

Impact of the U parameter on the predicted defect chemistry of materials: The example of $\text{PuO}_{2\pm x}$ Reece Bedford^{✉*} and Samuel Murphy[†]*School of Engineering, Lancaster University, Lancaster LA1 4YW, United Kingdom*

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Density functional theory (DFT) provides a powerful tool for describing the electronic properties of materials, however, self-interaction errors in semilocal functionals complicate the accurate modeling of correlated materials. The DFT + U method is a popular and computationally cost-effective solution for mitigating self-interaction; though, this reduces the *ab initio* aspect of DFT calculations, as the outcome now becomes dependent on the user's choice of U parameters. Atomistic modeling of plutonium dioxide (PuO_2) is employed to provide insight into its evolution in storage or into its properties as mixed-oxide fuel. There is no single U parameter that can reproduce all the experimental properties of PuO_2 accurately and, as such, it is important that the U parameter is selected with careful consideration. In this work, we use noncollinear DFT + U simulations to thoroughly examine the defect chemistry of PuO_2 using $U = 4$ and 7 eV, in order to understand the implication the choice of U parameter can have on the predicted defect chemistry. We find that both U parameters predict the same intrinsic defect chemistry, with the main discrepancy being on the preferred charge state of the oxygen vacancies: +2 for $U = 4$ eV and neutral for $U = 7$ eV. Additionally, we show that the choice of U can impact the defect formation energies and preferred charge states of a dopant. When uranium is placed onto a plutonium lattice site, it tends to favor the neutral and +1 charge state (indicative of U^{4+} and U^{5+}) with $U = 4$ eV, whereas with $U = 7$ eV the -1 and neutral charge states are more stable.

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The addition of the U parameter, inspired by the Hubbard model, increases the Coulomb repulsion felt by the correlated d or f electrons in density functional theory (DFT), preventing excessive delocalization in these orbitals [1]. This approach is attractive as the computational cost is comparable to typical local and semilocal functionals, enabling the simulation of large systems containing defects. The efficiency of the Hubbard model depends on the accurate determination of the U parameter [1,2]. It is possible to determine the U parameter self-consistently from first principles, ensuring the method remains entirely *ab initio* [3,4]; however, in the

majority of cases, the value is fitted to reproduce experimental properties. This is a reasonable approach, given that the accuracy of DFT is determined by comparing predicted properties to those observed in experiments. Unfortunately, it is often the case that there is no single value of the U parameter that enables the reproduction of all experimentally measured quantities [5–8]. This poses a problem for novel materials, or those where the experimental properties are not defined with certainty and, as a consequence, there are materials where different authors select various U parameters depending on which property is fitted to.

A particular example is PuO_2 : the experimental band gap ranges between 1.8 and 4.1 eV, depending on the method used [9–11]. To reproduce these band gaps, U parameters for PuO_2 ranging from 3 to 10 eV are required [5]. Within this range, authors have selected a few specific U parameters. For example, Neilson *et al.* [12] set $U = 7$ eV, based on the band gap of PuO_2 calculated using the HSE06 hybrid functional ($E_b = 3.04$ eV). The rationale was that the analysis of a material's defect chemistry required an accurate description of the band-gap width, and the HSE06 functional has been shown to reliably reproduce experimental band gaps [13]. A

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similarly large U parameter has been used for americium dioxide (AmO_2) [14]; larger U parameters would be expected when traversing across the actinide series, as electron correlation effects are more dominant. By contrast, Chen and Kaltsayannis [5] recommend $U = 4$ eV for antiferromagnetic PuO_2 , as this retained the experimentally observed $\text{Pu-}f$ and $\text{O-}p$ character of the valence band [15–17], while predicting a band gap at the lower end of the experimental range. This U parameter is also in keeping with other defect studies of actinide dioxides [18–24]. It should be noted that Neilson *et al.* [12,25,26] used noncollinear magnetism and spin-orbit coupling, while the other studies do not, which can lead to the requirement for a different U parameter. It has been shown previously that the choice of U parameter can change predicted defect formation energies and charge transition levels [27–34], however, thus far it is unclear how a material's overall defect chemistry is impacted.

Understanding the defect chemistry of materials is crucial because defects often control key properties such as ionic conductivity, diffusion, mechanical strength, and radiation tolerance, enabling the creation of advanced electronic devices and the safe management of hazardous materials. Understanding of such properties is of key importance for the Sellafield site in the UK, as it possesses one of the world's largest civilian stockpiles of separated plutonium in the world [35]. The stockpile is generally stored as a powder within two nested containers, with the outer canister welded shut. As it ages, the defect chemistry of PuO_2 evolves due to the introduction of decay products, such as uranium and americium, potentially changing how the powder interacts with the gaseous species entrained during packaging [25,26]. This has the possibility of leading to pressurization of the canisters. As the packages are sealed, it is difficult to perform experimental analysis of the powder *in situ*. Therefore, developing accurate models of the powder in the conditions inside the packages can support the future management of the stockpile. Especially now, with the UK government's recent policy change for the immobilization of all plutonium material [36].

In this work, the impact of the choice of the U parameter on the predicted defect chemistry is performed utilizing PuO_2 as an example where significantly different values have been employed previously (i.e., $U = 4$ and 7 eV). In addition to analyzing how the choice of U parameter impacts the intrinsic defect chemistry, the selection of a separate U parameter for dopants, in this case uranium, is explored.

II. METHODOLOGY

A. Simulation procedure

DFT + U simulations were performed using the Vienna *ab initio* simulation package (VASP) [37–40], employing the frozen-core projector-augmented wave (PAW) [41] pseudopotentials. All simulations utilized the generalized gradient approximation (GGA) formulation of Perdew-Burke-Ernzerhof that was revised for solids (PBEsol) [42]. We compare the defect chemistry of PuO_2 when applying a Hubbard correction of $U = 4$ and 7 eV to the $5f$ electrons of plutonium, utilizing the rotationally invariant method of Liechtenstein *et al.* [43]. We set $J = 0$ eV throughout all calculations, hence,

the methods of Liechtenstein *et al.* [43] and Dudarev *et al.* [44] are equivalent, where $U - J = U_{\text{eff}}$. Spin-orbit coupling [45] (SOC) and a $3k$ longitudinal antiferromagnetic (AFM) configuration were utilized, as this configuration has been shown by Pegg *et al.* [46] to be the lowest-energy configuration for PuO_2 in DFT.

The energy of the 12-atom PuO_2 unit cell was converged to less than 10 meV per formula unit (pfu) when using a plane-wave cutoff energy of 500 eV and a $4 \times 4 \times 4$ Monkhorst-Pack k -point mesh. For the calculation of the density of states (DoS), the k -point grid was increased to $8 \times 8 \times 8$. The thresholds for electronic and atomic force convergence were set to 1×10^{-5} eV and 1×10^{-2} eV/Å, respectively.

Vacancy and interstitial defects of plutonium and oxygen were inserted into a $2 \times 2 \times 2$ 96-atom supercell by adding or removing the corresponding atom. The k -point grid was reduced to $2 \times 2 \times 2$ for the supercell, accordingly. The atomic positions were then subjected to random perturbations in order to further reduce the symmetry of the defect structure, as adopted by the Shake'n'break method [47–49]. A modified version of this procedure is adopted by randomly and uniformly perturbing individual atoms by up to $\pm 2.5\%$ of the PuO_2 lattice parameter. No other distortion was applied, as ionic materials are particularly sensitive to high forces when highly distorted. The initial magnetic configuration for all defect simulations was set equal to that of the perfect supercell; it was assumed that the self-consistent field (SCF) cycle would determine the ground-state magnetic moments surrounding each individual defect. The exception was for the incorporation of uranium and excess plutonium (interstitial and antisite defects), where multiple initial magnetic moments were specified (e.g., $\mu_{\text{M}} = [111], [\bar{1}\bar{1}\bar{1}], [\bar{1}\bar{1}1], [1\bar{1}\bar{1}]$) for the defect atom, and the lowest energy was taken as final. It was found that the defect energies were not sensitive to the direction of the relaxed magnetic moment (of the defect atom), but some initial magnetic configurations relaxed into higher-energy nonmagnetic states.

Defects are then denoted in notation akin to Kröger-Vink: X_S^q , where X is the element (or V for a vacancy), S is the lattice site of the defect (Pu, O, or i), and q is the relative charge of the defect in the simulation supercell. The assortment of defect charge states was obtained by increasing or decreasing the total number of electrons within the supercell. For all defect calculations, symmetry impositions were removed, and the lattice parameters were fixed to be the same as the perfect supercell.

The DFT + U method is renowned for giving rise to metastable states, where depending on the initial occupation at the beginning of the SCF cycle, the U parameter may enforce an electron occupation that is not the true ground state of the material but provides a valid solution to the Kohn-Sham equations. It comes as no surprise that the strongly correlated f orbitals of the actinides are sensitive to such effects. In fact, the desire to determine the true ground state of UO_2 and PuO_2 , for their applicability in the nuclear industry, has been a driving force behind developing methods to circumvent metastable states [5,50–52]. One such method is the U -ramping method [50]; this method involves slowly incrementing the U parameter up to a desired value and has the effect of smoothing out the initial potential energy surface.

This increases the probability of relaxing into the ground state, but careful monitoring is still required as it is not guaranteed. Occupation matrix control (OMC) [53] is another technique for obtaining the true ground-state electronic structure. The method involves fixing a specific electron occupation for a number of initial SCF cycles, after which the occupation is removed, and the calculation is left to converge naturally. This encourages the calculation to relax into the desired occupation and can be used to determine the ground state by scanning across all possible occupation configurations of the orbitals.

The U ramping and OMC methods are typically applied when using the collinear $1k$ AFM approximations for UO_2 and PuO_2 [5,18–24,54]. The use of such a magnetic configuration is clearly susceptible to the aforementioned metastable states. While OMC can perhaps reach the true ground state of bulk materials more reliably, the U -ramping method is more popular for the calculation of defects. The application of OMC across all charge states for every defect would be a rather laborious process. Additionally, many studies avoid employing the $3k$ AFM configuration with SOC due to the elevated computation cost. However, it has been shown in UO_2 that the use of SOC can achieve the same ground state with and without applying OMC [51,55]. The magnetic configuration is tied to the electron occupation, and it appears that the increased number of degrees of freedom when SOC is involved reduces the possibility of falling into a metastable state. For this reason, unless specified, it can be assumed that the use of the $3k$ AFM configuration and SOC is enough to achieve the ground state of PuO_2 and its associated defects.

B. Defect formalism

The formation energy of a defect ΔG_f^i can be calculated from the equation devised by Zhang and Northrup [56]. In this work, the contribution of vibrational entropies to the defect formation energies is not included; therefore, we approximate ΔG_f^i with ΔE_f^i :

$$\Delta E_f^i = E_{\text{defect}}^{\text{DFT}} - E_{\text{perfect}}^{\text{DFT}} - \sum_{\alpha} n_{\alpha} \mu_{\alpha} + q_i \mu_e + E_{\text{corr}}, \quad (1)$$

where $E_{\text{defect}}^{\text{DFT}}$ and $E_{\text{perfect}}^{\text{DFT}}$ are the total DFT energies of defective and perfect supercells, n_{α} is the number of atoms added to or removed from the system to create the defect, and μ_{α} is the corresponding chemical potential of the atom. The charge of the defect q_i is multiplied by the electron chemical potential μ_e , defined as the sum of the energy of the valence band maximum (E_{VBM}) and the position of the Fermi level within the band gap, $\mu_e = E_{\text{VBM}} + \varepsilon_F$. Finally, a finite-size correction term E_{corr} is added to mitigate energy contributions from the interactions of charged defects across periodic boundaries, and is discussed further in Sec. IID.

The concentration of a defect can then be calculated from its formation energy using Boltzmann statistics:

$$c_i = m_i \exp\left(\frac{-\Delta E_f^i}{k_B T}\right), \quad (2)$$

where m_i is the multiplicity of the defect, T is the temperature, and k_B is Boltzmann's constant.

To maintain charge neutrality in the crystal, the concentrations of charged defects must balance with the concentration of electrons and holes [57]. In this work, we apply Fermi-Dirac statistics to the density of states to calculate charge carrier concentrations:

$$\sum_i q_i c_i - \int_{E_{\text{CBM}}}^{\infty} g_c(E) \frac{dE}{1 + \exp\left(\frac{E - \varepsilon_F}{k_B T}\right)} + \int_{-\infty}^{E_{\text{VBM}}} g_v(E) \frac{dE}{1 + \exp\left(\frac{\varepsilon_F - E}{k_B T}\right)} = 0, \quad (3)$$

where the first term refers to the sum of ionic defect charges, the second term to the concentration of electrons in the conduction band, and the third term refers to the concentration of holes in the valence band. The terms $g_c(E)$ and $g_v(E)$ represent the total electronic density of states in the conduction and valence bands (per formula unit), where E_{CBM} is the energy of the conduction band minimum. The density of states is calculated with each respective U parameter.

Finally, the deviation of x in PuO_{2+x} can be determined by comparing the total concentration of oxygen to the total concentration of plutonium in the defect model:

$$x = \frac{2 + [\text{O}_i] - [\text{V}_\text{O}]}{1 + [\text{Pu}_i] - [\text{V}_\text{Pu}]} - 2. \quad (4)$$

C. Chemical potentials

The chemical potential of any compound must be equal to the sum of the chemical potentials of its constituent elements. For example, the binary metal oxide $\text{M}_\alpha\text{O}_\beta$ can be defined as

$$\alpha \mu_{\text{M}}(P_{\text{O}_2}, T) + \beta \mu_{\text{O}}(P_{\text{O}_2}, T) = \mu_{\text{M}_\alpha\text{O}_\beta}. \quad (5)$$

For solids, $\mu(P_{\text{O}_2}^\circ, T^\circ) \approx \mu(0, 0)$, therefore, the pressure and temperature dependencies can be neglected, and the chemical potentials $\mu_{\text{M}_\alpha\text{O}_\beta}$ and μ_{M} can be calculated using DFT. To calculate $\mu_{\text{O}}(P_{\text{O}_2}, T)$, we adopt the method of Finnis *et al.* [58], using the known standard formation energy of the compound in order to first calculate the chemical potential of oxygen under standard conditions:

$$\Delta H_{\text{M}_\alpha\text{O}_\beta}^f = \mu_{\text{M}_\alpha\text{O}_\beta} - \alpha \mu_{\text{M}} - \beta \mu_{\text{O}}^\circ. \quad (6)$$

To calculate the chemical potential of oxygen under desired conditions, we extrapolate from μ_{O}° using real gas relations:

$$\mu_{\text{O}}(P_{\text{O}_2}, T) = \mu_{\text{O}}^\circ + \Delta \mu(T) + \frac{1}{2} k_B T \log\left(\frac{P_{\text{O}_2}}{P^\circ}\right), \quad (7)$$

where the second and third terms on the right side of the equation refer to the temperature and pressure contributions to the chemical potential of oxygen.

Temperature contributions are determined by calculating the change in free energy from standard conditions ($T^\circ = 298.15$ K) as a function of temperature equation (8). The enthalpy H and entropy S terms are calculated as functions of temperature using the Shomate equations, where the coefficients for Eqs. (10) and (11) are taken from [59]:

$$\Delta \mu(T) = G(T) - G(T^\circ), \quad (8)$$

$$G(T) = H(T) - TS(T), \quad (9)$$

TABLE I. Calculated μ_o° from Eq. (6) using various binary oxides. All solid phases calculated using PBEsol, SOC, and a 500-eV cutoff energy; the criteria for convergence was as stipulated in Sec. II A. The k points used were as recommended by The Materials Project [63] and the plutonium metal U parameters were as per Neilson *et al.* [12].

Metal	Oxide	μ_o°/eV
α -Pu	PuO ₂	-3.57
Li	Li ₂ O	-4.57
Mg	MgO	-4.51
Al	Al ₂ O ₃	-4.56

$$\frac{H(T)}{1000} = At + \frac{1}{2}Bt^2 + \frac{1}{3}Ct^3 - \frac{1}{4}Dt^4 - \frac{E}{t} + F - G, \quad (10)$$

$$S(T) = A \ln t + Bt + \frac{1}{2}Ct^2 + \frac{1}{3}Dt^3 - \frac{E}{2t^2} + G, \quad (11)$$

$$t = \frac{T}{1000}. \quad (12)$$

In principle, any reference system can be used in Eq. (6) for the calculation of the standard chemical potential of oxygen μ_o° , as it should be the same for a given level of theory and set of DFT parameters used [60]. However, Table I shows that a discrepancy arises in the calculated μ_o° when using PuO₂ and α -Pu metal in comparison to the other less correlated materials. The U parameters used in PuO₂ and α -Pu metal are different, and as the total DFT energies are dependent on these U parameters, comparison of these energies introduces an unphysical contribution to the oxygen chemical potential. Therefore, in this work, we set $\mu_o^\circ = -4.51$ eV [i.e., using Mg/MgO as a reference for Eq. (6)] and extrapolate the chemical potential of oxygen to desired conditions using Eq. (7). Then, μ_{Pu} can be obtained from Eq. (5) using this calculated μ_o . This is the same procedure employed by Neilson *et al.* [61] to calculate chemical potentials in UO₂.

We formulate our defect models by employing the defect analysis package (DefAP) [62].

D. Finite-size correction

The introduction of charged defects into small simulation supercells leads to finite-size effects being incurred. Most notable are long-range Coulombic interactions that can make a significant contribution to the total energies. Using increasingly larger supercells to mitigate this is unfeasible due to computational constraints and, accordingly, *post hoc* corrections are applied to correct for this finite-size effect.

In this work, the charge correction scheme of Kumagai and Oba [64] is utilized, which extended upon the anisotropic scheme of Murphy and Hine [65]. The method utilizes a Makov and Payne [66] formulated image charge correction, applying a first-order point-charge correction and a third-order potential alignment term with respect to the supercell volume:

$$E_{\text{corr}}^{\text{KO}} = E_{\text{PC}} + E_{\text{PA}}. \quad (13)$$

For a cubic system, such as PuO₂, the point-charge correction can be simply calculated as

$$E_{\text{PC}} = \frac{\alpha q^2}{2\epsilon L}, \quad (14)$$

where $\alpha = 2.837$ is the lattice-type dependent Madelung constant, $\epsilon = 19.66$ [12] is the static dielectric constant, and L is the supercell lattice constant.

The potential alignment term in Kumagai and Oba's method is calculated using atomic site electronic potentials of supercells with a defect ($V_{\text{def},q}$) and without (V_{perf}):

$$E_{\text{PA}} = -q\Delta V_{\text{PC},d/p}|_{\text{far}}, \quad (15)$$

$$V_{d/p} = V_{\text{defect},q} - V_{\text{perf}}, \quad (16)$$

$$\Delta V_{\text{PC},d/p} = V_{d/p} - V_{\text{PC},q}, \quad (17)$$

where $\Delta V_{\text{PC},d/p}$ is the change in potential between the defect-induced potential $V_{d/p}$ and the point-charge potential $V_{\text{PC},q}$. $\Delta V_{\text{PC},d/p}|_{\text{far}}$ is the change in potential calculated at a distance far from the defect but within the supercell. The convergence of the V_{Pu}^{4-} defect formation energy with respect to the supercell size can be seen in Fig. S1 in the Supplemental Material [67].

E. Magnetic moments

The magnetic moment of an individual ion, μ_B , can be calculated from the magnitude of the ion's magnetic x , y , and z components:

$$\mu_B = \sqrt{\mu_x^2 + \mu_y^2 + \mu_z^2}. \quad (18)$$

The overall magnetic moment for a group of ions, denoted in this work as μ_k , can be calculated from the magnitude of the sum of magnetic x , y , and z components across the series of ions:

$$\mu_k = \sqrt{\left(\sum \mu_x\right)^2 + \left(\sum \mu_y\right)^2 + \left(\sum \mu_z\right)^2}. \quad (19)$$

For an antiferromagnetic (and nonmagnetic) crystal, $\mu_k = 0$.

III. RESULTS AND DISCUSSION

A. Electronic structure

First, we examine the impact on the electronic structure of PuO₂ with each selected U parameter. This is plotted in Fig. 1, along with the corresponding electronic structure calculated by the HSE06 hybrid functional. Details of the HSE06 calculation are as per Pegg *et al.* [46].

For $U = 4$ eV, a direct band gap of 2.2 eV along the k point L has been calculated. The valence band constitutes a mix of Pu- f and O- p orbitals, while the conduction band is almost entirely Pu- f states. This electronic structure is similar to that calculated by Chen and Kaltsoyannis [5] with $U = 4$ eV, despite the different AFM configurations used. For $U = 7$ eV, the greater degree of localization of the Pu- f states from the larger U parameter is apparent; the Pu- f states occupy energies over 4 eV below the valence band maximum, resulting in the character of the high-energy states in the valence band

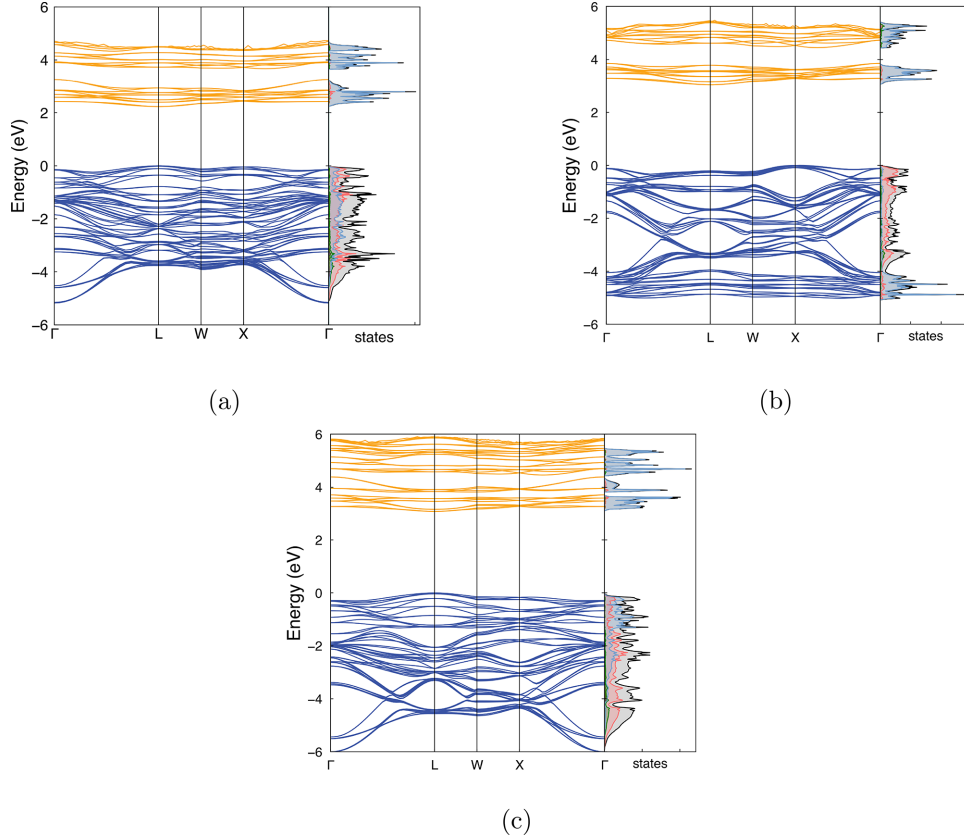


FIG. 1. Electronic band structure and density of states for $3k$ longitudinal AFM PuO_2 , calculated with (a) $U = 4$ eV and (b) $U = 7$ eV using PBEsol, as well as (c) HSE06. For the density of states, the Pu- f , Pu- d , and O- p states are represented by blue, green, and red colors, respectively. In Eq. (3), $g_c(E)$ and $g_v(E)$ are calculated by integrating over the density of states. Higher U values diminish the prominence of plutonium f states at the valence band maximum.

being solely O- p orbitals. The electronic structure of PuO_2 calculated with $U = 5$ and 6 eV in Fig. S2 of the Supplemental Material [67] shows that such character of the valence band quickly arises for $U > 4$ eV. The shift in the Pu- f states away from the Fermi energy results in a wider indirect band gap of 3.03 eV between the k points X and L .

In comparison, the HSE06 hybrid functional predicts a direct band gap of 3.04 eV along the k point L , with a valence band consisting of hybridized Pu- f and O- p states. It is clear that there is no single U parameter that can reproduce the electronic structure of the hybrid functional exactly. Each U parameter has a tradeoff between retaining the Pu- f and O- p hybridized valence band or the width of the band gap. It can be envisioned that defect states that appear within the band gap will be influenced by both of these properties, and to what degree shall be explored in later sections.

B. Unique lattice sites

Within the $Fm\bar{3}m$ fluorite crystal structure, it would be expected that there would be a single unique site for both the plutonium and oxygen sublattices due to the symmetry of the crystal. As such, for full clarity, defect formation energies for the formally charged V_{Pu}^{4-} and V_{O}^{2+} defects were calculated on multiple lattice sites with both U parameters.

For V_{Pu}^{4-} , all four plutonium sites were found to be equivalent; however, there were deviations in the predicted energies

of V_{O}^{2+} at different sites. Table II shows the relative difference in energies for eight selected V_{O} sites, representing the eight oxygen lattice sites present in the conventional PuO_2 unit cell. The relative energies of additional sites that encompass a broader range of equivalent positions can be found in Table S1 of the Supplemental Material [67]. Two of the

TABLE II. Relative energies (E_{rel}), with respect to the site at the coordinates $(\frac{1}{8}, \frac{1}{8}, \frac{3}{8})$, the average magnetic moment of plutonium atoms ($\bar{\mu}_{\text{B}}$), and the overall magnetic moment (μ_k) of V_{O}^{2+} at different locations. Magnetic moments considered are the first-nearest-neighbor plutonium atoms to the V_{O} site only. $V_{\text{O}1}$ and $V_{\text{O}2}$ sites denoted with superscript a and b , respectively.

V_{O}^{2+} Site	$U = 4$ eV			$U = 7$ eV		
	E_{rel} (eV)	$\bar{\mu}_{\text{B}}$	μ_k	E_{rel} (eV)	$\bar{\mu}_{\text{B}}$	μ_k
$(\frac{1}{8}, \frac{1}{8}, \frac{1}{8})^a$	0.20	3.72	4.44	0.22	3.81	0.56
$(\frac{3}{8}, \frac{1}{8}, \frac{3}{8})^b$	0.03	3.71	0.08	0.22	3.81	0.42
$(\frac{1}{8}, \frac{1}{8}, \frac{3}{8})$	0.00	3.74	0.00	0.00	3.81	0.02
$(\frac{1}{8}, \frac{3}{8}, \frac{1}{8})$	0.00	3.74	0.00	0.00	3.81	0.01
$(\frac{1}{8}, \frac{3}{8}, \frac{3}{8})$	0.00	3.74	0.00	0.00	3.81	0.06
$(\frac{3}{8}, \frac{1}{8}, \frac{1}{8})$	0.00	3.74	0.00	0.00	3.81	0.04
$(\frac{3}{8}, \frac{1}{8}, \frac{3}{8})$	0.00	3.74	0.00	0.00	3.81	0.05
$(\frac{3}{8}, \frac{3}{8}, \frac{1}{8})$	0.00	3.74	0.00	0.00	3.81	0.03

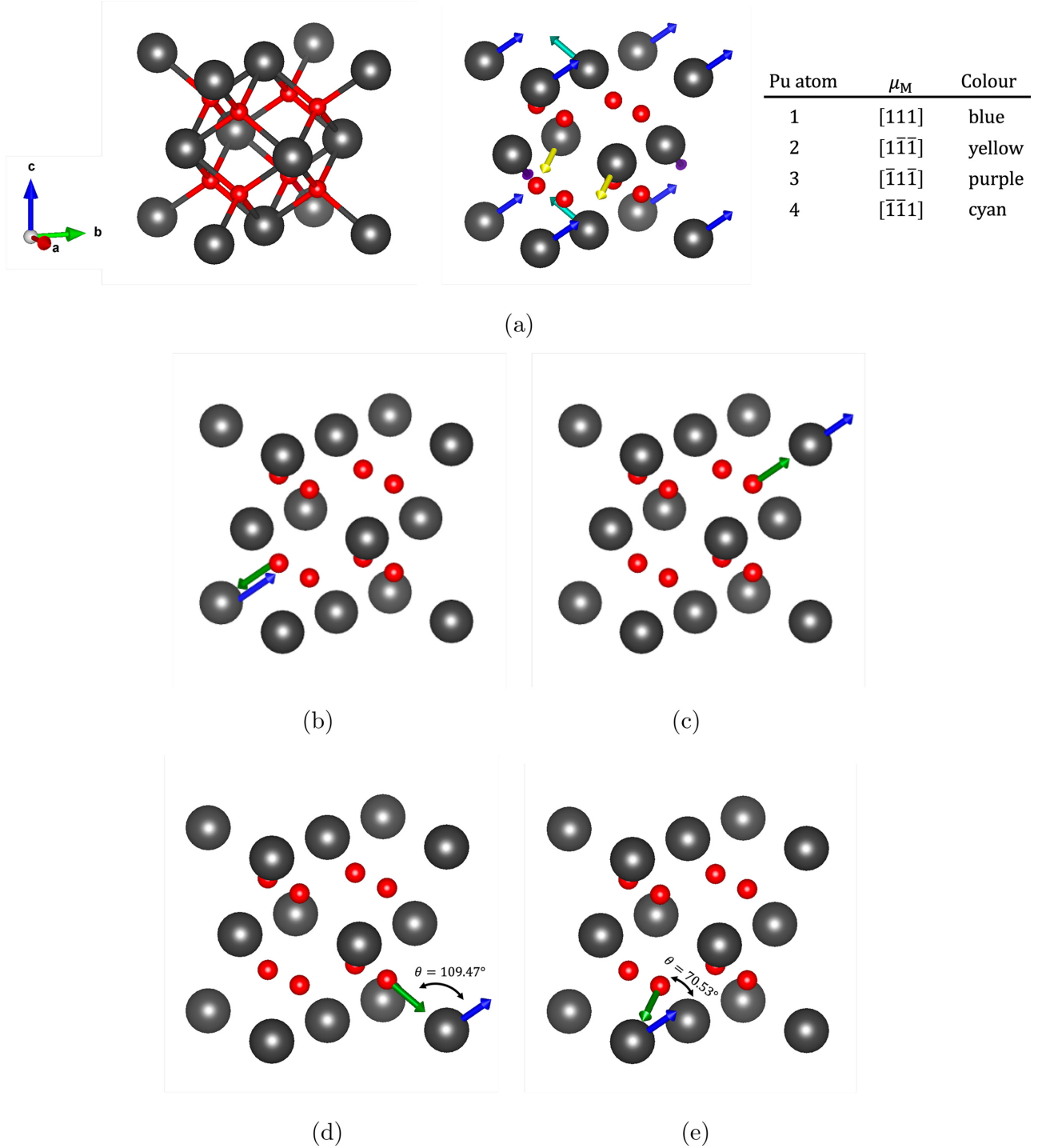


FIG. 2. (a) PuO₂ unit cell and the four magnetic vectors of the 3k AFM longitudinal configuration, and (b)–(e) the $\mu_M \cdot v_{OPu}$ of four different oxygen atoms bonded to plutonium atom number 1. The blue arrow represents $\mu_M = [111]$ and the green arrow represents v_{OPu} . Black and red spheres denote plutonium and oxygen atoms, respectively. (b) O1: $\mu_M \cdot v_{OPu} = -3$, (c) O2: $\mu_M \cdot v_{OPu} = 3$, (d) O3: $\mu_M \cdot v_{OPu} = -1$, and (e) O4: $\mu_M \cdot v_{OPu} = 1$.

oxygen lattice sites were found to be higher in energy and are denoted as V_{O1} and V_{O2} . Irrespective of the selected U parameter, the V_{O1} and V_{O2} sites are approximately 0.2–0.3 eV higher in energy than the other oxygen sites. One exception was found for a V_{O2} site with $U = 4$ eV, only being 0.03 eV higher in energy, though Table S1 [67] shows that an equivalent site in the supercell relaxed into the higher-energy state.

While all the oxygen sites are symmetrically equivalent in three-dimensional (3D) space, the application of the 3k AFM longitudinal magnetic configuration generates four oxygen sites subject to different *local* magnetic moments from the bonded plutonium atoms. We illustrate this in Fig. 2 by taking the dot product between the unit magnetic vector of a plutonium ion μ_M and the unit vector that represents the

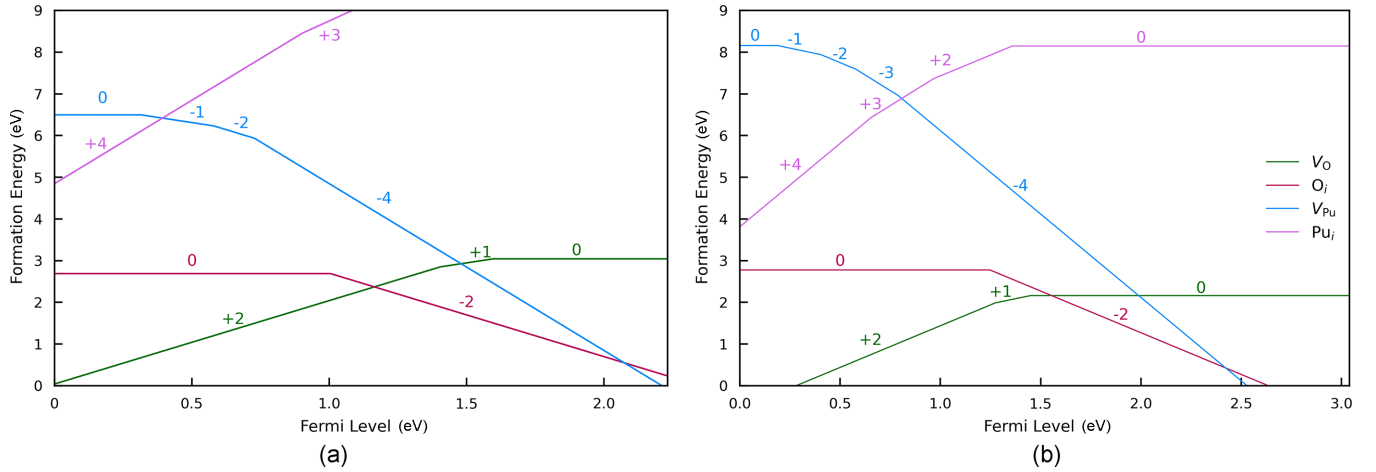


FIG. 3. Intrinsic defect formation energies for PuO_2 calculated as a function of the Fermi level. The temperature was fixed at 600 K and P_{O_2} at 10^{-20} atm. Only defect formation energies in the range of 0 to 9 eV are plotted, and the labeled numbers correspond to the charge state with the lowest formation energy at that point in the band gap. (a) $U = 4$ eV and (b) $U = 7$ eV.

bond from an oxygen atom to the same plutonium ion v_{Opu} . The resultant dot product for a particular oxygen atom is the same regardless of which of the bonded plutonium atoms is selected. The common denominator between the V_{O1} and V_{O2} sites is that the bond directions lie parallel (or antiparallel) to the magnetic vectors of the bonded plutonium atoms, and is shown by the dot product of the two vectors being equal to 3 (or -3). The other oxygen sites form an angle of either 70.53° or 109.47° between the bond direction and magnetic vector, the sum of which is 180° ; thus, these two sites form alternate angles to one another and are degenerately equivalent.

For as to why the V_{O1} and V_{O2} sites are higher in relative energy, we theorize that the removal of an oxygen atom that forms a bond parallel to the magnetic vector creates an instability in the $3k$ longitudinal AFM structure. This is shown in Table II, as the supercells containing the V_{O1} and V_{O2} defects express a greater degree of ferromagnetism, while the other sites with the same U parameter largely retain the AFM configuration (i.e., $\mu_k \approx 0$). While the magnetic moments of the individual plutonium atoms are largely unaffected in comparison to perfect PuO_2 ($\mu_B = 3.75$ with $U = 4$ eV; $\mu_B = 3.82$ with $U = 7$ eV), the direction of the magnetic vectors becomes misaligned with respect to the $3k$ AFM configuration for the nearest-neighbor plutonium atoms to the V_{O} site. This includes the plutonium atoms surrounding the V_{O2} site at coordinates $(\frac{3}{8}, \frac{3}{8}, \frac{3}{8})$ with $U = 4$ eV, despite showing a lower degree of ferromagnetism.

Further exploration of this disparity can be found in Tables S2–S5 in the Supplemental Material [67]. We observe that the difference in energy is not a consequence of a finite-size effect, as the $3 \times 3 \times 3$ supercell produced the same result. As did attempting to improve the orbital occupation of plutonium atoms through the U -ramping method, symmetry constraints, or by imposing the $3k$ AFM configuration through a constrained local moment approach. The latter test being perhaps the most interesting, as despite converging closer to a $3k$ AFM longitudinal solution, the relative energy remained higher. It is conceivable that occupation matrix control could circumvent the difference in calculated energies, although this method would be laborious for a full noncollinear defect analysis.

While Table II shows that a V_{O2} site with $U = 4$ eV almost relaxed into the same ground state as the other lattice sites, Tables S2–S5 [67] show it cannot be consistently and reliably achieved. A relative difference in energy of 0.2–0.3 eV is unlikely to substantially change the defect chemistry of a material, though, we still recommend that a plethora of defect sites are checked when using noncollinear magnetism to ensure that no anomalies in defect energies arise for sites that should theoretically be equivalent. Subsequently, in this work, we utilize the lowest-energy site of V_{O} obtained for all proceeding calculations.

C. Intrinsic defect formation energies

Figure 3 plots the defect formation energies of the intrinsic defects in PuO_2 as a function of the Fermi level for (a) $U = 4$ eV and (b) $U = 7$ eV. The range of the Fermi level is equivalent to the magnitude of band gap (E_b) of PuO_2 calculated with each U parameter. At a temperature of 600 K and an oxygen partial pressure of 10^{-20} atm, the formation energies between $U = 4$ and 7 eV show broadly similar trends. Both U parameters predict oxygen defects to be dominant, with V_{O}^{2+} having the lowest formation energies at Fermi levels closer to the valence band, while the more negatively charged O_i^{2-} defect becomes dominant towards the conduction band. The formation energies of V_{O} are notably lower in energy for $U = 7$ eV than $U = 4$ eV at equivalent Fermi levels. This is due to the reduced orbital interaction between plutonium and oxygen atoms when $U = 7$ eV in comparison to $U = 4$ eV; this is shown by the reduced Pu- f and O- p orbital hybridization in Fig. 1 for $U = 7$ eV. A reduced covalent interaction results in a weaker interaction between plutonium and oxygen, hence, less energy is required to break the Pu–O bond and create the vacancy.

The formally charged V_{Pu}^{4-} is the dominant plutonium vacancy charge state across the band gap with both U parameters, although the formation energies for $U = 4$ eV are lower than for $U = 7$ eV. One might expect the formation energies of V_{Pu} to be larger for $U = 4$ eV, due to the stronger Pu–O interaction, as stipulated with V_{O} . However, the opposite is

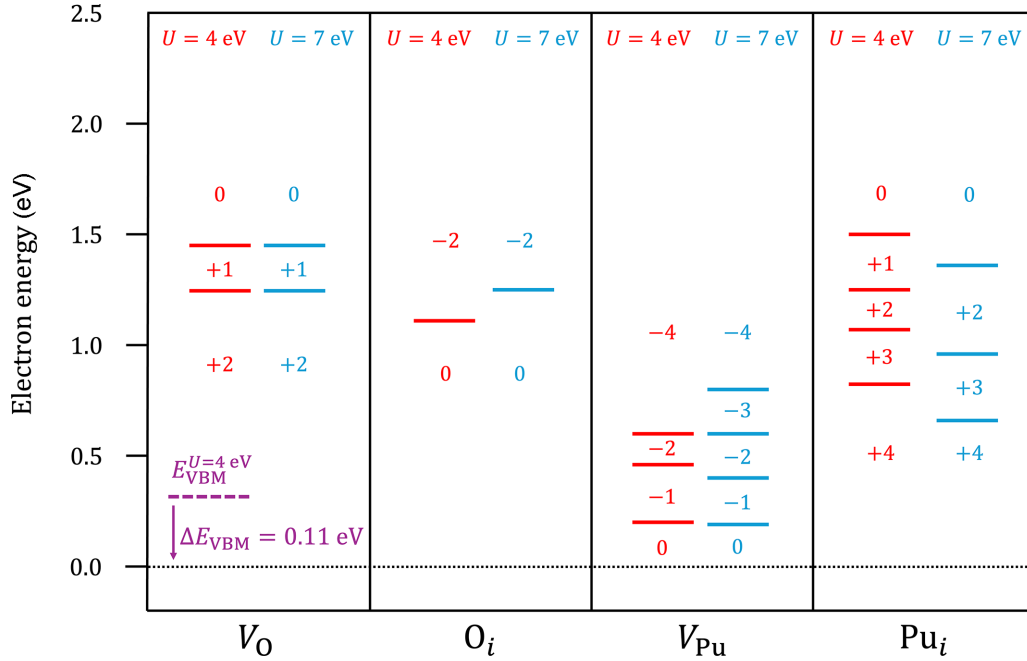


FIG. 4. Charge transition levels (CTL) of V_O , O_i , V_{Pu} , and Pu_i with $U = 4$ eV (red) and $U = 7$ eV (blue). Labeled numbers indicate the most stable charge state in that region. The bands were aligned by shifting the valence band of $U = 4$ eV down by 0.11 eV, such that the $+1|+2$ V_O CTL with both U parameters was equal.

true, and can be attributed to a shift in μ_{Pu} to satisfy Eq. (5). The value of μ_O is dependent only on P_{O_2} and temperature, and is equivalent in both U parameter models due to the common reference system used in Eq. (6). Meanwhile, μ_{PuO_2} increases as a function of increasing U parameter, thereby μ_{Pu} also increases. Larger values of μ_{Pu} disfavor V_{Pu} formation, as this represents an increase in the energy required to transfer Pu from PuO_2 to an infinite reservoir of Pu metal. Through the same inverted logic, the formation energies of Pu_i are higher for $U = 4$ eV than for $U = 7$ eV.

Another difference between the selected U parameters can be observed in the preferred charged states of V_O across the band gap; the formally charged V_O^{2+} occupies the widest range of Fermi levels when $U = 4$ eV, in contrast to the neutrally charged V_O^0 for $U = 7$ eV. The charge transition levels for all defects are, generally, slightly shifted towards the valence band for $U = 7$ eV in comparison to $U = 4$ eV. However, this observed shift can be attributed to the changing position of the valence band maximum with the U parameter [60,68]; the charge transition levels can be found to be approximately equal if the bands from both U parameters are aligned. Following the method of Freysoldt *et al.* [60], we shift the valence band maximum of $U = 4$ eV down by 0.11 eV, such that the $+1|+2$ charge transition level of V_O was equal with both U parameters. A comparison of the aligned charge transition levels is displayed in Fig. 4. The charge transition levels of V_O and V_{Pu} show strong agreement between U parameters. For the interstitial defects, the charge transition levels of Pu_i are within 0.1 eV across both U parameters, while the $0|-2$ transition of O_i differs by 0.3 eV. The work of Freysoldt *et al.* [60] and Alkauskas *et al.* [68] suggest that differences in transition levels around 0.2 eV show respectable agreement. Considering that the relative positions of the charge transition levels with both U parameters are approximately equal when

the bands are aligned, defects with more negative charge have an increased favorability when $U = 7$ eV due to the wider band gap. Consequently, charge compensation mechanisms and defect interactions through the Fermi level will vary with each U parameter, particularly in the regions of PuO_{2-x} , as there is a notable difference in the regions where the $+2$ and neutral charge states dominate for V_O . Next, we consider the following Frenkel pair (FP) and Schottky reactions in PuO_2 :

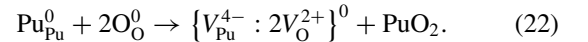
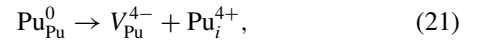
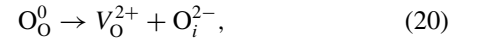


Table III compares the reaction energies of the unbound FP and Schottky defects with each U parameter, to those calculated by Neilson *et al.* [12] as well as the many-body Cooper-Grimes-Rushton (CRG) potential for the actinide dioxides [69]. Reaction energies are calculated by summing the defect formation energies of the reaction product defects at the valence band maximum. Table III shows a strong

TABLE III. Frenkel pair and Schottky reaction energies (in eV), calculated with $U = 4$ and 7 eV in this work, as well as the energies calculated by Neilson *et al.* [12] (PBEsol; $U = 7$ eV; 3k AFM long) and the CRG potential.

Reaction	This work		Neilson <i>et al.</i> [12]	CRG [69]
	$U = 4$ eV	$U = 7$ eV	$U = 7$ eV	Empirical
O-FP	4.74	4.71	4.89	4.94
Pu-FP	14.48	13.93	13.86	12.98
Schottky	8.83	8.99	7.65	10.38

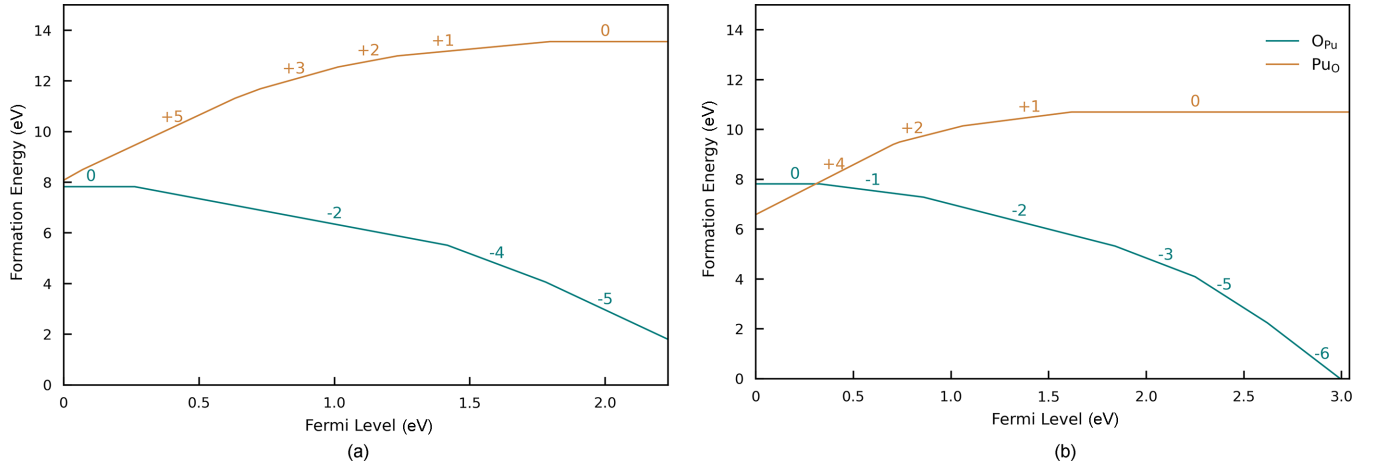


FIG. 5. Formation energies of the O_{Pu} and Pu_O antisite defects as a function of the Fermi level. Temperature was fixed at 600 K and P_{O_2} at 10^{-20} atm. (a) $U = 4$ eV and (b) $U = 7$ eV.

agreement in the oxygen FP reaction energies with both U parameters and closely corresponds with the energy calculated by Neilson *et al.* [12] and with the CRG potential. The Schottky reaction energy is also in close agreement with both U parameters. On the other hand, a significant difference was found for the plutonium FP energy with the selected U parameter, with $U = 4$ eV predicting this reaction to be approximately 0.5 eV higher in energy. Interestingly, while the FP reaction energies are in close agreement, Neilson *et al.* [12] predicted a lower Schottky reaction energy than we have, despite using the same set of DFT parameters (with $U = 7$ eV). It is possible the inclusion of vibration entropy in the defect formation energies has contributed to this, which we have not incorporated into this work. However, as noted by Neilson *et al.* [12], there is clear agreement in the reaction energies calculated from DFT and empirically; the oxygen FP has the lowest energy while the plutonium FP has the largest.

D. Antisite defects

It has recently been suggested that the Pu_O^{6+} and O_{Pu}^{6-} antisite defects, in addition to an assortment of other intrinsic defect cluster arrangements, may have an impact on the defect chemistry of PuO_2 [70]. However, it is not apparent whether a finite-size correction term was applied to the defect energies in this work. If no correction was applied to the defect energies,

the large charge magnitudes of these defects will be artificially stabilized by attraction to the neutralizing background jellium charge used in DFT calculations. Singh *et al.* [71] calculated defect formation energies of antisites in AnO_2 ($An = U, Pu, Th$), finding the formation energies to be significantly larger than all other defects. However, only charge-neutral defect configurations were considered. To further explore antisite defects, we calculated the formation energies of the Pu_O and O_{Pu} defects with an applied charge correction.

Figure 5 plots the formation energies of Pu_O and O_{Pu} as a function of the Fermi level, calculated under the same conditions as Fig. 3, with (a) $U = 4$ eV and (b) $U = 7$ eV. Figure 5 shows that the trends in the formation energies between the selected value of U are broadly similar. The formally charged Pu_O^{6+} and O_{Pu}^{6-} defects do not show much prominence in the calculated formation energies in the case of both $U = 4$ and 7 eV; only O_{Pu}^{6-} appears at the extremities of the band gap when $U = 7$ eV. For O_{Pu} , there is little discrepancy in the calculated formation energies with both U parameters, with the -2 charge state dominant across the band gap for both U parameters. Observation of the final relaxed defect structure in Fig. 6(a) shows that the antisite oxygen atom does not reside at the center of the plutonium vacancy, but rather, as a triple O-O-O bridge. The bond lengths in the bridge are 1.45 Å, corresponding with the O-O peroxide bond length in other oxide materials [72].

The lattice oxygen atoms bonded to the antisite oxygen have a Bader charge between $-0.66e$ and $-0.70e$. In comparison, the Bader charge of the lattice oxygen atoms in bulk PuO_2 ranges between $-1.20e$ and $-1.25e$, depending on the U parameter and defect charge state. The increase in Bader charge is possibly indicative of the formation of O^{1-} (or O_0^{1+}). It is rather interesting that DFT simulations prefer this mechanism for the accommodation of an antisite oxygen atom, as opposed to the oxidation of Pu^{4+} to Pu^{5+} . The Bader charge of the antisite oxygen was determined to be $0.00e$, and assuming this represents O^0 , then the sum of the charges of the constituents of the O_{Pu} defect, $V_{Pu}^{4-} + 2O_O^{1+} + O_{Pu}^0$, creates an overall charge of -2 . When the defect charge state is more negative, the additional electrons are accommodated as Pu^{3+} dispersed throughout the supercell, and do not localize around

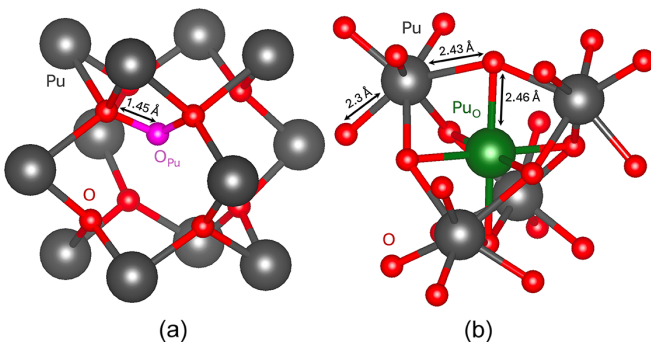


FIG. 6. Antisite defect structures for (a) O_{Pu}^{2-} and (b) Pu_O^{1+} with $U = 4$ eV.

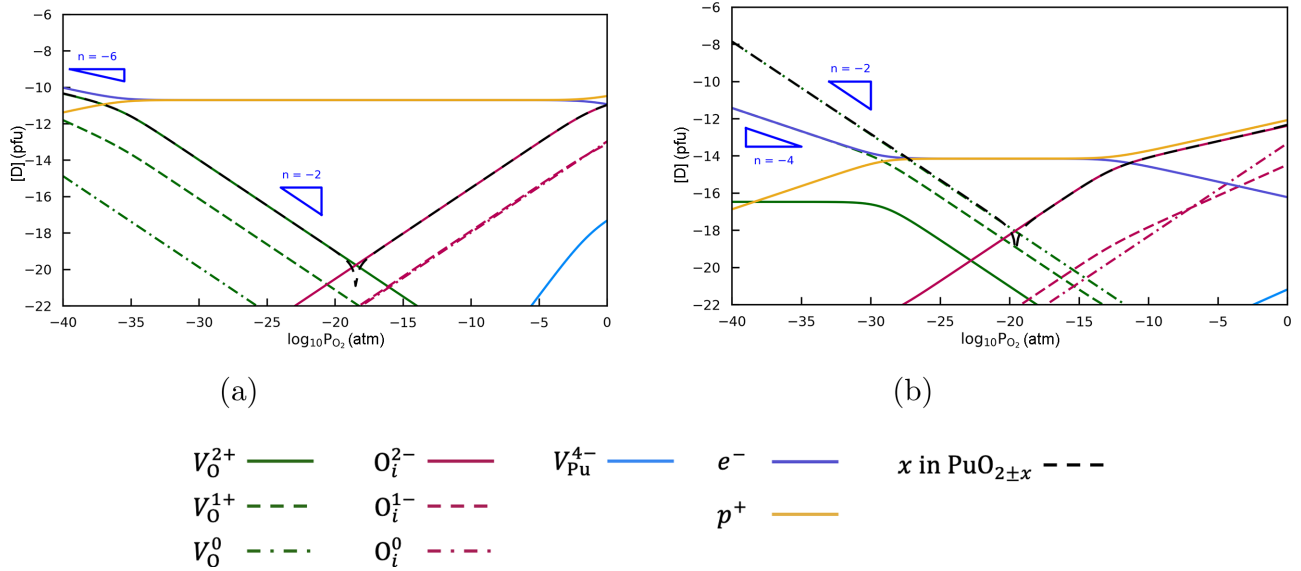


FIG. 7. Intrinsic defect concentrations of PuO_2 (per formula unit), as a function of P_{O_2} (standard atmosphere), at a fixed temperature of 600 K, where (a) $U = 4$ eV and (b) $U = 7$ eV. The blue triangles show the values of the exponent n in Eq. (29) at different regions.

the antisite defect. This explains why the -2 charge state is the most prominent across the band gap.

In the case of PuO , the $+1$, $+2$, and $+3$ are prominent at the center of the band gap with $U = 4$ eV, while for $U = 7$ eV, the wider band gap promotes the neutral and $+1$ charge states. The formation of PuO causes significant strain in the crystal, as per Fig. 6(b). The surrounding oxygen atoms surrounding the antisite contract to form bonds with the antisite plutonium atom, thereby causing a significant shift in bond lengths of the other neighboring atoms. With $U = 4$ eV, the $\text{PuO}-\text{O}_\text{O}$ bond length ranges from 2.25 Å for the $+6$ charge state, to 2.47 Å when the charge is neutral. Meanwhile, for $U = 7$ eV, the bond lengths range from 2.36 to 2.49 Å for the same charge states. This coincides with the lower formation energies of PuO predicted for $U = 7$ eV, whereby the increased bond lengths mitigate the likewise Coulombic forces surrounding the antisite, in addition to the generally lower formation energy of V_{O} .

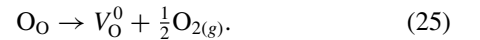
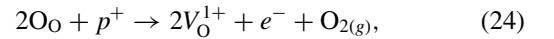
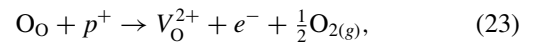
E. Defect chemistry of PuO_2

Figures 7(a) and 7(b) plot the defect concentrations of intrinsic PuO_2 as a function of P_{O_2} , where (a) $U = 4$ eV and (b) $U = 7$ eV. Only defects with concentrations greater than 10^{-22} pfu are displayed. Figure 7 shows that the defect chemistry of intrinsic PuO_2 with both U parameters is entirely governed by oxygen defects, as also found in the work of Neilson *et al.* [12] and Lu *et al.* [73]; the presence of V_{Pu} will not be significant until P_{O_2} becomes much greater than atmospheric pressure, corresponding with the stability of the cation sublattice. The absence of Pu_i , O_{Pu} , and PuO in both models also suggests that these defects will have a negligible contribution to the defect chemistry of PuO_2 , as also suggested by Singh *et al.* [71].

The predicted defect chemistry with each of the selected U parameters shows the difference in the formation energies of V_{O} and its preferred charge state. For $U = 4$ eV, V_{O}^{2+}

dominates at perfect stoichiometry, and requires charge compensation by free electrons at lower P_{O_2} . For $U = 7$ eV, the neutrally charged V_{O}^0 defect possesses the highest concentration of oxygen vacancies throughout all partial pressures quoted, as previously found by Neilson *et al.* [12]. The lack of charge compensation required for V_{O}^0 allows for the hypostoichiometric region to grow unrestricted with P_{O_2} , in contrast to $U = 4$ eV, where it is clear the total V_{O} concentration will become inhibited by the availability of free electrons.

Considering that oxygen defects are the main contributor to the predicted defect chemistry of PuO_2 , we can attribute the change in the stoichiometry of $\text{PuO}_{2\pm x}$ using these defects only. For the PuO_{2-x} region, the defect reactions governing the change in x at near stoichiometry are as follows:



The corresponding rate constants for each reaction are then

$$k_1 = [V_{\text{O}}^{2+}][e^-][p^+]^{-1}P_{\text{O}_2}^{\frac{1}{2}}, \quad (26)$$

$$k_2 = [V_{\text{O}}^{1+}]^2[e^-][p^+]^{-1}P_{\text{O}_2}, \quad (27)$$

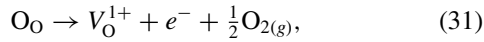
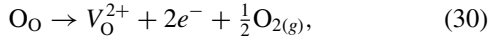
$$k_3 = [V_{\text{O}}^0]P_{\text{O}_2}^{\frac{1}{2}}. \quad (28)$$

Within the region of perfect stoichiometry in PuO_2 , Figs. 6(a) and 6(b) show that $[e^-] = [p^+]$. Substituting this equality into each of the rate equations finds that for all charge states

$$[V_{\text{O}}^q] \propto P_{\text{O}_2}^{\frac{1}{2}}, \quad (29)$$

where $n = -2$. Indeed, our defect models with both $U = 4$ and 7 eV show that the concentrations of all V_{O} charge states grow at a rate of $n = -2$ in the near-stoichiometric region.

As P_{O_2} continues to decrease, the concentrations of the charged defects, namely V_O^{2+} and V_O^{1+} , become limited due to the requirement for charge compensation by free electrons. As such, the concentration of electrons, and thus the conductivity of PuO_2 , becomes proportional to the charge of V_O . The defect reactions for the charge-compensating processes are as follows:



where the rate constants for the reactions are

$$k_4 = [V_O^{2+}][e^-]^2 P_{O_2}^{\frac{1}{2}}, \quad (32)$$

$$k_5 = [V_O^{1+}][e^-] P_{O_2}^{\frac{1}{2}}. \quad (33)$$

In Eq. (32), substituting $\frac{1}{2}[V_O^{2+}]$ for $[e^-]$ shows that the concentration of V_O^{2+} has a dependence of $n = -6$:

$$k_4 = [V_O^{2+}] \left(\frac{1}{2}[V_O^{2+}] \right)^2 P_{O_2}^{\frac{1}{2}}, \quad (34)$$

$$4k_4 = [V_O^{2+}]^3 P_{O_2}^{\frac{1}{2}}. \quad (35)$$

Thus,

$$[V_O^{2+}] \propto P_{O_2}^{-\frac{1}{6}}. \quad (36)$$

In Eq. (33), a dependence of $n = -4$ can be obtained by substituting $[V_O^{1+}]$ for $[e^-]$:

$$k_5 = [V_O^{1+}][V_O^{1+}] P_{O_2}^{\frac{1}{2}}, \quad (37)$$

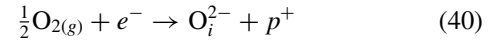
$$k_5 = [V_O^{1+}]^2 P_{O_2}^{\frac{1}{2}}, \quad (38)$$

$$[V_O^{1+}] \propto P_{O_2}^{-\frac{1}{4}}. \quad (39)$$

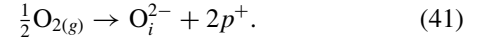
The conductive properties of PuO_{2-x} are, therefore, also dependent on whether V_O^{1+} or V_O^{2+} is the dominant charged defect, and Fig. 7 shows how this changes with the U parameter. When $U = 4$ eV, greater reducing conditions are required before the charge compensation of V_O^{2+} occurs, providing a region of conductivity with $n = -6$ dependence. This is due to the concentration of electrons and holes being notably several orders of magnitude larger for $U = 4$ eV than $U = 7$ eV, and can simply be attributed to smaller band gap reducing the formation energies of free electrons and holes. For $U = 7$ eV, the concentration of electrons in the hypostoichiometric region becomes equal to the concentration of V_O^{1+} . Thus, the conductivity of PuO_2 in this region has a dependence of $n = -4$, and corresponds with high-temperature experimental observations [74,75].

The hyperstoichiometric PuO_{2+x} region is governed by O_i^{2-} only for both $U = 4$ and 7 eV. At 600 K, the nonformally charged states are not significant until P_{O_2} becomes greater than atmospheric conditions. As such, the following defect reaction can be attributed to PuO_{2+x} in the near-stoichiometric

region:



or for larger x in PuO_{2+x} ,



Using similar logic as before, the concentration of O_i^{2-} can be found to have a dependence of $n = 2$ at near-stoichiometric conditions and $n = 6$ at larger x in PuO_{2+x} . Again, Fig 7 shows that, when $U = 4$ eV, the concentration of O_i^{2-} , and thus the degree of hyperstoichiometry, grows proportionally with $n = 2$ until larger P_{O_2} . In contrast, when $U = 7$ eV, the growth of the PuO_{2+x} region becomes inhibited, with a rate proportional to $n = 6$, due to holes providing charge compensation [12]. The formation of hyperstoichiometric PuO_{2+x} is still somewhat debated experimentally [76,77], with the mechanism suggested being the adsorption of H_2O on the surface [78]. This would evolve into H_2 gas, but no detectable quantities have been measured inside PuO_2 canisters in the UK [79], thus far. The total P_{O_2} measured in all cases has also been low [79]; as such, it is expected that the degree of hyperstoichiometry of PuO_2 inside the canisters, if any, will remain small.

Figure 8 shows how the predicted change in hypostoichiometry of PuO_2 in our defect models compares to the experimental observations of Swanson [80], Komeno [81], and Woodley [82] (data collated by Vauchy *et al.* [83]). The hypostoichiometric region of PuO_2 has been indicated to have a $n = -4$ dependence at high temperatures from experiments [74,83], suggesting that V_O^{1+} is the defect that governs both the conductivity and stoichiometry of PuO_{2-x} . This contrasts with the change in stoichiometry predicted when using $U = 7$ eV, showing a dependence of $n = -2$, a consequence of the wider band gap favoring the formation of V_O^0 . For a given P_{O_2} when using $U = 7$ eV, the values of x in PuO_{2-x} are larger in comparison to experimental results, suggesting an increased favorability of the hypostoichiometric region. This can also be related to the reduced hybridization of the Pu- f and O- p states in the valence band (Fig. 1).

For $U = 4$ eV, the predicted change in stoichiometry shows a strong agreement with the results of Woodley [82]. It is worth noting that Woodley [82] used a different method to calculate oxygen potentials in PuO_{2-x} , and cited higher concentrations of impurities in their samples than Swanson [80] and Komeno [81]. This has likely influenced the discrepancy in the calculated experimental oxygen potentials between the authors. Overall, the experimental data indicate a trend of $n = -2$ to -4 as P_{O_2} increases in Fig. 8. At low P_{O_2} , the reducing conditions result in the formation of V_O^0 , as with $U = 7$ eV, and has a dependence of $n = -2$; as P_{O_2} increases, the preference to form V_O^{1+} at higher temperatures arises, resulting in $n = -4$ when charge compensated by electrons. Within this small region, the $U = 4$ eV model agrees with the experimental trends, though the values of x predicted by our defect model are at least an order of magnitude smaller than experimental values. Our $U = 4$ eV defect model also predicts regions of $n = -6$ at a lower temperature of 600 K [Fig. 7(a)], which would be more representative of the conditions inside the PuO_2 canisters. The $n = -6$ region has

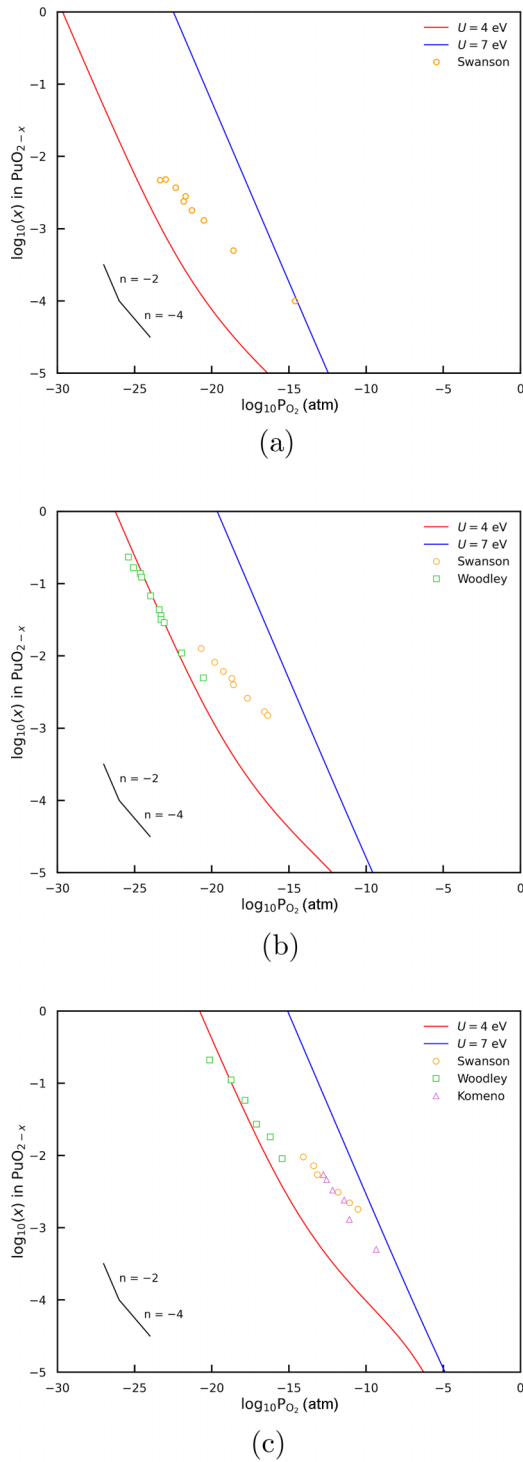


FIG. 8. The deviation in stoichiometry x in PuO_{2-x} as a function of P_{O_2} , calculated at a temperature of (a) 1173 K, (b) 1273 K, and (c) 1469–1473 K. Red and blue lines represent the defect models using $U = 4$ and 7 eV, respectively.

been theorized by the defect reactions and the predicted defect chemistry here, though, to our knowledge, it has not been measured in PuO_2 . This region is challenging to experimentally observe, however, as lower temperatures produce smaller values of x , and as noted by Vauchy *et al.* [83],

the measurement error scales logarithmically as x becomes smaller.

As when fitting to the electronic structure of the HSE06 hybrid functional, neither U parameter reproduces the exact experimental properties. Changes in stoichiometry and oxygen potential are more closely reproduced with $U = 4$ eV, while $U = 7$ eV shows the experimental $n = -4$ dependence on the conductivity of PuO_{2-x} as well as the mitigation of the hyperstoichiometric region. These are additional experimental properties that may also need to be considered when selecting a desirable U parameter. Qualitatively, both U parameters can be argued to be a reasonable approximation of the experimental trends for PuO_2 . However, hypostoichiometry is certainly more prominent for PuO_2 , thus, using $U = 4$ eV to reproduce the mechanisms for the change in stoichiometry will be a better approximation of the PuO_2 defect chemistry in this region.

F. Uranium defect formation energies

The defect chemistry of PuO_2 constantly evolves due to the radioactivity of plutonium. Nuclear transmutation of plutonium results in the concentrations of daughter elements increasing over time, many of which have differing redox potentials, causing a change in the conductive properties of PuO_2 . Uranium-234, produced via the α -decay of plutonium-238, is expected to be present in small concentrations in PuO_2 over longer periods of time ($^{238}\text{Pu } t_{1/2} \approx 88$ years). As such, understanding how the ingrowth of uranium affects the properties of PuO_2 is of interest.

Here, we study uranium as a defect substituted on a plutonium-lattice site (U_{Pu}), and how the choice of the selected U parameters affects the calculated defect formation energies. As uranium is a defect, selecting its desired U parameter cannot be simply fitted to bulk material properties, leaving the user with an arbitrary choice. One option is to simply apply the same U parameter to uranium as plutonium in the bulk (i.e., $U = 4$ or 7 eV). Another possible solution is to apply the same U parameter to uranium as in bulk UO_2 . Typical values have been found to be in the range of 3–4.6 eV [5,21,51,54,84–86].

Figure 9 illustrates how the choice of the U parameter for both plutonium and uranium impacts the defect formation energies of U_{Pu} . We compare the formation energies of U_{Pu} when the same U parameter has been applied to both plutonium and uranium ($U = 4$ and 7 eV), as well as when $U = 3.35$ eV for uranium, a value recommended by Pegg *et al.* [87] and recently used by Neilson *et al.* [61] to predict the defect chemistry of noncollinear AFM UO_2 . The charge states considered were $-1, 0, +1$, and $+2$, as this would represent the oxidation states of $+3$ to $+6$ if the charge in the simulation localized on the uranium atom.

When the $U = 4$ eV for plutonium [Fig. 3(a)], there is little difference between the selected U parameters for uranium on the defect formation energies predicted. This is unsurprising, given only the small difference in the U parameter assigned to uranium and that on the host plutonium. Table IV reflects this too, as the Bader charges and magnetic moments for uranium between $U = 3.35$ and 4 eV are almost identical, showing similar charge localization on the defect.

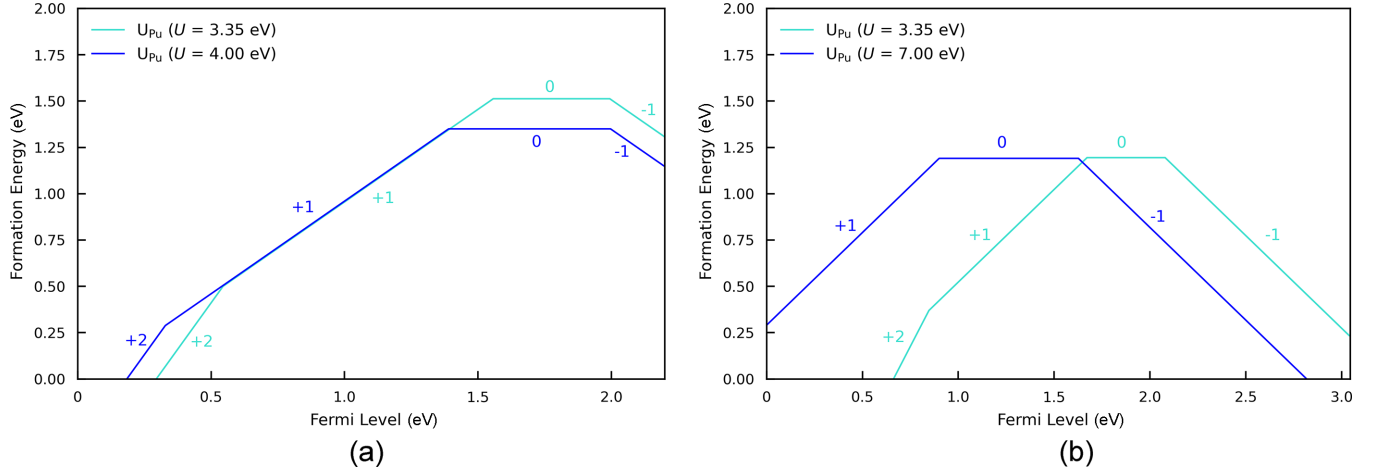


FIG. 9. Defect formation energies of U_{Pu} in bulk PuO_2 , calculated at $T = 600$ K and $P_{O_2} = 10^{-20}$ atm. Total uranium concentration fixed at 10^{-10} pfu; such a concentration was arbitrary, though was selected so that all favorable charge states had $E_f > 0$ eV in the band gap. Only the charge states with the smallest formation energy at each point across the band gap are displayed. The light blue lines represent uranium with a Hubbard correction of $U = 3.35$ eV, while the dark blue lines represent uranium with a Hubbard correction equal to plutonium in the bulk, (a) $U = 4$ eV and (b) $U = 7$ eV, respectively.

Near the top of the valence band in Fig. 3(a), the +2 charge state is preferred for U_{Pu} . Table IV shows the magnetic moment of uranium is almost zero in this charge state, and as the magnetic moments of the actinide elements stem from unpaired electrons in the f orbital, U_{Pu}^{2+} implies the accommodation of U^{6+} . Interestingly, the Bader charges of uranium in U_{Pu}^{2+} do not align with that of uranium in UO_3 , though this is likely due to the difference in coordination number with the oxygen atoms. For U_{Pu}^{1+} , the most dominant charge state for U_{Pu} , the average Bader charge with both U parameters for uranium is $2.80 e$, residing at the midpoint between the Bader charges of uranium in UO_2 and UO_3 . Considering that the known oxidation states of uranium in UO_2 and UO_3 are +4 and +6, respectively, this indicates that U_{Pu}^{1+} correlates with the accommodation of U^{5+} . Additionally, a magnetic moment of $0.42 \mu_B$ has been calculated for uranium, lower than that calculated for U^{4+} in bulk UO_2 , which is to be expected as there are fewer electrons localized in uranium's f orbital. At a Fermi level around 1.5 eV, there is a transition from the +1 to the charge-neutral state, followed closely by the -1 charge state close to the conduction band. Table IV shows that

TABLE IV. Bader charge (e) and magnetic moment (μ_B) of uranium in U_{Pu} when applying $U = 3.35$ and 4 eV to uranium's $5f$ orbitals; $U = 4$ eV for plutonium in the bulk. UO_2 ($3k$ AFM transverse [87]) and UO_3 (nonmagnetic) provided as reference for U^{4+} and U^{6+} .

Defect charge	$U = 3.35$ eV		$U = 4$ eV	
	Bader charge	μ_B	Bader charge	μ_B
-1	2.51	1.33	2.53	1.36
0	2.52	1.31	2.54	1.33
1	2.79	0.42	2.82	0.43
2	2.91	0.05	2.94	0.06
UO_2	2.53	1.36	2.54	1.36
UO_3	3.16	0.00	3.18	0.00

uranium in U_{Pu}^0 and U_{Pu}^{1-} has approximately the same Bader charge and magnetic moments as that of uranium in bulk UO_2 . This indicates that both these defect charge states represent U^{4+} , and that the extra electron in U_{Pu}^{1-} has localized to form Pu^{3+} . Indeed, examination of the plutonium Bader charges in the U_{Pu}^{1-} simulation cell shows that one plutonium atom possesses a Bader charge of $2.07 e$, in comparison to the average Bader charge of $2.42 e$ for plutonium in perfect PuO_2 . This depicts the formation of Pu^{3+} . The preferred charge states, and the localization of the charge in the supercells, align with the knowledge that oxidation and reduction is easier in UO_2 and PuO_2 , respectively.

In contrast, when $U = 7$ eV for plutonium [Fig. 9(b)], the choice of the U parameter for uranium can have a significant impact on the defect formation energies of U_{Pu} , causing a considerable shift in the charge transition levels predicted. Setting $U = 7$ eV for both plutonium and uranium suggests that U_{Pu}^{2+} is not favorable to form within the band gap of PuO_2 . Additionally, the +1 charge state is less dominant than when $U = 4$ eV and is only prevalent up to Fermi levels of 1 eV above the valence band. The charge neutral U_{Pu}^0 is preferred at the intermediate Fermi-level regions of 0.7 to 1.7 eV, and due to the wider band gap, U_{Pu}^{1-} is more dominant. One would assume that a larger U parameter on uranium would increase the propensity to form U^{3+} ; however, the Bader charges in Table V indicate that U_{Pu}^{1-} still consists of $U^{4+} + Pu^{3+}$. The formation of U^{3+} is not observed, even with a larger U parameter. On the other hand, if $U = 3.35$ eV for uranium, the +2 charge state is found to be favorable up to a Fermi level of 0.75 eV, where then the +1 charge state dominates up until the center of the band gap. This is more in accordance with the observations with $U = 4$ eV. The large disparity between the selected U parameters of uranium causes a considerable shift in charge transition levels of U_{Pu} . Moreover, the large disparity in the U parameters between plutonium and uranium appear to create anomalies in the trends of the Bader charges and magnetic moment of uranium, such that the defect

TABLE V. Bader charge (e) and magnetic moment (μ_B) of uranium in U_{Pu} when applying $U = 3.35$ and 7 eV to uranium's $5f$ orbitals; $U = 7$ eV for plutonium in the bulk. UO_2 ($3k$ AFM transverse [87]) and UO_3 (nonmagnetic) provided as reference for U^{4+} and U^{6+} .

Defect charge	$U = 3.35$ eV		$U = 7$ eV	
	Bader charge	μ_B	Bader charge	μ_B
-1	2.51	1.59	2.59	1.38
0	2.79	0.42	2.60	1.39
1	2.78	0.42	2.89	0.47
2	2.91	0.03	3.34	0.04
UO_2	2.53	1.36	2.54	1.40
UO_3	3.16	0.00	3.18	0.00

charge states do not directly correlate with the oxidation state of uranium. For $U = 3.35$ eV in Table V, the Bader charge and magnetic moment for uranium in U_{Pu}^0 suggests the formation of the defect complex $U^{5+} + Pu^{3+}$, rather than U^{4+} . The large difference in the U parameters between plutonium and uranium enforces a greater localization of electrons on plutonium, thus, there is a greater preference to form Pu^{3+} . When $q = -1$, the Bader charge of uranium corresponds with that of U^{4+} in bulk UO_2 , though there is a notable increase in its magnetic moment.

While we have shown that a range of U parameters could be adopted for uranium, it is important that the predicted defect chemistry remains in alignment with experimental observations. It is known that in UO_2 , uranium predominantly adopts a +4 oxidation state. Under oxidizing conditions, the +5 and +6 oxidation states of uranium can be accessed, providing charge compensation for the formation of hyperstoichiometric UO_{2+x} . Intuitively, it would therefore be desirable for the defect charge states of U_{Pu} to directly correspond with the different oxidation states of uranium. As such, the results from Tables IV and V indicate it may be preferable to have no more than a small difference in the U parameters between bulk and defect atoms. When the difference in U parameters is relatively large, the preference for an electron to localize on a plutonium atom over uranium results in no single charge state that represents an isolated U^{4+} defect; the defect containing U^{4+} is coupled with Pu^{3+} in the -1 charge state. This can lead to ambiguity of the different oxidation states of uranium in the defect model, as the concentration of U^{4+} will depend on charge-compensating mechanisms for Pu^{3+} .

G. Uranium defect chemistry

Figures 10(a)–10(d) show the defect chemistry of PuO_2 with a fixed dilute concentration of uranium at 10^{-4} pfu. This concentration represents the 0.1% concentration of uranium expected to be present in PuO_2 after 100 years of storage. Figures 10(a) and 10(b) set $U = 3.35$ eV for uranium, while Figs. 10(c) and 10(d) set the U parameter for uranium equal to that of plutonium in the bulk ($U = 4$ and 7 eV, respectively).

Considering the cases of $U = 4$ eV for plutonium in Figs. 10(a) and 10(c) first, we observe that the selected U parameter for uranium has little impact on the overall defect

chemistry, as would be expected, given the similar formation energies calculated in Fig. 9(a). Both figures indicate that uranium is mostly accommodated as U_{Pu}^0 , but with a significant contribution from U_{Pu}^{1+} . There is also a large concentration of U_{Pu}^{1-} , though this defect is essentially U_{Pu}^0 plus a nearby localized electron. In contrast, the concentration of U_{Pu}^{2+} remains small relative to the other charge states, and so it is not expected that U^{6+} will significantly contribute to the accommodation of uranium in PuO_2 . In the near-stoichiometric regions, charge compensation for U_{Pu}^{1+} is mostly provided by free electrons from the conduction band, while a not-insignificant proportion is also provided in the form of Pu^{3+} from U_{Pu}^{1-} . As P_{O_2} increases, O_i^{2-} takes over as the charge-compensating mechanism, as the presence of U_{Pu}^{1+} shifts the Fermi level further towards the conduction band, promoting hyperstoichiometry. Additionally, the concentration of V_{Pu}^{4-} is notably higher in concentration for the same aforementioned reasons.

The choice of U parameter for uranium when $U = 7$ eV for plutonium becomes much more significant. When $U = 3.35$ eV for uranium, the charge-compensating mechanism for U_{Pu}^{1+} at high P_{O_2} is V_{Pu}^{4-} , rather than O_i^{2-} . While both V_{Pu}^{4-} and O_i^{2-} are representative of hyperstoichiometry, they can have profoundly differing effects on the overall material properties of PuO_2 at higher length scales. Additionally, U^{5+} is predicted to be the most prominent oxidation state for uranium, as the U_{Pu}^0 defect, which has the largest concentration, represents a complex of $U^{5+} + Pu^{3+}$. On the other hand, utilizing $U = 7$ eV for uranium suggests that the presence of uranium in PuO_2 promotes hypostoichiometry. As per Fig. 9(b), the charge transition levels of U_{Pu} are substantially shifted towards the valence band at larger U values, resulting in an increased concentration of positively charged V_O defects. Considering that all our other defect models, as well as experimental observations, indicating that the presence of uranium in PuO_2 promotes hyperstoichiometry, it is likely the case that $U = 7$ eV is too large to be applied for uranium as a defect.

IV. SUMMARY

In this work, the impact of the selection of Hubbard- U parameter on the predicted defect chemistry of PuO_2 is explored. The results show that, regardless of the chosen U parameter, the intrinsic defect chemistry of PuO_2 remains dominated by oxygen defects, however, this choice does influence more nuanced details within the defect model. In particular, the chosen U parameter changes the preferred charge state of V_O at near stoichiometry: V_O^{2+} in the case of $U = 4$ eV, and V_O^0 for $U = 7$ eV. This is a consequence of the wider band gap and shifting of charge transition levels towards the valence band when $U = 7$ eV, favoring less positively charged defects. Furthermore, the formation energies for V_O are generally lower for $U = 7$ eV, due to the decreased hybridization between $Pu-f$ and $O-p$ states. These factors combine to create a different relationship between the predicted stoichiometry in $PuO_{2\pm x}$ as a function of the oxygen partial pressure. While neither tested U parameter exactly reproduces all experimental characteristics of the defect chemistry of PuO_2 , $U = 7$ eV predicts the $n = -4$ dependence on the conductivity in the

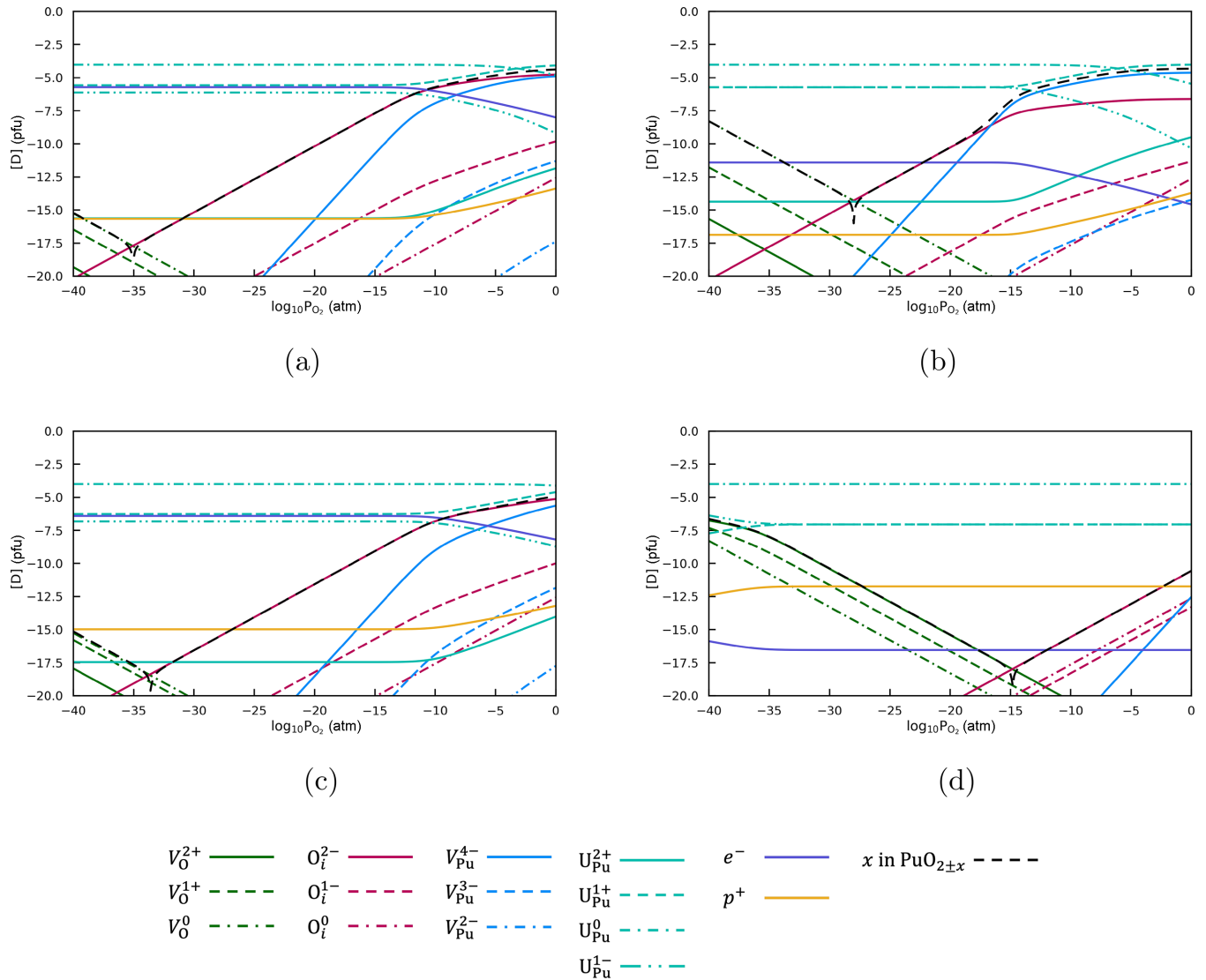


FIG. 10. Effect of the selected U parameters on the defect concentrations (per formula unit) in PuO_2 , with a fixed concentration of uranium at 10^{-4} per PuO_2 , calculated as a function of P_{O_2} (standard atmosphere). Temperature was fixed at 600 K. (a) $U(Pu) = 4$ eV; $U(U) = 3.35$ eV, (b) $U(Pu) = 7$ eV; $U(U) = 3.35$ eV, (c) $U(Pu) = 4$ eV; $U(U) = 4$ eV, and (d) $U(Pu) = 7$ eV; $U(U) = 7$ eV.

hypostoichiometric region and that the hyperstoichiometric region is less favorable, while $U = 4$ eV shows close alignment with how the stoichiometry of PuO_{2-x} changes with the oxygen partial pressure. Perhaps an intermediate U parameter of $U = 5$ or 6 eV could enable prediction of all of these characteristics; however, this would result in an electronic structure that is not fitted to the HSE06 hybrid functional band gap width, nor the characteristic Pu- f and O- p hybridized valence band from experiments. Therefore, this indicates that the choice of the U parameter can have a significant impact on the intrinsic defect chemistry of materials.

Additionally, it is shown that the selection of U parameters for any dopant ions should be carefully considered, particularly its relative value to U for any intrinsic species. For the accommodation of uranium in PuO_2 , applying $U = 7$ eV for both plutonium and uranium results in the promotion of hypostoichiometry in PuO_2 , where it may be expected that the opposite is true. Additionally, when there is a large disparity

between the U parameters of plutonium and uranium, the charge of a defect may not appropriately localize. This resulted in the formation of $U^{5+} + Pu^{3+}$ rather than the expected U^{4+} for the charge-neutral defect. Of course, the relative charge of a defect is *not* necessarily equivalent to the oxidation state of a particular ion, though, from our intuition, they can be correlated. As such, it is recommended that defect formation energies for dopants that require a U parameter are calculated using a few different values for U . This can help gauge how much the charge transition levels shift as a consequence of the selected U parameter of the dopant, and how the charge around the defect is localizing.

Overall, this work highlights how the selection of the U parameter can have important implications for the predicted defect chemistry of materials, and this should also be considered in the overall assessment of the model. Of crucial importance is the selection of the relative U parameters for any dopants. This has significant consequences and suggests

that it could possibly be inappropriate to employ widely adopted U parameters for elements in their bulk phases when as dopants. Looking specifically at PuO_2 , the results suggest that $U = 4 \text{ eV}$ for plutonium provides a closer agreement of the relationship between hypostoichiometry and oxygen partial pressure. The hypostoichiometric region is of course more apparent experimentally for PuO_2 . As the value of $U = 4 \text{ eV}$ was selected to offer a better description of hybridization in the valence band, this may provide a better approach to selection of the U parameter than selecting a value to match the band-gap width.

Crystal structures were visualised using VESTA [88]; charge corrections calculated using PYMATGEN [89]; plots generated using GNPLOT [90] and MATPLOTLIB [91]; density of states plotted using SUMO [92]; Bader charges calculated using scripts provided by the Henkelman Group [93].

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DATA AVAILABILITY

The data that support the findings of this article are openly available [94].

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