Density functional theory calculations on magnetic properties of actinide compounds

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We have performed a detailed analysis of the magnetic (collinear and non-collinear) order and the atomic and electron structures of UO₂, PuO₂ and UN on the basis of density functional theory with the Hubbard electron correlation correction (DFT + U). We have shown that the 3-k magnetic structure of UO₂ is the lowest in energy for the Hubbard parameter value of \( U = 4.6 \text{ eV} \) (and \( J = 0.5 \text{ eV} \)) consistent with experiments when Dudarev’s formalism is used. In contrast to UO₂, UN and PuO₂ show no trend for a distortion towards rhombohedral structure and, thus, no complex 3-k magnetic structure is to be anticipated in these materials.

1. Introduction

Actinide compounds continue to attract a great interest for both materials scientists and nuclear engineers. Their properties combine a strong electron correlation and relativistic effects of 5f valence electrons. In this paper, we study collinear and non-collinear magnetic structures of three basic actinide materials UO₂, PuO₂ and UN. All these materials have face-centred cubic (f.c.c.) actinide sub-lattice: the two oxides have fluorite structure and UN rock-salt structure. Experiments suggest that at low temperatures UN is anti-ferromagnetic whereas UO₂ and PuO₂ are diamagnetic.

In contrast to UN and PuO₂, the magnetic properties of UO₂ and UN have been performed so far. The X-ray diffraction measurements on UN revealed no significant tetragonal distortion, which would be a consequence of the AFM spin alignment along the (001) direction.
In the present study, we consider possible collinear and non-collinear magnetic structures of UO₂ also using the DFT + U technique, but implemented in another code, Vienna Ab initio Simulation Package (VASP). First, we test the ability of this method and the code to reproduce experimentally observed non-collinear magnetic order in UO₂ using experimental values of the Hubbard parameter \( U = 4.6 \) eV, \( J = 0.5 \) eV.\(^{24}\) Second, we explore different possible magnetic structures in UN and PuO₂ using the same DFT + U technique and try to determine which of the \((001)\) and \((111)\) structures is more stable. Section 2 describes computational details used in the present simulations. Descriptions of studied magnetic structures are given in Section 3. The results of our computations are provided and discussed in Section 4. Lastly, the conclusions are summarized in Section 5.

2. Computational details

In the present first-principles simulations we used the VASP (version 4.6)\(^{21,22}\) computer code employing the DFT + U method. The VASP code treats core electrons using pseudo-potentials, whereas the semi-core electrons at U atoms and all the valence electrons are represented by plane waves. The electronic structure is calculated within the projector augmented wave (PAW) method.\(^{23}\) The simplified rotationally-invariant Dudarev’s form\(^{17}\) for the Hubbard interaction was used for UO₂ and UN. It uses exclusively the difference, \( U_{\text{eff}} = U - J \), of the Hubbard parameter \( U \) and the exchange parameter \( J \). In contrast to uranium compounds, PuO₂ shows a significant role of exchange part requiring the use of Liechtenstein’s form\(^{16}\) for the energy correction. The double counting correction in all our calculations was treated with account for spin-polarization.\(^{15-17}\) Computations of UO₂ were done including the SOI effects, whereas computations of PuO₂ and UN employed only scalar relativistic approximation. Both unit cell parameters and atomic positions were optimized until the energy convergence reached \( 10^{-5} \) eV. The calculations were performed with the cut-off energy of 520 eV. The integrations in the reciprocal space over the Brillouin zone (BZ) of the tetragonal unit cell of PuO₂ and UN (used to calculate the \((001)\) AFM magnetic structure) were performed using \( 10 \times 10 \times 8 \) and \( 12 \times 12 \times 10 \) Monkhorst–Pack meshes,\(^{25}\) respectively. Computations of the rhombohedral PuO₂ and UN with the \((111)\) magnetic structure were performed with \( 12 \times 12 \times 12 \) and \( 14 \times 14 \times 14 \) Monkhorst–Pack meshes. Similarly, the integrations over the BZ for the conventional unit cell of UO₂ were performed using \( 6 \times 6 \times 6 \) Monkhorst–Pack meshes. The conventional 12-atom unit cell was necessary for modelling of UO₂ with non-collinear magnetic structures. It was possible to use the smaller unit cell for a collinear magnetic ordering (the 1-k AFM \((001)\) and \((111)\) magnetic structures) in UO₂. Correspondingly, in these cases we applied larger \( 14 \times 14 \times 10 \) and \( 12 \times 12 \times 12 \) k-meshes. The applied meshes in the reciprocal space were sufficient to reach a convergence of \( 10^{-4} \) eV for one-electron energies. Fractional electron occupancies were estimated with the Gaussian method using the smearing parameter of 0.25 eV. Calculations, which included SOI, were done with lifted symmetry constraints.

Photoemission spectroscopy (PS) measurements by Baer and Schoenes\(^{24}\) suggest that the Hubbard correlation parameter \( U \) is 4.6 eV for UO₂ assuming that exchange parameter \( J \) is 0.5 eV. These values were applied later by Dudarev et al.\(^{17}\) In their calculations\(^{17}\) the band gap becomes open and equal to 1.3 eV within the LSDA + U, being, however, smaller than the experimental value of 2.0 eV. A somewhat better agreement is observed within the generalized gradient approximation,\(^{26}\) i.e. GGA + U.\(^{10,27-29}\) Note that following Dudarev’s calculations, we employed recently the same values of \( U \) and \( J \) in our study on bulk properties and defects behaviour in UO₂.\(^{10}\) In the present simulations we used the same set of correlation \( U \) and exchange \( J \) parameters for computations of UO₂. The parameter \( U_{\text{eff}} = 1.875 \) eV for UN was fitted\(^{30}\) to reproduce the magnetic moment of uranium ions and UN unit cell volume in the low-temperature phase. The band gap of \( \sim 1.8 \) eV\(^{31}\) for PuO₂ is known from the electrical conductivity measurements which is similar to the band gap in UO₂. Previous theoretical studies\(^{8-9}\) also agreed on the AFM solution for PuO₂ within the 1-k magnetism and, therefore, used the tetragonal structure as described above. Despite the relatively similar band gaps in both oxides, their electronic structures are quite different which is clearly seen in the corresponding PS measurements.\(^{32}\) Parameters \( U = 3.0 \) eV and \( J = 1.5 \) eV were fitted for PuO₂ to describe correctly its experimental lattice constant, band gap, and position of Pu 5f band.

3. Magnetic structures

The dependence of atomic magnetic moments on the position in a lattice can be expressed as expansion in plane waves:

\[
M_j = \sum_{\mathbf{k}} e^{i \mathbf{k} \cdot (r_j - r_0)} M_{0}^\mathbf{k},
\]

where \( M_j \) is the magnetic moment of the atom in unit cell \( j \) and at position \( r_j, r_0 \) is the position of the same atom in the 0th unit cell, \( k \) and \( M_{0}^\mathbf{k} \) are, respectively, the wave vector and amplitude of the magnetic wave \( w \).

In the collinear 1-k magnetic structures magnetic moments of U atoms are collinear and changes in the magnetic moments can be described by a single wave \( (k = 1) \). For the \((001)\) magnetic structure choosing the Oz axis along the direction of alternation of magnetic moments, the wave vector is \( k_1 = 2\pi/a \) (0, 0, 1), where \( a \) is a cubic lattice constant. Similarly, for the \((111)\) structure the wave vector is \( k_1 = \pi/a \) (1, 1, 1). These two collinear 1-k magnetic structures were modelled for all three materials considered here. These magnetic structures have symmetry reduced from the cubic one. In the \((001)\) structure the lattice has a tetragonal symmetry, and in the \((111)\) structure the lattice becomes rhombohedral, as can be seen from the next section.

Farber et al.\(^{18}\) suggested the 2-k transverse magnetic structure for UO₂ which is associated with a transverse phonon. If we choose the direction of the phonon propagation as the Oy axis, then magnetic waves propagate along the Ox and Oz axes \( (k_1 = 2\pi/a (1, 0, 0), k_2 = 2\pi/a (0, 0, 1)) \) with amplitudes \( M_{0}^\mathbf{k} = M_0 (0, 1, 0), M_{0}^\mathbf{k} = M_0 (1, 0, 0) \), where \( M_0 \) is...
the magnitude of atomic magnetic moment. Magnetic moments of U atoms lie on the Oxy plane and point along various [110] directions. The transverse phonon in this structure can be described as O atoms in odd and even {010} oxygen planes shift in opposite directions along the Ox axis. While later experiments showed that this structure is not the most stable one, we included it into our simulations to compare energies of all previously considered magnetic structures of UO₂.

According to the experiment,¹¹ UO₂ has transverse 3-k magnetic structure. The wave vectors for three waves in 3-k structures are \( k_1 = 2\pi/a (1, 0, 0), k_2 = 2\pi/a (0, 1, 0), \) and \( k_3 = 2\pi/a (0, 0, 1) \). There are two equivalent transverse structures with this symmetry in the fluorite lattice. The first structure has amplitudes \( M_{01}^i = M_0 (0, 1, 0), M_{02}^i = M_0 (0, 0, 1), M_{03}^i = M_0 (1, 0, 0) \). The second one has amplitudes \( M_{01}^i = M_0 (0, 1, 0), M_{02}^i = M_0 (1, 0, 0), M_{03}^i = M_0 (0, 0, 1) \). The two O atoms nearest to each U atom in the direction of its magnetic moment shift from their sites toward this U atom. Both structures have the same total energies. We used the first one in our simulations.

4. Results and discussion

In the present study, we assess the difference between the two (111) and (001) AFM magnetic collinear structures, as a function of the \( U \) and \( J \) parameters for UN and PuO₂ (Fig. 1).

The energy difference between the two magnetic structures for UN (Fig. 1a) is very small and negative at small values of \( U_{\text{eff}} = U - J \). It slowly grows for \( U_{\text{eff}} \) between 0.0 eV and 1.5 eV, then noticeably increases from 2.0 to 5 eV, and likely saturates for the higher values of \( U_{\text{eff}} \). For the optimized value of \( U_{\text{eff}} = 1.875 \) eV the (001) structure of UN is already more stable than the (111) structure (see inset in Fig. 1a). At this value of \( U_{\text{eff}} \) the lattice constants for UN in the (001) magnetic structure are \( a = 4.974 \) Å and \( c = 4.859 \) Å, and lattice parameters in the (111) magnetic structure are the lattice constant \( a = 4.942 \) Å and the rhombohedral angle \( \gamma = 88.2 \)°. In both cases the cubic unit cell is distorted along the direction of alternation of magnetic moments. In the (001) structure it is compressed along the Oz axis, for the (111) structure the unit cell is elongated along [111] direction. It is experimentally known that UN is cubic with the lattice constant \( a = 4.886 \) Å.³³ The calculated spin magnetic moments of U atoms are 1.47 \( \mu_B \) in the (001) structure and 1.82 \( \mu_B \) in the (111) structure. The magnetic moment of U atoms measured at low temperatures is 0.75 \( \mu_B \). Inclusion of the SOI allows revealing substantial orbital moments in actinide compounds which would lead to much better alignment of U atom magnetic moment with experimental value.³⁰ It is important also that the value of \( U_{\text{eff}} = 1.875 \) eV is sufficient to stabilize the AFM structure with respect to the FM one in contrast to standard DFT calculations.³⁰,³⁴

Due to the Liechtenstein form of the DFT + \( U \) functional applied to PuO₂, we have to vary the \( U \)- and \( J \)-parameters independently. It was done by varying \( U \)- with the \( J \)-parameter fixed at 1.5 eV and by varying \( J \) at \( U = 3.0 \) eV, correspondingly. As seen in Fig. 1b, the (001) magnetic structure of PuO₂ is energetically more stable than the (111) one, except for very small values of Hubbard parameter \( U \). It suggests no preference of the (111) magnetic structure, in contrast to UO₂ (see discussion below), for realistic values of \( U \)- and \( J \)-parameters. The difference increases with both parameters, indicating further stabilization of the (001) magnetic structure in a comparison to the (111) one. The energy difference between the two magnetic structures (Fig. 1b) is almost linear for PuO₂, independently of which parameter is varied or fixed. For chosen values of the parameters \( U = 3.0 \) eV and \( J = 1.5 \) eV), lattice constants for PuO₂ in the (001) structure are \( a = 5.402 \) Å and \( c = 5.513 \) Å, and lattice parameters in the (111) magnetic structure are \( a = 5.430 \) Å and \( \gamma = 88.9 \)°. In the case of PuO₂ a cubic unit cell becomes elongated in the direction of alternation of magnetic moments. The calculated spin magnetic moments of Pu atoms are 3.81 \( \mu_B \). Experimentally, PuO₂ is cubic with lattice constant \( a = 5.398 \) Å and diamagnetic.

In Fig. 2 we present the total densities of states (DOS) for the discussed tetragonal AFM unit cell of PuO₂, when the strong correlation effects are neglected (dashed line) and for the employed values of \( U = 3.0 \) eV and \( J = 1.5 \) eV (solid line). The DOS clearly demonstrates that PuO₂, like UO₂, tends to be metallic if the strong correlation effects are not treated.
properly, whereas the band gap of 1.5 eV appears for the chosen parameters of the GGA + U scheme. The latter value of the band gap is slightly smaller than the experimental value (1.8 eV).

The case of UO₂ differs from the discussed above trends for UN and PuO₂ due to the fact that the <111> magnetic structure in UO₂ is more stable than the <001> one by 62 meV per formula unit at \( U = 4.6 \) eV and \( J = 0.5 \) eV. This result confirms the previously published hybrid functional calculations\(^{19}\) with atomic basis set. Due to the SOI the total energy is reduced almost by 2.66 eV per UO₂ primitive unit cell. This does not affect relative energies of all studied magnetic structures (3-k, 2-k and both (001) and (111) 1-k structures). Relative energies for all considered magnetic structures are provided in Table 1 with respect to the 3-k magnetic structure. The transverse 3-k magnetic structure appears to be the most energetically preferable. This is in accord with inelastic neutron scattering experiments.\(^{11}\) The 2-k structure proposed by Faber and Lander\(^{18}\) has just a little bit lower energy (5 meV per formula unit) than the (111) collinear structure but noticeably higher than the transverse 3-k structure.

Both the (001) and (111) collinear structures have unit cells compressed along the direction of alternation of magnetic moment (see Table 1). Magnetic moments of U atoms in both structures point in the same [001] and [111] directions.

All lattice constants in the 2-k structure are different. The lattice of the 2-k structure becomes orthorhombic. As expected (see Section 3 and ref. 18), odd and even oxygen \{010\} planes are shifted along the Ox axis in the opposite directions. The obtained shift is \( \Delta = 9.7 \times 10^{-3}a \) (compare with \( \Delta = 2.6 \times 10^{-3}a \) obtained in ref. 10). However, directions of magnetic moments are very different from those suggested in ref. 11: the magnetic moments point almost along the [010] directions, but are slightly tilted towards shorter square diagonal (the squares are perpendicular to the [001] direction). This can be expressed by amplitudes of magnetic waves \( M_i^0 = (0, 1, 0)1.79 \mu_B, M_i^0 = (1, 0, 0)0.24 \mu_B \).

Unit cell in the transverse 3-k structure keeps cubic shape. Magnetic moments are aligned according to the transverse 3-k symmetry. The pair of O atoms nearest to each U atom in the direction of its magnetic moment is shifted toward this U atom by \( 9.6 \times 10^{-3} \sqrt{3}a \) (or 0.092 Å). Somewhat smaller distortion was derived from experiments.\(^{18}\)

For the total magnetic moments of U atoms in the most stable transverse 3-k structure we obtained a value of 1.99 \( \mu_B \), which slightly exceeds the experimental value of 1.74 \( \mu_B \). Magnetic moments obtained for the (001) 1-k and for the 2-k structures are much closer to the experimental value, but these structures have higher energies and are not consistent with inelastic neutron scattering data.\(^ {11}\) According to Ippolito et al.\(^ {20}\) the magnetic moment reduction can be explained by a dynamic Jahn–Teller mixing, while our modelling includes only a static Jahn–Teller mixing. The obtained values of magnetic moments are still noticeably lower than the magnetic moment of 2.06 \( \mu_B \) of U ions in the ground state expected from the intermediate coupling of moments.\(^ {35}\) We have to notice that the intermediate coupling theory includes a multi-determinant form of wavefunction, while the present simulations are done in a single-determinant form of wavefunction.

In Fig. 3 we compare the total DOS for different magnetic UO₂ structures. In all considered structures, the highest valence band consists predominantly of U 5f orbitals and the next highest valence band is mostly built from O 2p orbitals. The conduction bands contain U 6d and U 5f orbitals. Our calculations reproduce the band gaps in various magnetic structures of UO₂ (see Table 1) very close to the experimental value (2.0 eV).\(^ {24}\) The band gaps in both considered non-collinear structures are a little larger, by several tenths of eV. In calculations\(^ {19}\) with hybrid

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**Table 1** Results of calculations for UO₂. \( \Delta E \) is the total energy (in meV per molecule) for various magnetic structures in UO₂ with respect to transverse 3-k structure, which has the lowest energy. The energy calculations included SOI. \( a, b \) and \( c \) are lattice constants, \( z, \beta \) and \( \gamma \) are angles between lattice vectors of conventional unit cell. \( E_g \) is band gap, \( \mu \) is the total magnetic moment of U atom (in Bohr’s magnetons \( \mu_B \)) and the values in parentheses are spin contributions to the magnetic moments. The experimental value of magnetic moment is 1.74 \( \mu_B \).

<table>
<thead>
<tr>
<th>Magnetic structure</th>
<th>(001) 1-k</th>
<th>(111) 1-k</th>
<th>Faber–Lander 2-k</th>
<th>Transverse 3-k</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta E )/meV per molecule</td>
<td>95</td>
<td>33</td>
<td>28</td>
<td>0</td>
</tr>
<tr>
<td>( a )/Å</td>
<td>5.566</td>
<td>5.550</td>
<td>5.555</td>
<td>5.547</td>
</tr>
<tr>
<td>( b )/Å</td>
<td>5.566</td>
<td>5.550</td>
<td>5.562</td>
<td>5.547</td>
</tr>
<tr>
<td>( c )/Å</td>
<td>5.508</td>
<td>5.550</td>
<td>5.521</td>
<td>5.547</td>
</tr>
<tr>
<td>( z = \beta = \gamma )/Å</td>
<td>90</td>
<td>91.7</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>( E_g )/eV</td>
<td>1.95</td>
<td>2.03</td>
<td>2.50</td>
<td>2.38</td>
</tr>
<tr>
<td>( \mu/\mu_B )</td>
<td>1.76 (1.95)</td>
<td>2.00 (1.98)</td>
<td>1.81 (2.04)</td>
<td>1.99 (2.00)</td>
</tr>
</tbody>
</table>
As a result, O 2p band shifts, following the narrowing of U 5f valence bands is small, of O 2p band varies little among considered structures. The (U GGA + B) non-collinear 3-k structure of UO 2 is the most stable one for this material. UO 2 retains a cubic shape in this structure. Two O atoms nearest to each U atom in the direction of its magnetic moment move toward this U atom. This is consistent with both experiment and previous computer simulation employing the LDA + U technique within the Wien2k code. It is important that such agreement is achieved with the standard functional the band gap for the (111) structure is significantly (by ~1.5 eV) overestimated.

The U 5f band width is 1.5 eV for the collinear magnetic structures and gets much narrower for the non-collinear cases (0.76 eV and 0.86 eV in case of 2-k and 3-k structures, respectively). This band splits into two separate sub-bands: U 5f(5/2) and U 5f(7/2) in the 3-k structure with a gap of ~0.1 eV and distance between peaks ~0.38 eV. The width (~4.2 eV for (111) structure and ~4.4 eV for other structures) of O 2p band varies little among considered structures. The gap between O 2p and U 5f valence bands is small, ~0.3–0.5 eV. As a result, O 2p band shifts, following the narrowing of U 5f valence band, and becomes by ~0.5 eV closer to the Fermi level in the non-collinear structures than in the collinear ones.

5. Conclusions

We have compared several possible magnetic structures of several key actinides UO2, UN and PuO2 based on the GGA + U technique. Our modelling shows that the transverse non-collinear 3-k structure of UO2 is the most stable one for this material. UO2 retains a cubic shape in this structure. Two O atoms nearest to each U atom in the direction of its magnetic moment move toward this U atom. This is consistent with both experiment and previous computer simulation employing the LDA + U technique within the Wien2k code. It is important that such agreement is achieved with the standard values of Hubbard and exchange parameters (U = 4.6 eV, J = 0.5 eV) within Dudarev’s form of the DFT + U approach. Still, a reason for overestimated U atom magnetic moment remains unclear.

The collinear magnetic order causes breaking of cubic symmetry in UN and PuO2. In contrast to UO2, neither UN nor PuO2 show the energetical preference for the rhombohedral distortion. Both materials have the AFM tetragonal (001) structure for a reasonable choice of parameters U and J. The total DOS of PuO2 is successfully reproduced using the Liechtenstein form for the Hubbard correction with the parameters U = 3.0 eV and J = 1.5 eV. However, as well as in the previous computational studies, we obtained that the AFM state of PuO2 is more stable than the experimentally observed diamagnetic state.

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Notes and references

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