 1, 1)</td>
</tr>
</tbody>
</table>

The magnetic wavevectors are directed along the main axes of the crystal unit cell. The final magnetic moment of each ion is calculated using the Pythagorean theorem in Eq. (1).

$$\|\mu\|^2 = \sum_{k=1}^{3} \|\mu_k\|^2$$

The magnitude of the vector ($\mu$) is calculated from its orthogonal ($\mu_k$) components. SOI must be considered to access the noncollinear 2-3$k$ AFM states.
The crystal structure is coupled by SOI\textsuperscript{12} to the magnetic state. In the high-temperature PM state, the Fm\textoverline{3}m (No. 255) crystal structure is stabilized by the intrinsic magnetic disorder (Fig. 2). At low-temperature (T = 30.8 K), the ordered FM and AFM configurations can cause a crystallographic distortion due to an imbalance of magnetic forces. The nature of the crystallographic distortion and its exact relation to the magnetic state is presently unknown.

The extent of the disruption is dependent upon the magnitude of the magnetic forces within the crystal. In this paper, the low-temperature magnetic structure of UO\textsubscript{2} and NpO\textsubscript{2} is investigated using first-principle methods. In addition, a computationally tractable method for the inclusion of magnetic order in the AnO\textsubscript{2} has been developed that can be applied to larger systems. Low-temperature (T < 30.8 K) measurements of the AnO\textsubscript{2} magnetic ground-state are extremely challenging, due to thermal energy generated by the radioactive decay of the actinide nuclei, the inhomogeneity of samples and high chemical sensitivity to environmental conditions.\textsuperscript{21-28}

**Fig. 2** Illustration of the actinide dioxide (AnO\textsubscript{2}) crystal structure: left) cubic Fm\textoverline{3}m symmetry, right) cubic Pa\textoverline{3} symmetry. The colours in the parentheses indicate the An\textsuperscript{4+} (blue) and O\textsuperscript{2-} (red) ions.

A key difficulty in the computational investigation of the AnO\textsubscript{2} is the treatment of relativistic effects, electron-correlation, and complex magnetic structures. The correct electronic structure of the AnO\textsubscript{2} cannot be calculated by conventional density functional theory (DFT) based methods,\textsuperscript{29,30} due to the high degree of electron-correlation,\textsuperscript{31} which often manifests as an underestimation of the electronic band-gap.\textsuperscript{8,32} To compensate, numerous methods have been developed such as, the self-interaction correction (SIC) method,\textsuperscript{33} modified density functional theory (DFT+U),\textsuperscript{29,30,34-36} dynamic mean field theory (DMFT),\textsuperscript{37} and hybrid density functionals.\textsuperscript{38-40} Of these methods, DFT+U offers a computationally tractable means of investigation by treating the on-site Coulomb repulsion of the f-electrons with tuneable U and J modifiers, essentially adding an energy penalty to partial occupation of what should be localized f-electrons. The ground-state characteristics of f-electron compounds can be captured by DFT+U when SOI are included.\textsuperscript{41} By comparison, hybrid functionals offer one of the more accurate, but computationally highly expensive methods. The computationally intense nature of DMFT has been highlighted by a number of authors, but even this method has incorrectly calculated the early AnO\textsubscript{2} as charge-transfer insulators.\textsuperscript{37,42-45}
Identifying and modelling the correct ground-state magnetic structure in these materials is also complicated. Indeed, only a limited number of publications have investigated noncollinear contributions to the magnetic structure. In the majority of cases, due to the computational expense of modelling these systems, AnO₂ studies have been restricted to discussions of collinear 1k magnetic order due to the computational expense of the systems. In addition, although the importance of spin-orbit interactions (SOI) for the treatment of the actinide elements has been highlighted in numerous investigations, few consider SOI effects in their fully relativistic studies.

The magnetic structure of UO₂ displays interesting characteristics. In the Russel-Saunders (low-spin) coupling scheme, the ground-state of the U⁴⁺ ion is a ³H₄ (Γ₅ triplet) multiplet. Low-temperature measurements of (U₁₋ₓThₓ)O₂ confirm a Γ₅ triplet magnetic ground-state, whereas a discontinuous first-order phase transition at the Néel temperature, T₉N = 30.8 K, indicative of magnetic order, has been established by heat capacity, magnetic susceptibility and neutron diffraction measurements. The exact nature of the magnetic ground-state has been investigated in numerous studies. Initial neutron diffraction measurements indicated a collinear 1k AFM ground-state, coupled with a homogeneous lattice distortion. Later studies suggested an internal Jahn-Teller distortion of the O²⁻ ions, but no evidence has been found for a reduction in the external cubic crystal symmetry. On further investigation, noncollinear 2k AFM order was proposed due to internal distortion.

Finally, low-temperature (T < 30.8 K) neutron diffraction measurements of UO₂ have confirmed an internal Pa₃ (No. 205) crystallographic distortion, where the displacement of the O²⁻ ions is 0.014 Å, which is indicative of transverse 3k AFM order. Anti-ferroquadrupolar ordering favours Pa₃ (No. 205) crystal symmetry by minimizing quadrupolar and exchange terms. Neutron diffraction measurements have determined an ordered effective magnetic moment of 1.74 µₑU ion, whereas the transverse 3k AFM ground-state has been inferred by inelastic neutron scattering (INS), resonant X-ray scattering (RXS) and nuclear magnetic resonance (NMR) measurements. In terms of the electronic structure, the f-f Mott-Hubbard insulating character of UO₂ with a band-gap of 2.00-2.50 eV has been established by optical adsorption, X-ray adsorption (XAS), X-ray photoemission (XPS), bremsstrahlung isochromatic spectroscopy (BIS), resonant photoemission spectroscopy (RPES), inverse photoemission spectroscopy (IPES) and theoretical methods. In the past, multiple investigations of UO₂ have focused on the experimental AFM ground-state, the energetics of the DM and FM configurations have been considered for comparison with previous theoretical considerations.

By comparison, the magnetic ground-state of NpO₂ is highly complex and marred by several inconsistencies. In crystal field theory, the Np⁴⁺ ion results in the ⁴I₀/² (I₈ quartet) configuration. Indeed, the tetravalent f⁴ nature of the Np⁴⁺ ion has been confirmed by Mossbauer isomer shift spectroscopy. At low-temperature (T = 25.4 K), a first-order PM-AFM phase transition has been indicated by magnetic susceptibility and specific heat capacity measurements. In addition, a longitudinal 3k AFM ground-state coupled to Fm.₃m (No. 225) crystal symmetry has been inferred from resonant X-ray scattering (10 K < T < 17 K) and O NMR measurements (T = 17 K). The absence of an external distortion of the cubic cell further indicates noncollinear 3k AFM behavior. In contrast, low-temperature
Mossbauer (T = 1.5 K)\textsuperscript{90} and neutron diffraction (12 K < T < 30 K)\textsuperscript{95} measurements have failed to identify a magnetic moment. The upper limit for the magnetic moment set by muon spin rotation measurements (0.3 K < T < 25.4 K) is 0.06-0.15 $\mu_B$/Np ion,\textsuperscript{20,96} whereas the upper limit for the magnetic moment set by Mössbauer spectroscopy is 0.01 $\mu_B$/Np ion.\textsuperscript{90} The absence of a measurable local magnetic moment is inconsistent with the idea of magnetic order and the nature of the small-moment AFM state is unresolved.\textsuperscript{20} As a Kramers ion, i.e. an ion with an uneven number of valence electrons, the ground Np\textsuperscript{4+} state should order magnetically in the absence of interactions that break time-reversal symmetry conditions. A mechanism by which the magnetic moment of the Np\textsuperscript{4+} ion can be suppressed is AFM super-exchange,\textsuperscript{20} which is the coupling between moment-bearing cations via nominally diamagnetic anions.\textsuperscript{97,98}

The inhomogeneous nature of NpO\textsubscript{2} samples has hindered experimental investigation.\textsuperscript{93,99} For instance, the extreme difficulty in manufacturing large single-crystal samples impacts the search for low-temperature (T < 25.4 K) crystallographic distortions.\textsuperscript{93,100} In the past, the detection threshold of neutron diffraction measurements was limited to 0.02-0.03 Å.\textsuperscript{20} By comparison, crystallographic distortions of isostructural UO\textsubscript{2} are of the order of 0.01-0.02 Å.\textsuperscript{17} In a search for low-temperature (T < 25.4 K) anharmonic effects in NpO\textsubscript{2} by neutron diffraction (12 K < T < 30 K)\textsuperscript{95} and in an independent RXS (9 K < T < 25 K) study,\textsuperscript{93} no evidence of a dynamical distortion of the O\textsuperscript{2−} ions was found. However, Mossbauer spectroscopy (T = 1.5 K) of NpO\textsubscript{2} has indicated an internal O\textsuperscript{2−} ion distortion inferred by the small broadening of spectroscopic lines.\textsuperscript{90} In addition, inelastic neutron scattering (INS) (5 K < T < 25 K) studies\textsuperscript{101,102} indicate an internal O\textsuperscript{2−} ion distortion of 0.02 Å, which is reminiscent of the internal O\textsuperscript{2−} ion distortion in UO\textsubscript{2}. The internal O\textsuperscript{2−} ion distortion may result in Pa\textsuperscript{3} (No. 205) crystal symmetry that is indicative of transverse 3k AFM behaviour, although this has yet to be experimentally confirmed.

The upper-limit of the magnetic moment (0.01-0.15 $\mu_B$/Np ion) indicates that NpO\textsubscript{2} is a small-moment system.\textsuperscript{20,90,93,96} To our knowledge, small moments have only been identified in heavy-fermion metals\textsuperscript{103-105} and has yet to be identified in insulators. In this regard, computational investigations of PuO\textsubscript{2} have indicated the existence of an unconfirmed small-moment insulating magnetic ground-state.\textsuperscript{106} For instance, multiple DFT calculations have indicated an AFM ground-state, which contrasts with the DM state established by experimental methods.\textsuperscript{107-110} The mechanisms behind such an intriguing electronic states are not yet fully understood and the crystal and magnetic structures of NpO\textsubscript{2} have still not been resolved.

2 Computational Methodology

2.1 Calculation Details

The Vienna Ab-initio Simulation Package (VASP)\textsuperscript{33,37,111} was used to perform density functional theory (DFT) based calculations, using the revised Perdew–Burke–Ernzerhof for solids (PBEsol)\textsuperscript{29,30} PBEsol+$U$\textsuperscript{34-36} and hybrid Heyd–Scuseria–Ernzerhof (HSE06)\textsuperscript{38-40} functionals \textsuperscript{29,30,34-36} and a plane wave basis set with a kinetic energy cut-off of 500 eV. The uranium (6s\textsuperscript{2}, 7s\textsuperscript{2}, 6p\textsuperscript{6}, 6d\textsuperscript{2} 5f\textsuperscript{2}), neptunium (6s\textsuperscript{2}, 7s\textsuperscript{2}, 6p\textsuperscript{6}, 6d\textsuperscript{2} 5f\textsuperscript{3}), and oxygen (2s\textsuperscript{2}, 2p\textsuperscript{4}) valence electrons are implicitly considered, as are the SOI\textsuperscript{12} and contributions to noncollinear magnetic wave-vectors. The cut-off energy and k-point grid for each calculation have been validated in our previous work\textsuperscript{31} and the conjugate gradient algorithm has been used to
evaluate the ionic forces. In our previous study, the performance of multiple DFT functionals on the AnO$_2$ was tested and for the standard DFT functionals, the PBEsol functional had been proven to be the most effective. Images are visualized by the VESTA code.

DFT+U calculations offer a computationally tractable method of investigating actinides where pure DFT fails. The on-site Coulomb repulsion of the An 5f-electrons is treated by the rotationally invariant Liechtenstein et al. DFT+U formulism, where the Coulomb (U) and exchange (J) modifiers are treated as independent variables:

$$E_{dc}(\hat{n}) = \frac{U}{2} \hat{n}_{\text{tot}}(\hat{n}_{\text{tot}} - 1) \frac{1}{2} \sum_{\sigma} \hat{n}_{\text{tot}}^{\sigma}(\hat{n}_{\text{tot}}^{\sigma} - 1)$$  \hspace{1cm} (1)$$

The double counting energy term ($E_{dc}$), the main quantum number (n) and the spin index (σ) are denoted by the terms in parentheses. As such, the Dudarev et al. formulism and Liechtenstein et al. formulism are equivalent when J = 0.00 eV. In the past, the influence of J on noncollinear magnetic materials, and the performance of numerous exchange-correlation functionals, has been investigated. Therefore we have kept the J modifier at a constant value of 0.00 eV and referenced against past investigations. The integration of the Brillouin zone is performed with a Γ-centred (5·5·5) k-point grid, using the Blöchl tetrahedron method. The exchange-correlation energy is evaluated by the PBEsol functional. Self-consistent calculations were performed until convergence was reached for the respective electronic and ionic thresholds of 1 x 10$^{-8}$ eV and 1 x 10$^{-3}$ eV·Å$^{-1}$. For the optical absorbance calculation, the k-point mesh is 15 x 15 x 15; for band structure calculations, the Fmmm (No. 69) k-point pathway is Γ→Y→X→Z→Γ→L, whereas, the Pa3̅ (No. 205) k-point pathway is Γ→M→R→X→Γ→R.

As a more computationally intensive method, hybrid functionals incorporate Hartree-Fock (HF) exchange energy into the DFT formulism. In this study, the hybrid HSE06 functional is employed with the integration of the Brillouin zone performed by the conventional Gaussian method and a Γ-centred (4 x 4 x 4) k-point grid.

$$E_{XC}^{HSE} = (a)E_{X}^{HF,SR}(\mu) + (1 - a)E_{X}^{PBE,SR}(\mu) + E_{X}^{PBE,LR}(\mu) + E_{C}^{PBE}$$  \hspace{1cm} (2)$$

The terms in the parentheses define the exchange-correlation HSE06 energy ($E_{XC}^{HSE}$), an adjustable constant (a), the short-range (SR) interaction energy and the long-range (LR) interaction energy. The adjustable screening (μ) modifier in the HSE06 functional is 0.207 Å$^{-1}$. Calculations were performed until self-consistency was reached for the electronic and ionic thresholds of 1 x 10$^{-6}$ eV and 1 x 10$^{-2}$ eV·Å$^{-1}$, respectively.
3 Results & Discussions

3.1 Uranium Dioxide

3.1.1 Magnetic Structure

In our calculations, the electronic and crystallographic nature of UO$_2$ is influenced by the magnetic state. An energetically degenerate transverse $1\text{-}2k$ AFM HSE06 ground-state has been calculated (Table 2). In addition, the initial DM HSE06 state is unstable and a metastable, highly-energetic, weakly FM (852) configuration (0.85 $\mu$B/U ion) has been identified. A comparatively insignificant low-index FM and AFM state (1.42-1.53 $\mu$B/U ion) energy difference has been found. In relation to the experimental transverse $3k$ AFM ground-state, the FM (001), FM (111), longitudinal $1k$ AFM and transverse $1\text{-}2k$ AFM states are marginally lower in energy by -0.01 eV\text{-}formula unit$^{-1}$.

A band-gap of 2.42-2.57 eV (for the low-index FM states) and 2.82-3.02 eV (for the AFM states) has been calculated. This is considerably higher than current experimental measurements. In contrast with experimental measurements indicating $\text{Pa}_3\overline{5}$ crystal symmetry, an actinide $\text{Fmmm}$ (No. 69) or $\text{Pbca}$ (No.61) crystallographic distortion in the transverse $1\text{-}2k$ AFM states has been found. It is noted that the transverse $1k$ AFM state is consistent with experimental static and low-frequency dynamical magnetic measurements.

Table 2 The relative energy (eV), band-gap (eV), magnetic moment ($\mu$B/U ion), lattice volume ($\text{Å}^3$) and space group (number) for each UO$_2$ magnetic configuration. Calculated by the HSE06 Functional. The energetics of the magnetic configurations are calculated relative to the degenerate transverse $1\text{-}2k$ antiferromagnetic ground-state. Note: The initial DM HSE06 state is unstable. Instead, a relaxed, highly-energetic FM (852) state has been calculated.

<table>
<thead>
<tr>
<th>Initial Configuration</th>
<th>Relative Energy (eV)</th>
<th>Band-gap (eV)</th>
<th>Magnetic Moment ($\mu$B/U ion)</th>
<th>Lattice Volume ($\text{Å}^3$)</th>
<th>Space Group (Number)</th>
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<tr>
<td>Diamagnetic</td>
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<td>(001)</td>
<td>0.010</td>
<td>2.42</td>
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<td>1.45</td>
<td>162.81</td>
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<td>1.44</td>
<td>162.60</td>
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<td>1.49</td>
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<td>2.99</td>
<td>1.43</td>
<td>162.57</td>
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<tr>
<td></td>
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<td>2.00-2.50$^{76, 119}$</td>
<td>1.74$^{65, 67, 70}$</td>
<td>163.85$^{65, 70}$</td>
<td>$\text{Pa\bar{3}}$ (No. 205)$^{72}$</td>
</tr>
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</table>

To probe the magnetic ground-state, the relative energetics of competing magnetic phases have been calculated with PBEsol+U, where the magnitude of the U influences the relative
energetics of the magnetic states (Fig. 3). In contrast to hybrid HSE06 calculations, the highly-energetic PBESol+U DM state is stable.

Fig. 3 The relative ground-state energies, band-gaps, and effective magnetic moments against the Coulomb modifier (U) for diamagnetic (DM), ferromagnetic (FM), and antiferromagnetic (AFM) states of UO$_2$, calculated with PBESol+U. The antiferromagnetic transverse (T) and longitudinal (L) domains are also represented. The k-prefix denotes the number of independent wave vectors: Above, the calculated energy of magnetic states relative to the transverse 3k antiferromagnetic ground-state; Middle, the direct band-gap; Below, the effective magnetic moment of the uranium ions. The DM (yellow), FM (Orange), longitudinal AFM (Green) and transverse AFM (Blue) states are denoted by the colours in the parentheses.

In our calculations, the metallic FM (111) ground-state, calculated by PBESol (U = 0 eV), is inconsistent with the experimental data. Indeed, under no circumstance is the insulating nature of UO$_2$ reproduced when U = 0 eV, which illustrates the failure of pure DFT to account
for the highly localized character of the 5f electrons. The insulating nature of UO$_2$, which is well-described experimentally, can be reproduced computationally when $U = 3$-$4$ eV. The introduction of the U modifier immediately results in an AFM ground-state. The nature of the AFM ground-state is, however, dependent on the U constraint. In general, a degenerate longitudinal 2-3k AFM and transverse 1-3k AFM ground-state is formed when $U = 1$-$7$ eV. In relation to past theory, the DM is considerably higher in energy and therefore physically unrealistic.

The low-temperature crystal structure of UO$_2$ shows $P\bar{a}3$ crystal symmetry indicated by neutron scattering and X-ray diffraction measurements. In our calculations, the transverse 3k AFM state results in $P\bar{a}3$ (No. 205) crystal symmetry. This is consistent with experimental information. The transverse 1k AFM with Fmmm (No. 69) orthorhombic symmetry differs from the longitudinal 1k AFM state with $I4/mmm$ (No. 139) tetragonal symmetry. Therefore, the collinear 1k AFM states are an invalid approximation of the cubic crystal structure at low temperatures.

The magnetic moment of UO$_2$ is 1.74 $\mu_B/U$ ion, reported by neutron diffraction measurements. In our calculations, the magnetic moment of the U ion is underestimated by DFT+U and the hybrid HSE06 functional with the closest approximation obtained by the FM (111) states. In terms of the lattice volume, no discernible change is detected between the ordered magnetic states, but the lattice volume is considerably lower in the DM state.

### 3.1.2 DFT+U Electronic Structure

The electronic structure of the transverse 3k AFM state for UO$_2$ has previously been calculated by first-principles methods ($U = 3.25$ eV). This is energetically unstable compared to the transverse 1k AFM ground-state. Here, we have also calculated the electronic structure of the transverse 1k AFM ground by DFT+U, where we have used $U = 3.50$ eV, consistent with the literature (Fig. 4). In contrast, collinear 1k AFM calculations by constrained random phase approximation (cRPA) methods were obtained with $U = 5.70$ eV and $J = 0.40$ eV, i.e. considerably higher than in the literature.

In the density of states (DoS), the valence band maximum (VBM) and conduction band minimum (CBM) are mainly comprised of uranium f-states. The U d-states are significantly higher in energy and should therefore have very little influence on bonding interactions. This electronic structure indicates that UO$_2$ is a Mott-Hubbard insulator, consistent with experimental information. This result is similar to that obtained for transverse 3k AFM order.

The band structure of UO$_2$ with the transverse 1k AFM ground-state results in an indirect band-gap of 2.27 eV from $\Gamma$ (VBM) to $\Gamma$-$Y$ (CBM). In contrast, the calculated optical absorption spectra generate a band-gap of 2.49 eV, so the direct band-gap and optical band-gap thus differ by 0.22 eV, although they are not strictly directly comparable. The direct band-gap defines the VBM-CBM energy difference, whereas, the optical band-gap defines the minimum allowed transition as controlled by symmetry rules. Nevertheless, the calculated band-gap and bulk modulus are in very good agreement with experimental information (Table 3).
Fig. 4 Left, the calculated band structure. Right, the density of states of the transverse 1k AFM ground-state of UO$_2$ with Fmmm (No. 69) crystal symmetry. Calculated from PBEsol+U where U = 3.50 eV.

Table 3 The direct band-gap (eV), optical band-gap (eV), lattice constant (Å), bulk modulus (GPa) and magnetic moment (μ$_B$/U ion) for the transverse 3k (T-3k) AFM state of UO$_2$.

<table>
<thead>
<tr>
<th>U (eV)</th>
<th>J (eV)</th>
<th>Direct Band-gap (eV)</th>
<th>Optical Band-gap (eV)</th>
<th>Lattice Constant (Å)</th>
<th>Bulk Modulus (GPa)</th>
<th>Magnetic Moment (μ$_B$/U ion)</th>
<th>Crystal Symmetry</th>
<th>Magnetic State</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.50</td>
<td>0.00</td>
<td>2.27</td>
<td>2.49</td>
<td>5.476</td>
<td>210</td>
<td>1.42</td>
<td>Fmmm (69)</td>
<td>T-1k AFM</td>
</tr>
<tr>
<td>3.35</td>
<td>0.00</td>
<td>2.06</td>
<td>2.20</td>
<td>5.474</td>
<td>210</td>
<td>1.35</td>
<td>Pa$\overline{3}$ (205)</td>
<td>T-3k AFM$^{11}$</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>2.00-2.50$^{76, 119}$</td>
<td>~5.473$^{65, 70}$</td>
<td></td>
<td></td>
<td>1.74$^{65, 67, 70}$</td>
<td>Pa$\overline{3}$ (205)</td>
<td>Experimental</td>
</tr>
</tbody>
</table>

3.2 Neptunium Dioxide

3.2.1 Magnetic Structure

In this section we have calculated the relative energetics for each magnetic state, the band-gap, the magnetic moment of the Np ion, and the crystal structure for NpO$_2$. Note, however, that due to the f$^3$ nature of the Np$^{4+}$ Kramers ion, the DM configuration is physically unrealistic.

In our hybrid functional HSE06 calculations, the transverse 3k AFM state is only 0.002 eV·formula unit$^{-1}$ higher in energy than the FM (111) ground-state (Table 4). The transverse 3k AFM state results in Pa$\overline{3}$ (No. 205) crystal symmetry, which satisfies observations of noncollinear magnetic behaviour and the inferred internal crystallographic distortion. However, the magnetic moment is anomalously high and does not fit the picture of a small-moment AFM state. As with UO$_2$ and PuO$_2$, the crystal symmetry and magnetic structure of NpO$_2$ are coupled by SOI. The low temperature crystal structure of NpO$_2$ is unresolved, but thus far, Pa$\overline{3}$ (No. 205) and Pn$\overline{3}$m (No 224) structures have been inferred from RXS measurements.$^{123}$
Table 4 The relative energy (eV), band-gap (eV), magnetic moment (μB/Np ion), lattice volume (Å³) and space group (number) for each NpO₂ magnetic configuration, calculated by the HSE06 functional. The energetics of the magnetic configurations are calculated relative to the ferromagnetic (111) ground-state.

<table>
<thead>
<tr>
<th>Initial Configuration</th>
<th>Relative Energy (eV)</th>
<th>Band-gap (eV)</th>
<th>Magnetic Moment (μB/Np ion)</th>
<th>Lattice Volume (Å³)</th>
<th>Space Group (Number)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferromagnetic</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(001)</td>
<td>0.081</td>
<td>2.65</td>
<td>2.63</td>
<td>158.74</td>
<td>I4/mmm (No. 139)</td>
</tr>
<tr>
<td>(011)</td>
<td>0.017</td>
<td>2.65</td>
<td>2.63</td>
<td>158.85</td>
<td>Immm (No. 71)</td>
</tr>
<tr>
<td>(111)</td>
<td>0.000</td>
<td>2.42</td>
<td>2.67</td>
<td>158.82</td>
<td>R̅3m (No. 166)</td>
</tr>
<tr>
<td>Antiferromagnetic</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Longitudinal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1k</td>
<td>0.079</td>
<td>2.65</td>
<td>2.60</td>
<td>158.78</td>
<td>I4/mmm (No. 139)</td>
</tr>
<tr>
<td>2k</td>
<td>0.083</td>
<td>3.14</td>
<td>2.52</td>
<td>158.69</td>
<td>I4/mmm (No. 139)</td>
</tr>
<tr>
<td>3k</td>
<td>0.004</td>
<td>2.88</td>
<td>2.64</td>
<td>158.69</td>
<td>Fm̅3m (No. 225)</td>
</tr>
<tr>
<td>Transverse</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1k</td>
<td>0.064</td>
<td>3.26</td>
<td>2.55</td>
<td>158.74</td>
<td>Fm̅mm (No. 69)</td>
</tr>
<tr>
<td>2k</td>
<td>0.001</td>
<td>3.20</td>
<td>2.64</td>
<td>158.79</td>
<td>Pbca (No. 61)</td>
</tr>
<tr>
<td>3k</td>
<td>0.002</td>
<td>3.20</td>
<td>2.64</td>
<td>158.71</td>
<td>Pa̅3 (No. 205)</td>
</tr>
<tr>
<td>Experimental</td>
<td></td>
<td>2.85-3.10124,125</td>
<td>~0.01-0.1090,93</td>
<td>159.8493</td>
<td>Fm̅3m (No. 225)93, Pa̅3 (No. 205)101,102</td>
</tr>
</tbody>
</table>

The HSE06 results above are emulated by PBEsol+U (Fig. 5). The FM (111) ground-state, calculated by PBEsol, independent of the U modifier, results in R̅3m (No. 166) symmetry as a result of a trigonal distortion of the unit cell. However, this structure is inconsistent with current experimental data. A number of experimental investigations have strongly indicated an AFM ground-state, although the nature of the magnetic moment has thus far not been determined. No evidence of a trigonal R̅3m (No. 166) crystallographic distortion has been reported, but noncollinear 3k AFM behaviour has been identified, where the domain is unresolved.93, 94, 102, 123, 126 From our calculations, only the noncollinear 3k AFM states result in cubic symmetry. The transverse 3k AFM state is marginally lower in energy than the longitudinal 3k AFM state (Table 4), with the external cubic symmetry retained in both cases.

The electronic structure of NpO₂ is influenced by the magnetic state. The band-gap, as measured by optical absorbance of NpO₂ epitaxial thin films, is 2.85 eV.124 In our calculations, the correct insulating nature of NpO₂ is reproduced when U = 4-6 eV for all magnetic states. In this range, the relative energy differences between the longitudinal 3k AFM, transverse 2-3K AFM, and the FM (111) states are minimal.

The longitudinal 3k AFM state results in Fm̅3m (No. 225) symmetry, which is supported by RXS measurements. In contrast, the transverse 3k AFM state results in Pa̅3 (No. 205) symmetry, characterized by an internal O²⁻ distortion of 0.011 Å. The distortion is equal to that implied by Mossbauer spectroscopy90 and INS101,102 measurements. In theory, the noncollinear AFM domain can be established by its crystalline environment, but the distortion cannot be confirmed as this is below the instrument resolution. In terms of the lattice volume, no discernible change between different magnetic states is observed.
Fig. 5 The relative ground-state energies, band-gaps, and effective magnetic moments against the Coulomb modifier (U) for diamagnetic (DM), ferromagnetic (FM), and antiferromagnetic (AFM) states of NpO$_2$, calculated with PBEsol+U. The antiferromagnetic transverse (T) and longitudinal (L) domains are additionally represented. The k-prefix denotes the number of independent wave vectors: Above, the calculated energy of magnetic states relative to the transverse 3k antiferromagnetic ground-state; Middle, the direct band-gap; Below, the effective magnetic moment of the Np ions. The FM (orange), longitudinal AFM (green) and transverse AFM (blue) states are denoted by the colours in the parentheses.

As mentioned above, the magnetic moment of the Np ions is unresolved. Experimentally, the NpO$_2$ system appears to be a small-moment system, but this picture cannot be confirmed by first-principle methods. The magnetic moment of the Np ions in the FM states decreases from 2.77 μ$_B$/Np ion to 2.68 μ$_B$/Np ion when U ranges from 0-7 eV, whereas in AFM states, it
increases from 2.35 μ_B/Np ion to 2.71 μ_B/Np ion for the same values of U = 0-7 eV. Although the calculated magnetic moment is considerably greater than the low-temperature measurement, it is consistent with that of the high-temperature PM state.

3.2.2 DFT+U Electronic Structure

No experimental information on NpO_2 exists to support a FM (111) ground-state. The unopposed and overwhelming consensus is that NpO_2 possesses an AFM ground-state. The influence of entropy on the low-temperature magnetic state is unknown and is believed to impact the magnetic ground-state. In addition, the influence of phonon activity on dynamic stability has yet to be studied. Our calculated transverse 3k AFM state is consistent with observations of noncollinear magnetic behaviour, the preservation of external cubic symmetry and indications of an internal O^2- distortion. This is identical to observations of Pa3̅ crystal symmetry in UO_2. We therefore employed the same approach used for UO_2, whereby the electronic structure of the transverse 3k AFM (U = 4.25 eV) has been calculated by the PBEsol functional (Fig. 6). In contrast, other investigations have reported that the longitudinal 3k AFM state retained the Fm3̅m crystal symmetry.31, 46

![Fig. 6](image.png)

Fig. 6 Left, the calculated band structure. Right, the density of states of the transverse 3k AFM ground-state of NpO_2 with the Pa3̅ (No. 205) crystal symmetry. Calculated from PBEsol+U where U = 3.50 eV.

In the transverse 3k AFM (theoretical) state, the CMB is formed equally of oxygen p-states and neptunium f-states, indicating that NpO_2 shares both Mott and charge-transfer characteristics. In contrast with previous investigations, the longitudinal 3k AFM state predominately results in a charge-transfer insulator.31 The charge-transfer characteristics are likely due to the absence of an exchange modifier that otherwise serves to reduce the effective Np magnetic moment. In both instances, the Np d-states have no significant role in chemical bonding interactions.
The band structure reveals a direct R-centred band-gap of 2.79 eV, which compares with a calculated optical absorbance of 2.81 eV. Finally, the calculated bulk modulus of NpO$_2$ for the longitudinal 3k AFM state is 214 GPa, whereas the bulk modulus for the transverse 3k AFM state is 215 GPa (Table 5).

4 Conclusions

The magnetic structures of UO$_2$ and NpO$_2$ have been investigated by first-principles methods based on three levels of theory. We consider that the influence of the magnetic structure of a material on its crystal structure, shown here for two AnO$_2$ systems, may be of pertinence in other actinide compounds as well, which will be the topic of future work.

Our calculations result in the a transverse 1k AFM ground-state for UO$_2$ in agreement with both static and low-frequency measurements of spin-wave excitations. In contrast, the transverse 3k AFM state linked to Pa$^3$ (No. 205) crystal symmetry is established by inelastic neutron scattering (INS), resonant X-ray scattering (RXS) and nuclear magnetic resonance (NMR) measurements. All ordered magnetic states are in close energetic proximity (< 0.26 eV/F.U.). Thus, thermal fluctuations are thought to play a significant role. The influence of entropy on the dynamic stability of the ordered magnetic states remains unknown.

The insulating nature of NpO$_2$ is reproduced by PBEsol when U = 4-6 eV for all magnetic configurations. In this study, the existence of a small-moment system cannot be confirmed. A FM (111) ground-state with R$^3$m (No. 166) has been found. This contradicts resonant X-ray scattering and $^{17}$O NMR measurements. In contrast, the transverse 3k AFM state with Pa$^3$ (No. 205) crystal symmetry is only 0.001 eV higher in energy. This magnetic structure has been linked to experimental measurements.

The results show that the crystal symmetry is strongly influenced by the magnetic environment. For instance, the experimental cubic environment is only preserved by noncollinear 3k AFM states. The longitudinal 3k AFM state results in Fm$\bar{3}$m (No. 225) crystal symmetry, whereas the energetically marginally more favourable transverse 3k AFM state results in Pa$^3$ (No. 205) crystal symmetry, with a distortion of the O$^2-$ ions of 0.011 Å. In contrast, the collinear 1k AFM states, often employed in past investigations, result in either an orthorhombic Fmmm (No. 69) or tetragonal I4/mmm (No. 139) distortion.
Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references


