Energetics of halogen impurities in thorium dioxide

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A B S T R A C T

Defect energies for halogen impurity atoms (Cl, Br and I) in thoria are calculated using the generalized gradient approximation and projector augmented plane wave potentials under the framework of density functional theory. The energy to place a halogen atom at a pre-existing lattice site is the incorporation energy. Seven sites are considered: octahedral interstitial, O vacancy, Th vacancy, Th-O di-vacancy cluster (DV) and the three O-Th-O tri-vacancy cluster (NTV) configurations. For point defects and vacancy clusters, neutral and all possible defect charge states up to full formal charge are considered. The most favourable incorporation site for Cl is the singly charged positive oxygen vacancy while for Br and I it is the NTV1 cluster. By considering the energy to form the defect sites, solution energies are generated. These show that in both ThO_{2-x} and ThO_2 the most favourable solution equilibrium site for halides is the single positively charged oxygen vacancy (although in ThO_2, I demonstrates the same solubility in the NTV1 and DV clusters). Solution energies are much lower in ThO_{2-x} than in ThO_2 indicating that stoichiometry is a significant factor in determining solubility. In ThO_2, all three halogens are highly insoluble and in ThO_{2-x} Br and I remain insoluble. Although ½Cl_2 is soluble in ThO_{2-x} alternative phases such as $ZrCl_4$ exist which are of lower energy.

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1. Introduction

The incorporation of impurity atoms in a ceramic can have a strong influence on the chemical, mechanical, optical and diffusional properties of the material [1,2]. The eventual location of impurity atoms, be that through incorporation via chemical doping or ion implantation or fission, depends on the relative and absolute site solution energies. Much effort has been expanded to study the effect of impurity atoms on the properties of ceramic materials [3,4]. However, the effect of impurity atoms in materials that are being used or proposed to be used in nuclear reactors, especially as fuels, is less well understood, mainly due to their radiotoxicity, making experimental studies especially challenging [5]. Here, we have considered thoria (stoichiometric ThO_2 and substoichiometric ThO_{2-x}), a prospective ceramic nuclear fuel, especially in the form of $(Th,U)O_2$ and $(Th,Pu)O_2$ mixed oxides (MOX) [6]. Burn-up of the fissile isotopes of MOX fuels generates many radioactive volatile fission products (e.g., Kr, Xe, Cl, Br, I, Cs, Rb, Te) [7]. The inert gasses

(Kr, Xe) degrade mechanical properties (by causing swelling of fuel pins, the development of micro cracks and void formation [7,8]) and thermal properties (by reduction of thermal conductance in fuel-clad gap [9]). Volatile halogens are produced in smaller quantities (compared to gaseous fission products) and are also present in fuel as impurity atoms but their high electro-negativity means they are especially reactive, leading to detrimental chemical interaction with the fuel. They also cause the eventual degradation of mechanical properties through stress corrosion cracking and brittle fracture of the clad [8,10]. Thus, it is important to establish the solution energies and site preferences of halogens in the fuel matrix and their chemical interactions with the fuel.

Despite the important chemical interactions of impurity halogens with ceramic nuclear fuels, few literature studies consider the issue. Nevertheless, experimental studies have been reported for halogen generation and diffusion in urania especially since chlorine (^{35}Cl: 75.77% and ^{37}Cl: 24.23%) is present as an impurity (<0.5 ppm) in urania and urania based MOX, prior to reaction operation. During reactor operation, ^{36}Cl is produced by neutron capture due to the $^{35}Cl(n, \gamma)^{36}Cl$ reaction, which exhibits a high cross-section for thermal neutrons [11,12]. Cl_2 has to be considered as it is volatile

and [36]Cl in particular given its long half-life (3.01 × 10^{5}) years. A number of investigations into the release and diffusion of iodine and other volatile fission products (Xe, Te, Cs) have also been reported [13−15], using gamma-ray and secondary ion mass spectrometry.

Generally, experimental studies describe macroscopic phenomena rather than explaining the basic atomic scale incorporation and diffusion mechanisms of impurity halogens and linking this to their effects on material properties. Atomic scale computer simulation predictions of solution energies and site occupancies in nuclear materials therefore provide useful complementary information to help understand macroscopic observations (be that of the fuel or clad cracking). Moreover, the use of [232]ThO$_2$ based MOX as a reactor fuel in place of urania based MOX is relatively new [6,7]; as a result, no previous experimental studies of halogen solution and migration in thoria have been reported.

Atomic scale density functional theory (DFT) based calculations have provided understanding of basic point defect behaviour in solids for over a decade [1]. Especially for urania, DFT based approaches have been used to predict the behaviour of point defects (vacancies and self-interstitials) and the effects of impurities (He, Kr, Xe, I, Cs, Sr etc.) in urania [16−20]. Conversely, thoria has been less well studied. Some atomic scale modelling studies on trapping and diffusion of the volatile fission products (Xe, Br, Rb and Cs) [18,20] have been reported but these only considered the incorporation of impurity atoms in neutral point defects and neutral clusters of defects, leaving aside the possibility of incorporation in charged defect configurations. A more extensive study of Xe and Kr has been made [21], which did consider charged as well as neutral defect sites. This also considered solution in stoichiometric ThO$_2$ and substoichiometric ThO$_{2-x}$.

The study here focuses on the stability and chemical interaction of halogen impurity atoms (Cl, Br and I) in thoria by considering seven incorporation sites for these atoms: the octahedral interstitial, O vacancy, Th vacancy, Th-O di-vacancy cluster (DV) and the O-Th-O neutral tri-vacancy cluster (NTV) (for which there are three configurations [21]). For point defects and vacancy clusters, both neutral and all charged defect configurations, up to full formal charge, are considered for the calculation of incorporation energies (i.e. the energy to place a halogen ion on a pre-existing defect site). The most probable incorporation site for a halogen impurity is that with the lowest incorporation energy. This assumes that the concentration of defect sites is greater than the concentration of halogen ions. Incorporation energies are then used as the basis for calculating solution energies by considering the energy to form the defect (trap) site. This assumes that the concentration of halogen ions is greater than the availability of defect sites (which is appropriate for all but the very lowest defect concentrations [21]). The effect of van der Waals (vdW) interactions is considered and included for all possible defect configurations.

2. Theoretical methods

2.1. Calculation models

ThO$_2$ exhibits a face-centered cubic fluorite type crystal structure. We used the conventional cell of ThO$_2$ (Th$_4$O$_8$) to calculate the equilibrium lattice parameters and electronic properties. In order to calculate defect formation energies and the interaction of halogens with these defects, we used a 2 × 2 × 2 supercell containing 96 atoms. Fig. 1 shows the seven defect sites considered in this study.

2.2. Calculation methodologies

The calculations were carried out using the spin-polarized mode

of density functional theory as implemented in the VASP package [22,23]. The exchange-correlation term was modelled using the generalized gradient approximation (GGA) parameterized by Perdew, Burke, and Ernzerhof (PBE) [24]. The standard projected augmented wave (PAW) potentials [25] and a plane-wave basis set with a cut off value of 500 eV were employed. The valence electronic configurations for Th, Cl, Br, I and O were 6s^2 6p^6 6d^2 7s^2, 3s^2 3p^5, 4s^2 4p^5, 5s^2 5p^5 and 2s^2 2p^4 respectively. In order to describe the behaviour of the localized Th f states we included the orbital-dependent, Coulomb potential (Hubbard U) and the exchange parameter J within the DFT + U calculations, as formulated by Liechtenstein et al. [26]. We applied the values of U = 4.5 eV and J = 0.5 eV to the localized f states of Th. Charged defects interact with their next periodic images. In our previous study [21] we described the methodology as implemented by Makov et al. [27] to compensate for image charges when calculating defect formation energies.

A 2 × 2 × 2 supercell containing 96 atoms was used for the defect calculations. A 2 × 2 × 2 Monkhorst-Pack [28] k point mesh, which yielded 8 k points was used in all calculations. Structural optimizations were performed using a conjugate gradient algorithm [29] and the forces on the atoms were obtained from the Hellman-Feymann theorem including Pulay corrections. In all optimized structures, forces on the atoms were smaller than 0.001 eV/Å and the stress tensor was less than 0.002 GPa.

Halogen atoms and diatomic halogen molecules were relaxed in a 12 Å periodic cubic cell using only one k point (gamma point). We use both the energies of a halogen atom and half the total energy of a molecule to calculate incorporation energies.

The inclusion of van der Waals (vdW) interactions is particularly important for the incorporation of highly polarizable halogen atoms into ThO$_2$. In this work, dispersion has been included by using the pair-wise force field as implemented by Grimme et al. [30] in the VASP package.

In previous work [21] we partially demonstrated the validity of the parameters by showing the good correspondence between predicted and experiment values for lattice constants and bulk modulus for Th and ThO$_2$.

2.3. Definition of energetics

Bond dissociation energies (BDE) for diatomic halogen molecules were calculated using the following equation:

$$BDE = 2E[X] - E[X_2] \qquad (1)$$

where $E[X]$ is the energy of halogen atom and $E[X_2]$ is the energy of diatomic halogen molecule.

The incorporation energy of a halogen atom in the octahedral interstitial site was calculated using the following equation:

$$E[X_i] = E[X_i Th_n O_{2n}] - E[Th_n O_{2n}] - E[X] \qquad (2)$$

where $E[X_i Th_n O_{2n}]$ is the energy of a halogen atom incorporated into a ThO$_2$ supercell, $E[Th_n O_{2n}]$ is the total energy of the defect-free ThO$_2$ supercell and $E[X]$ is the energy of a single halogen atom. The incorporation energy of a halogen atom at a defect site, for example I at an oxygen vacancy site, is given by,

$$E[I(V_O)] = E[I_O Th_n O_{2n-1}] - E[Th_n O_{2n-1}] - E[I] \qquad (3)$$

where $E[I_O Th_n O_{2n-1}]$ is the total energy of the supercell containing an I atom at an oxygen vacancy and $E[Th_n O_{2n-1}]$ is the total energy of the cell containing an unoccupied oxygen vacancy.

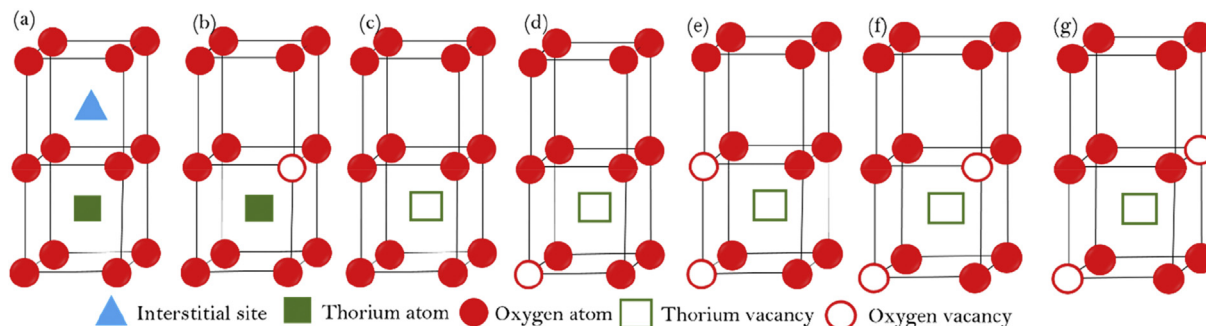Relative incorporation energies are important because

Fig. 1. Incorporation sites for halogen atoms considered in this study. (a) Interstitial site; (b) oxygen vacancy site; (c) thorium vacancy site; (d) di-vacancy (DV); (e), (f) and (g) neutral tri vacancies (NTV) 1, 2 and 3 respectively.

electronic charge is transported through the lattice much more rapidly than are fission products. Thus, whatever charge state the vacancy site into which the halide is placed may have had, the lattice will redistribute charge according to the balance between terms including site energy and charge neutrality. Incorporation energies are simply the building blocks from which we identify the most stable site and charge. Here, for example, the relative incorporation of I at an oxygen vacancy with +1 charge was calculated using the following equation:

$$E_{FC}\left[I(V_O^\bullet)\right] = E\left[I(V_O^\bullet)\right] + \left\{ E_f\left[(V_O^\bullet)\right] - E_f\left[(V_O^{\bullet\bullet})\right] \right\} \quad (4)$$

where $E_{FC}[I(V_O^\bullet)]$ is the incorporation energy of I with respect to an oxygen vacancy with +2 charge (i.e. the most favourable unoccupied charge state for an oxygen vacancy - see the supplementary data in reference [21] for details of defect charge preferences together with formation energy vs Fermi energy plots for different charge states), $E[I(V_O^\bullet)]$ is the incorporation energy of iodine, $E_f[(V_O^\bullet)]$ and $E_f[(V_O^{\bullet\bullet})]$ are the formation energies of oxygen vacancies with +1 and + 2 charges respectively. (Note: when comparing incorporation and relative incorporation energies, to differentiate, incorporation energies may be referred to as (absolute) incorporation energies).

3. Results and discussions

3.1. Energetics of halogen atoms

First we consider how the model parameters reproduce the halogen bond distances and bond dissociation enthalpies (BDE). Table 1 shows there is a reasonable agreement with the experiment but they are very similar to other theoretical values calculated using DFT.

3.2. Halogen atoms at interstitial sites

Calculations were first performed on a halogen atom occupying an octahedral interstitial site in defect-free ThO_2. In order to assess

the effect of vdW interactions, which describe the weak interaction of halogen atoms, the calculations were carried out with and without vdW corrections.

In all cases, the halogen atom occupies the symmetric octahedral interstitial position. The distortion introduced by the halogen, and the interatomic distances reported in Table 2, scale with atomic radius: the covalent radii of Cl, Br and I are 0.99 Å, 1.14 Å and 1.33 Å, respectively [33]. Thus the Th-Cl distance is shorter than the Th-I distance. While this is part due to the size of I compared to Cl, the electrostatic attraction between positively charged Th and negatively charged Cl compared to neutral I (as shown in Fig. 2) is also a contributing factor. This is a consequence of the difference in electron affinity [Cl: 349 kJmol^{-1}, Br: 324 kJmol^{-1} and I: 295 kJmol^{-1}] [32]. Similarly these two contributions (the charge on the halogen and the size of the halogen atom) also determine the X-O bond distance. Thus, while there will be a greater repulsion between negatively charged Cl and O than neutral I and O, the smaller atomic radius of Cl is also important and on balance, the Cl-O distance is shorter than the I-O distance. Overall, despite the charge transfer differences, the volume of the simulation supercell increases with the size of the halogen (see Table 2). The data in Table 2 also indicates that inclusion of the vdW dispersion correction (+D) does not significantly affect the bond distances. It does, however, reduce the supercell volume as dispersion is an attractive force.

In order to determine the stability of a halogen trapped at an octahedral interstitial site, we calculated the incorporation energies

Table 2
Calculated bond distances of Th/O-X and volume of the supercell containing a single interstitial halogen.

	Bond distances of Th/O-X (Å)				Volume (Å³)	
	Th-X		O-X		GGA	GGA + D
	GGA	GGA + D	GGA	GGA + D		
ThO_2	2.84	2.82	2.46	2.45	1460.23	1441.06
Cl:ThO_2	2.89	2.87	2.61	2.60	1473.50	1451.51
Br:ThO_2	2.93	2.92	2.64	2.62	1478.82	1457.71
I:ThO_2	3.01	2.99	2.67	2.66	1488.28	1467.00

Table 1
Computed bond lengths and bond dissociation energies of the three halogen diatomic molecules in this study. Comparison is made between experiment and a previous theoretical study.

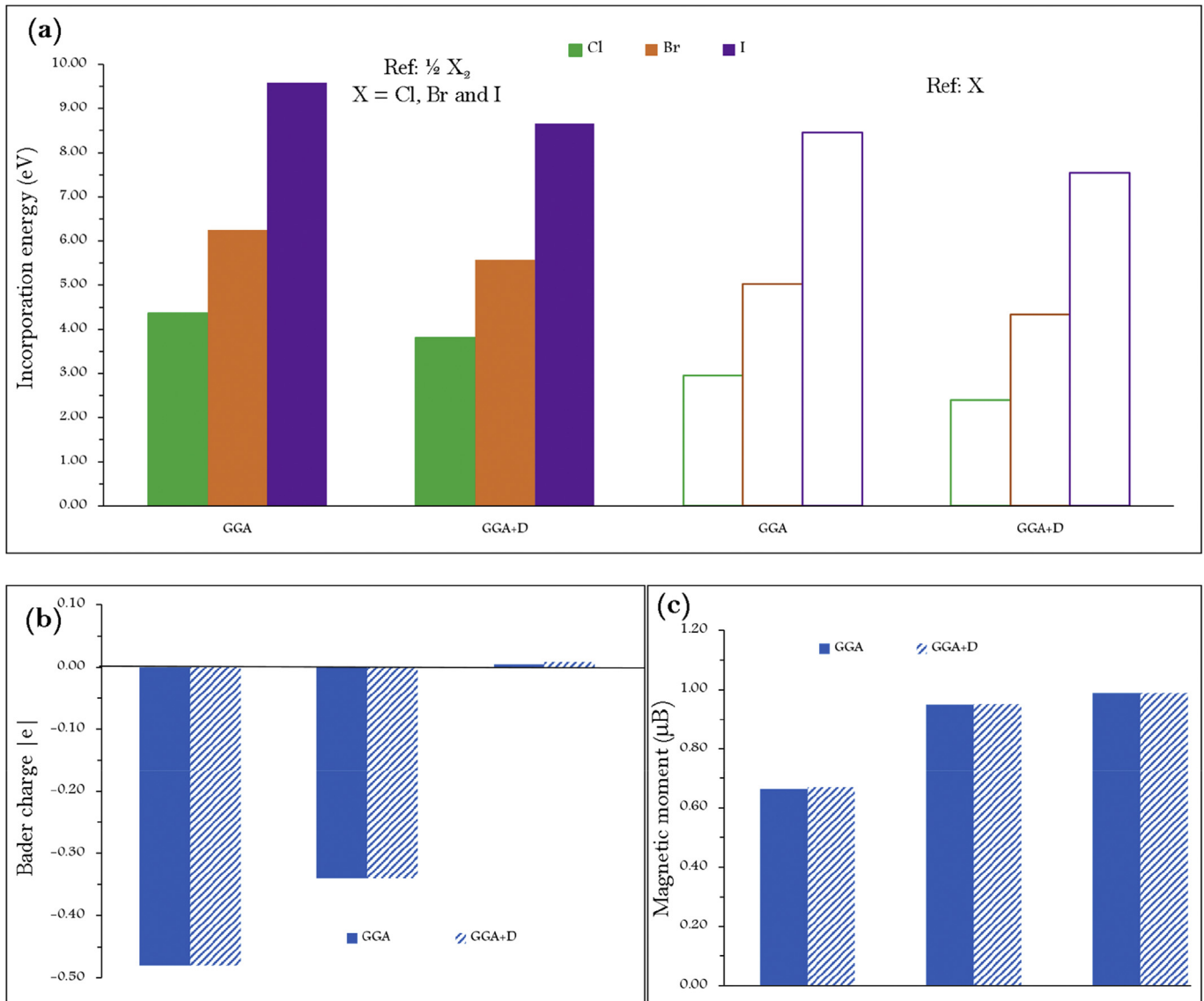| X-X	d(X-X)[Å]			Bond dissociation energy (eV)		
	This study	Other theory [31]	Expt [32]	This study	Other theory [31]	Expt [32]
Cl-Cl	1.998	2.023	1.988	2.82	2.68	2.51
Br-Br	2.315	2.321	2.281	2.47	2.38	1.99
I-I	2.686	2.700	2.665	2.24	2.12	1.57

Fig. 2. (a) Incorporation energies of halogen atoms at interstitial sites calculated using two halogen reference states with and without a dispersion correction (b) Bader charge on halogen atoms and (c) net magnetic moments of the supercell.

as defined by equation (2). To compare the current values with literature it was necessary to employ two different reference states for the halogen: the halogen atom (X) and half the halogen molecule (½ X_2). Positive values were predicted in all cases (see Fig. 2a) indicating that interstitial incorporation is highly endothermic. Clearly incorporation energies calculated using the energy of ½ X_2 are always more positive than for X as external energy must be provided to dissociate the X_2 molecule. The smaller Cl atom has a lower positive incorporation energy than Br, with I having the largest value, again showing the major influence of atom size. Fig. 2a also shows that dispersion facilitates incorporation because induced polarization is attractive but this is only a small perturbation.

Xio et al. [20] performed DFT + U calculations using the local density approximation on fission products including Br at an octahedral interstitial site, neutral vacancy defects and clusters in ThO_2 assuming a reference state of X (i.e. an isolated atom). Their calculated incorporation energy for a Br atom at octahedral interstitial site was 3.56 eV, which is less than the current value (due to

the effect of using the local density approximation compared to GGA [34]) but the value is still large and positive, consistent with incorporation being highly unfavourable.

Fig. 2b and c shows the Bader charges of the halogen atoms and the net magnetic moments of the supercells around the halogens respectively. The value of the Bader charge (and noting the approximations inherent in the Bader analysis [35,36]) depends on the relative electron affinity of the atom: Cl has the highest electron affinity and has gained 0.48 electrons from the surrounding lattice, Br gains 0.34 electrons (in good agreement with Xio et al. [20] who reported a charge transfer to Br of 0.22) while I is predicted to gain no charge.

Pure ThO_2 is non-magnetic (as reported elsewhere [37]). Once a halogen atom is introduced, the supercell will exhibit a magnetic moment, due to the electronic configuration of halogen, where the resultant spin is 1. In the supercell the spin is modified due to the influence of the charge transferred to the halogen so that for I the spin is 1 whereas for Cl it is 0.60. The overall magnetic moment associated with Br at an octahedral interstitial site predicted by Xio

et al. [20] is 0.88 agreeing well with the current prediction of 0.95. Since the addition of dispersion results in only very small changes to the relaxed structures of ions surrounding the interstitial species, it is not surprising that Fig. 2 shows there is no change in Bader charge or net spin.

3.3. Impurity atoms at oxygen vacancy site

We next consider incorporation of a single halogen species at a single oxygen vacancy with three possible (pre-existing) charge states (0, +1 and + 2) available (and including the dispersion correction here and in all subsequent calculations). Fig. 3 indicates that the incorporation energy is at least 4 eV lower compared to that in an interstitial site, reflecting the greater space available at the oxygen vacancy site. The oxygen vacancy into which it is most favourable to incorporate halogens is that with an overall +1 charge (i.e.$V_O^{\bullet}$). This is because the halogen will assume the single electron to complete its p-shell. The second most stable site is a neutral vacancy. Cl^- is the halogen ion closest in size to an oxygen ion, Cl therefore exhibits the most favourable incorporation energy, irrespective of the charge of the site. The Br atom is slightly larger and therefore its incorporation is less favourable. The incorporation of I is always energetically unfavourable.

In our previous work [21] we demonstrated that there is a formation energy preference in thoria for the fully (ionic) charged oxygen vacancy defect, $V_O^{\bullet\bullet}$, over $V_O^{\bullet}$, which is of lower energy than V_O^X. Thus, we have also calculated the 'relative incorporation energies' for halogens in oxygen vacancy sites (Fig. 3b) as we did in previous work on Xe and Kr incorporation [20] (i.e. relative to the lowest vacancy $V_O^{\bullet\bullet}$). The results (in Fig. 3) show that the $V_O^{\bullet}$, site remains the most favourable site for the incorporation of halogen. Also, since $V_O^{\bullet\bullet}$ formation is not much more preferable over $V_O^{\bullet}$, the

difference in relative incorporation v's (absolute) incorporation energies is slight — as will be evident, this is not the case for other defect sites.

For Xe and Kr, previous work [21] showed the highest charged oxygen vacancy ($V_O^{\bullet\bullet}$) provides the site with the lowest incorporation energy. This is because both the Xe and the Kr have complete outer electron shells and unlike halogens will not easily accommodate additional electrons.

Bader analysis shows (see Fig. 3c) that the charge gained by a halogen when it is incorporated at an oxygen vacancy again increases with the electron affinity of the halogen. Interestingly the magnetic moments of the supercells are almost zero except for I incorporated in a $V_O^{\bullet\bullet}$. In order to better understand the overall magnetic moments, we first calculated the magnetic moments of the halogen free oxygen vacancy containing supercells with 0, +1 and +2 charges: these are 0.00, 1.00 and 0.00 respectively. Thus, consider first the I atom, which has spin 1, residing in a $V_O^{\bullet\bullet}$. Since the halogen free supercell has spin zero and since I attracts little charge from the lattice, the overall spin of the halogen containing supercell is 1. Similarly, halogen atoms (spin 1) incorporated at a $V_O^{\bullet}$ (supercell spin 1) results in a halogen containing supercell of spin zero (this is consistent with the change in the Bader charge of the halogens which indicate that they are now negative ions — that is, they have incorporated the single electron to complete the halogen outer p-shell). What is less straight forward to explain is the incorporation of a spin 1 halogen into V_O^X supercells (of zero spin) leading to a halogen containing spin zero supercell. In these cases the halogen has no electron from the V_O^X site to associate (as the V_O^X site is charge neutral). However, the Bader charge (Fig. 3c) shows the halogens do attract charge from the lattice which completes their p-shell leading to spin zero.

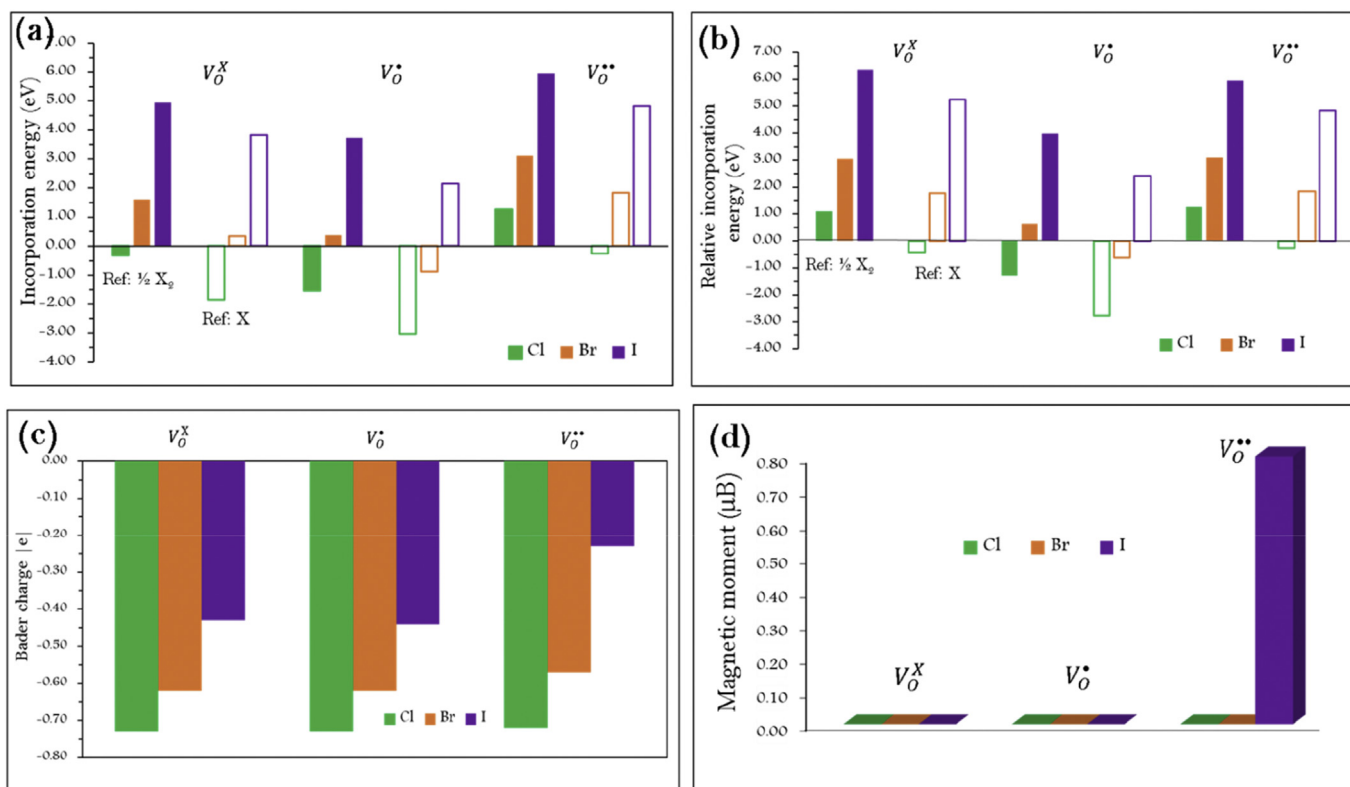According to the DFT calculation by Xio et al. [20], the calculated

Fig. 3. (a) Incorporation energy (b) relative incorporation energy (c) Bader charge on halogen atoms (d) net magnetic moments of supercells where Cl, Br or I occupies a vacant oxygen site.

incorporation energy, Bader charge and magnetic moment of Br occupying the V_O^X site are -0.38 eV, -0.50 and 0.00 respectively. While the Bader charge and magnetic moment agree with the current values of -0.62 and 0.00, the current incorporation energy is ~ 0.7 eV less favourable. This is because, as mentioned earlier, the local density approximation overestimates the binding energy — though we note that this site is the least favourable to be occupied and will therefore not be significant in overall defect processes.

3.4. Halogen atom incorporation at the thorium vacancy site

Five different charge states of the Th vacancy have been considered: neutral V_{Th}^x, the single negative charge V_{Th}', the double negative charge V_{Th}'', triple negative charge V_{Th}''' and quadruple negative charge V_{Th}''''. The incorporation energies (Fig. 4a) show a preference for halogens to occupy the neutral vacancy and in these cases incorporation is exothermic. This is because of there is a $4+$ charge around the vacancy to balance the lack of Th^{4+} cation, so that the halogen atom donates charge to part compensate for this, as evidenced by the positive Bader charges on the halogen ions. The degree of positive charge depends on the electronegativity of the halogen atom with the Cl atom exhibiting a less positive charge compared to the I atom. This is reflected in the incorporation energies so that the more highly positive charged I ion has a more favourable (negative) incorporation energy than Cl. The calculated incorporation energy, the Bader charge and magnetic moment for a Br atom occupying this neutral vacancy site were -3.16 eV, $+1.03$ and 1.00, agreeing reasonably with the corresponding values -4.69 eV, $+1.10$ and 0.83 calculated by Xio et al. [20].

The positive halogen Bader charge (Fig. 4c) decreases gradually when the halogen is incorporated from V_{Th}^x to V_{Th}'''', as negative charge is being introduced around the vacancy site. As a consequence, from V_{Th}^x to V_{Th}'', the preference in the (absolute) incorporation energy I > Br > Cl is maintained. However, in the case of V_{Th}''' and V_{Th}'''', the trend is reversed so that Cl > Br > I, since less charge is transferred from the halogen and the size of the halogen atom becomes the dominant factor.

The relative incorporation energy (Fig. 4b) is then calculated (see equation (4)) by adding the energy to charge of the vacancy from its most stable to the alternative charge. Relative incorporation energies favour Cl and Br atoms occupying the V_{Th}''' defect and I occupying (by a small margin) the V_{Th}'' defect. If we assume that a halogen atom occupies the most favourable V_{Th}'''' vacancy defect (e.g. Cl_{Th}''''), then the process of gaining an electron from the lattice to become Cl_{Th}''' is exothermic. Importantly, however, the relative incorporation energies are all positive — that is, the overall process of halogen relative incorporation into thorium vacancy sites is endothermic.

If we compare relative incorporation at the most favoured thorium vacancy sites to that in the most favoured oxygen vacancy site (i.e. into $V_O^\bullet$ compared to V_{Th}''' or V_{Th}''), incorporation of Cl and Br is clearly favoured at $V_O^\bullet$ but I is favoured at V_{Th}'' marginally over $V_O^\bullet$. This is a result of the higher electron affinities of Cl and Br, which therefore more readily assume the single charge of the $V_O^\bullet$ site compared to the lower electron affinity of I, which therefore more readily donates charge to the V_{Th}'' site.

Since of thorium vacancy sites, only I at a V_{Th}'' site is energetically important, consider first the calculated magnetic moment of the halogen free V_{Th}'' containing supercell, which is ~ 2. Then, the magnetic moment of a supercell with an I atom is ~ 3 (see Fig. 4d). The Bader analysis (Fig. 4c), shows the I atom has transferred ~ 1 electron to the lattice leaving its p shell open with a spin of 2 but pairing one of the two surrounding oxygen hole states, so that the overall spin of the supercell is 3. Other halogen spin states can be explained
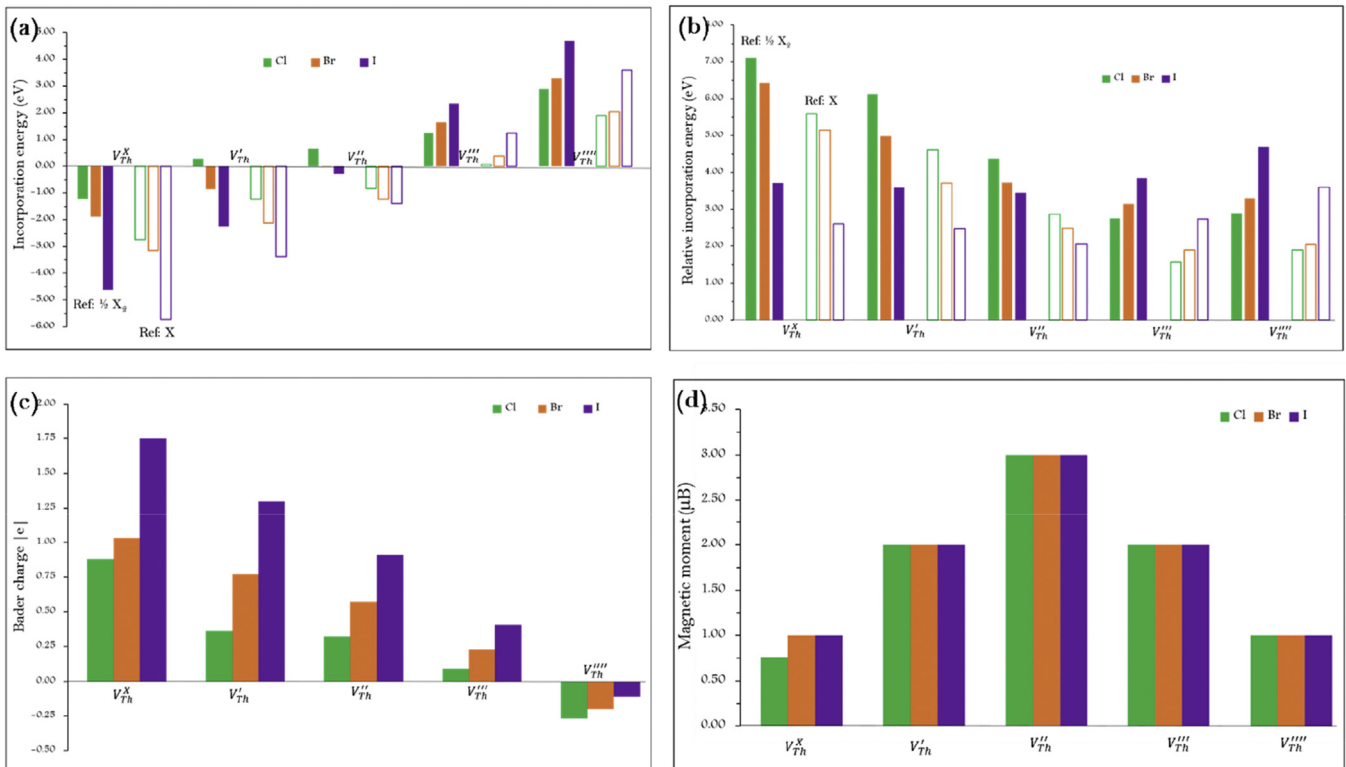

Fig. 4. (a) Incorporation energy (b) relative incorporation energy (c) Bader charge on halogen atoms and (d) net magnetic moments of the supercell containing Cl, Br and I atoms occupying the Th vacancy site with five different possible charge states.

similarly. (Note: The magnetic moment of the neutral thorium vacancy defect calculated by Xio et al. [20] is 3.37 agreeing reasonably well with the current value of 3.79).

3.5. Halogen atoms incorporated at the di-vacancy (DV) cluster

A di-vacancy (DV) cluster consists of a thorium vacancy adjacent to a nearest neighbour oxygen vacancy. We consider three charge states: DV(2-), DV(1-) and DV(0). Fig. 5a indicates that incorporation energy of Br and I is negative and favoured at the DV(0) cluster over DV(1-) and DV(2-). Conversely, for Cl the incorporation energy is much closer to zero and essentially independent of cluster charge. The negative energies for Br and I are a consequence of the charge transfer from Br and I to fill a hole state on adjacent oxygen ions - that form as a consequence of the missing Th^{4+} ion (see the Bader charges for Br and I in Fig. 5c). Cl being more electronegative does not donate charge (see Fig. 5c) and thus the incorporation energy is not as favourable. For the charged clusters, DV(1-) and DV(2-), incorporation energies become less favourable due to the reduced demand for charge transfer. According to the calculation by Xio et al. [20], for a neutral Br atom in a neutral di-vacancy cluster, the incorporation energy, the Bader charge and magnetic moment are −3.11 eV, +0.50 and 0.82 agreeing well with our calculated values of −2.87 eV, 0.53 and 0.99 respectively.

Since $V_{Th}^{''''}$ and $V_O^{\bullet\bullet}$ are the most favoured individual vacancy charge states, it is not unexpected that the DV(2-) cluster is the most favoured unoccupied di-vacancy charge state (for further discussion see Ref. [21]). Furthermore, when considering relative incorporation energies, in previous sections, it was demonstrated that $V_O^{\bullet}$ and $V_{Th}^{''''}$ are the favourable sites for halogens. If we combine these two vacancies we again obtain a DV(2-) host cluster. Fig. 5b

shows that there is a strong relative incorporation preference for accommodation of halide in the DV(2-) cluster. For ½Cl$_2$, however, the relative incorporation energy in DV(2-) is more than 1eV less favourable than in $V_O^{\bullet}$. Conversely for ½I$_2$, though positive, the relative incorporation energy is ~3eV lower in a DV(2-) cluster, while for ½Br$_2$, there is no preference. This simply reflects the relative sizes of the three halides and the greater space available in a DV cluster.

Given the preference to incorporate ½I$_2$ and ½Br$_2$ in a DV(2-) cluster, consider first that the magnetic moment of a halogen free supercell with a DV(2-) cluster is zero. Since, as Fig. 5c shows, there is little charge transfer to I or Br in a DV(2-) cluster, the incorporation of these spin 1 atoms therefore results in a supercell with an overall spin of 1. Again, the spins of other cluster combinations can be explained similarly.

3.6. Halogen atoms at the neutral tri-vacancy (NTV) cluster

The incorporation of a second near neighbour oxygen vacancy to a DV cluster results in a (charge) NTV. There are three possible NTV near neighbour cluster configurations (see Ref. [21]): with the two oxygen vacancies orientated closest together NTV1, furthest away NTV3 and intermediate NTV2 (see Fig. 1). Since the oxygen vacancies have opposite effective charge they repel so that the NTV3 configuration exhibits the lowest (unoccupied) cluster formation energy [21]. Fig. 6, however, shows that a single halogen atom is incorporated more favourably in the NTV1 cluster. This is because the NTV1 configuration provides a more effective volume for a large halide atom. Incorporation energies for all three halides are negative (exothermic) into a NTV1 cluster. Incorporation of Cl is most favoured due to its smaller size and higher electron affinity and
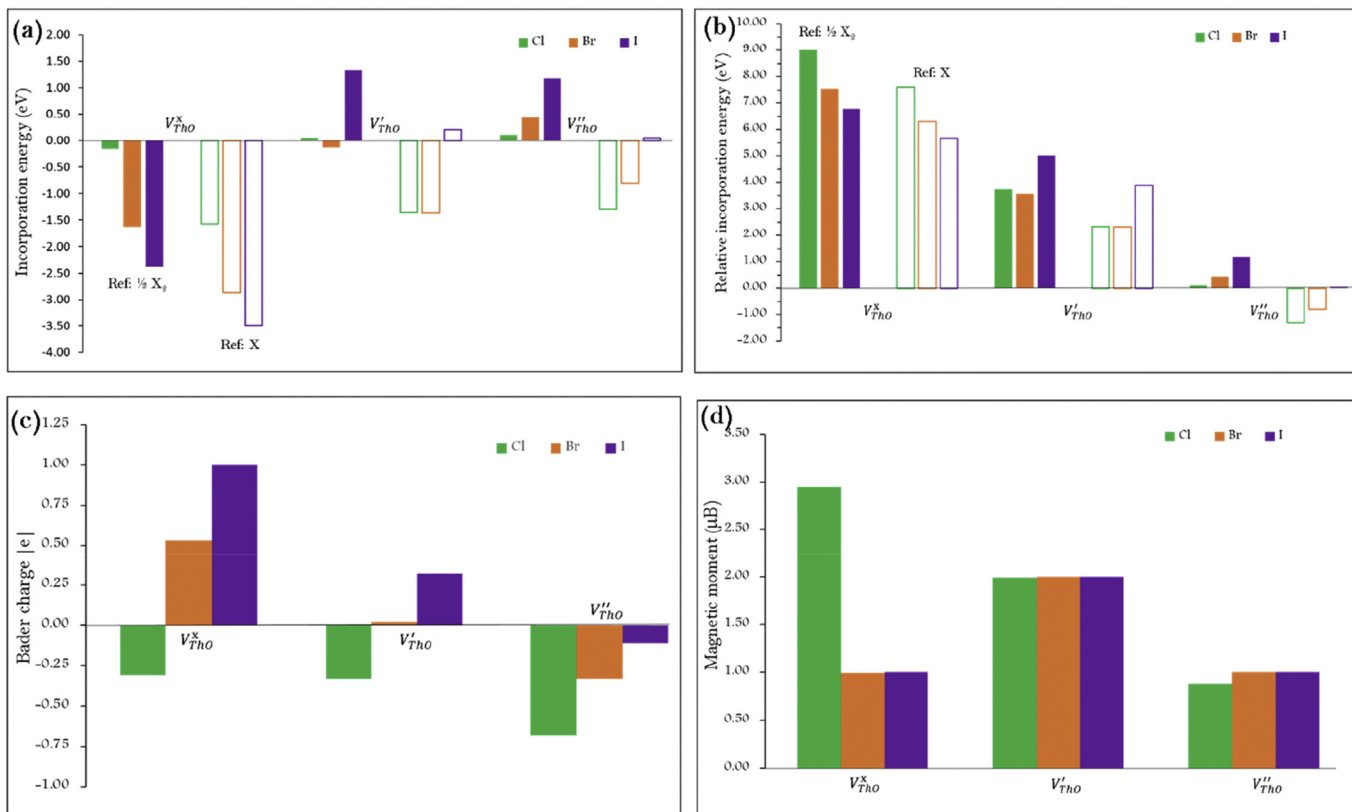

Fig. 5. (a) Incorporation energy (b) relative incorporation energy (c) Bader charge on halogen atoms and (d) net magnetic moments of the supercell containing Cl, Br and I occupying the DV cluster with three different charge states: DV(2-), DV(1-) and DV(0).
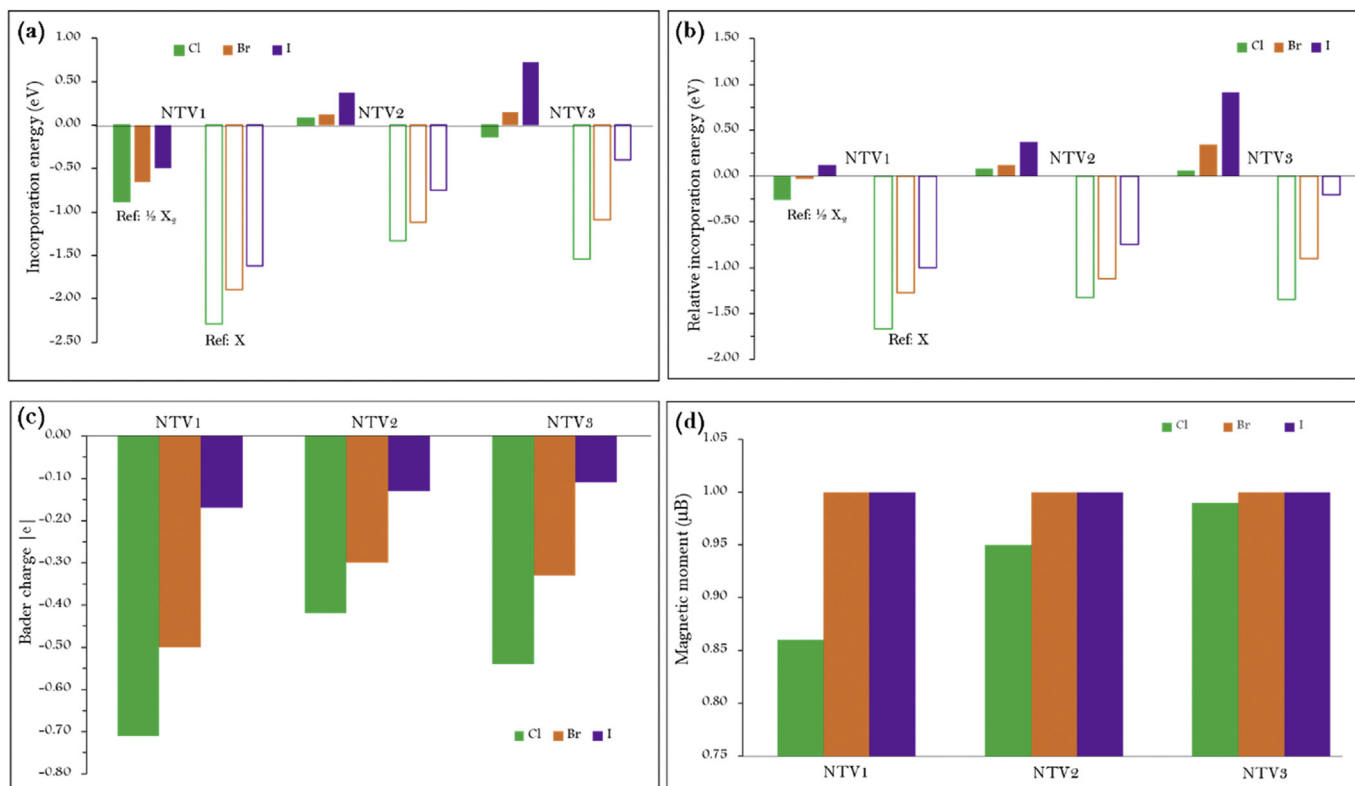
Fig. 6. (a) Incorporation energy (b) relative incorporation energy (c) Bader charge on halogen atoms and (d) net magnetic moments of the supercell containing a Cl, Br or I in each of the three NTV defect cluster configurations.

thus highest Bader charge (see Fig. 6c).

When relative incorporation energies are considered (relative to the most stable NTV cluster configuration), the overall preference for incorporation of halide into a NTV1 cluster remains. This is because, the difference in unoccupied cluster formation energies are smaller than the difference in halide incorporation preference. Nevertheless, it is important to consider relative incorporation because such energies take into account that oxygen vacancies can re-orientate more quickly than transport of halide atoms.

3.7. Overall relative incorporation energies

Incorporation energies assume that all trap sites are available for halide species, that is, the concentration of halide is much lower than the concentration of trap sites. Relative incorporation energies further assume that specific trap sites will assume their lowest charge or orientation configuration. By comparing the relative incorporation energies it is possible to predict into which trap sites the halide species will be preferentially incorporated. Table 3 suggests that $\frac{1}{2}Cl_2$ will occupy $V_O^{\bullet\bullet}$ sites but $\frac{1}{2}Br_2$ and $\frac{1}{2}I_2$ will occupy NTV1 clusters. Furthermore, the values suggest that $\frac{1}{2}Cl_2$ is readily

Table 3
Relative incorporation energies of halogen atoms (from $\frac{1}{2}X_2$) at the most favourable charge state or cluster configuration.

	Relative incorporation energy (eV)					
	Int	$V_O^{\bullet\bullet}$	V_{Th}''	V_{Th}''''	DV (2−)	NTV1
Cl	3.81	−1.27	4.38	2.73	0.11	−0.26
Br	5.57	0.64	3.73	3.15	0.44	−0.03
I	8.67	3.99	3.44	3.85	1.17	0.12

incorporated into $V_O^{\bullet\bullet}$ sites so that any chloride molecules will become trapped as single ions in these defects so long as such defects are available and chloride can be transported to the sites. Of course, these energies are enthalpies and at higher temperature entropy (particularly that exhibited by Cl_2 molecules) should be taken into account. However, although such terms will reduce the overall preference for trapping, the $\frac{1}{2}Cl_2$ trap energy is sufficiently high to overcome entropy contributions which are ~ kT. Conversely, $\frac{1}{2}I_2$ will not be readily incorporated into trap sites and will preferentially remain as a gas species — although the current study does not preclude $\frac{1}{2}I_2$ reacting in other ways and be bound into an alternative solid. $\frac{1}{2}Br_2$ exhibits such a small trap energy it too will not be strongly bound into trap sites although as with I_2, the kinetics of transport of these species through the fuel matrix may mean their release is gradual.

3.8. Solution energies

Solution energies are established by combining relative incorporation energies with the formation energies of the equilibrium solution sites. The methodology and formation energies of equilibrium solution sites have been reported previously [21] and allows us to consider and compare solution into stoichiometric ThO_2 and sub-stoichiometric ThO_{2-x}. Solution energies take into account that halide concentrations may be higher than the trap (solution) site concentrations (in the case of Cl this may be due to the original Cl concentration but in the case of I and Br the concentration will increase as burn-up proceeds). It is also now necessary to be cautious about what phase might be competing with solution in thoria (i.e. the alternative phase the halide might form with other species in the system). Here, initially, we assume gaseous species, $\frac{1}{2}$

I_2 etc., but these are reactive species.

The solution energies (Table 4) predict the most stable (equilibrium) solution sites for $\frac{1}{2}Cl_2$, $\frac{1}{2}Br_2$ and $\frac{1}{2}I_2$ in ThO_2 and ThO_{2-x}. In ThO_2, all values are positive indicating that halogen molecules are insoluble in thoria. Interestingly the most stable solution site for halides is $V_O^\bullet$, which is because this site has the lowest (but still significant) formation energy. In the case of $\frac{1}{2}I_2$, though, solution in $V_O^\bullet$, DV or NTV1 sites is essentially the same, a consequence of the larger size of I. In ThO_{2-x}, the lowest solution energy site is again $V_O^\bullet$ but since this site's formation energy in ThO_{2-x} is zero the solution energies are much lower (in fact, identical the incorporation energies). Thus, $\frac{1}{2}Cl_2$ is highly soluble in ThO_{2-x} but insoluble in ThO_2. $\frac{1}{2}Br_2$ and $\frac{1}{2}I_2$ remain insoluble in ThO_{2-x} (Note: in our previous study [21], we demonstrated that Xe and Kr are insoluble both in ThO_2 and ThO_{2-x}, which is because Xe and Kr are large unreactive species.).

The issue of another competing phase must now be considered. For ThO_2, however, solution energies for gaseous species are positive. Thus, whatever more stable competing phase might form, the solution energies for halides will only be more positive. The same conclusion holds for I and Br in ThO_{2-x} again making these species available to form alternative phases. Only then for Cl in ThO_{2-x} do we need to consider a possible competing phase.

Since fuel designers are concerned with the possibility that halides might attack the cladding, we considered $ZrCl_4$ as an alternative phase. In this case Zr metal is available in the cladding so that the reaction per $\frac{1}{2}Cl_2$ is simply:

$$\frac{1}{2}Cl_2 + \frac{1}{4}Zr \rightarrow \frac{1}{4}ZrCl_4 \tag{5}$$

for which the formation energy is -2.33 eV. Since this energy is considerably lower than -1.27 eV, the solution energy for $\frac{1}{2}Cl_2$ in ThO_{2-x}, the competing phase $ZrCl_4$ is more stable than solution of $\frac{1}{2}Cl_2$ in ThO_{2-x}. Thus, solution of Cl in ThO_{2-x} is not the equilibrium phase. Nevertheless, we do not know what the equilibrium phase is since there are many possible alternative phases given the number of fission products with which Cl might react. Further, kinetics of Cl transport will be influenced by the negative solution energy of Cl in ThO_{2-x}.

4. Conclusions

The incorporation and solution behaviour of halogen atoms (Cl, Br and I) in ThO_2 and ThO_{2-x} has been investigated using DFT simulations carried out with dispersion corrections. For all three halogen atoms, incorporation at octahedral interstitial sites is energetically unfavourable. Occupation at oxygen vacancy or thorium vacancy sites reduces the incorporation energy by at least 4 eV. The most favourable point defect site for the incorporation of Cl and Br is the singly charged positive oxygen vacancy $V_O^\bullet$ while for

I it is the doubly charged negative thorium vacancy, $V_{Th}^{''}$ (see Table 3). Incorporation in defect clusters is important, although the DV is a less favoured incorporation site than the NTV1. The incorporation site preference is determined by a combination of halide electronegativity (with charge transferring to or from the halide depending also upon the site charge) atom or ion size (which depends also on charge transfer), as well as the site size and in the case of defect clusters their configuration.

By considering the energy to form the defect sites, equilibrium solution energies were generated (see Table 4). These showed that in both ThO_{2-x} and ThO_2 the most favourable solution equilibrium site for Cl and Br is the $V_O^\bullet$. While $V_O^\bullet$ also provides the lowest solution energy for I in ThO_{2-x}, in stoichiometric ThO_2 the solution energy is essentially the same in $V_O^\bullet$, the DV and NTV1. Solution energies are much lower in ThO_{2-x} than in ThO_2 indicating that the solubility is significantly affected by non-stoichiometry. However, only $\frac{1}{2}Cl_2$ in ThO_{2-x} exhibits strong solubility. In ThO_2, all three halogens are highly insoluble as are Br and I in ThO_{2-x}. Thus, there is a strong driving force for the fission product I (and Br) to be released from fuel as gaseous species and be available to contribute to stress corrosion cracking of the clad [10]. While any Cl present may also be released as a gaseous product from ThO_2 it is much more stable in the fuel lattice than I or Br, especially in ThO_{2-x}. Nevertheless, while $\frac{1}{2}Cl_2$ is soluble in ThO_{2-x}, it will react with other species in the fuel system to form more stable alternative phases, such as $ZrCl_4$ and thus Cl solution in ThO_{2-x}, is not the equilibrium phase.

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Table 4
Solution energies of halogens at defect sites in ThO_2 and ThO_{2-x}. The most favourable solution equilibrium site is given in italics.

	Solution Energies (eV) in ThO_2				
	Int	$V_O^\bullet$	$V_{Th}^{'''}$ ($V_{Th}^{''}$ for I)	$V_{ThO}^{''}$ (DV)	NTV1
Cl	3.81	*1.04*	7.05	5.31	6.13
Br	5.57	*2.95*	7.47	5.64	6.36
I	8.67	*6.30*	7.76	6.37	6.51
	Solution Energies (eV) in ThO_{2-x}				
Cl	3.81	*−1.27*	11.67	6.21	6.13
Br	5.57	*0.64*	12.09	6.71	6.36
I	8.67	*3.99*	12.38	7.56	6.51

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