THE CRYSTAL STRUCTURE AND ELASTIC PROPERTIES OF PURE AND Dy DOPED URANIA

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Abstract

The structure of urania and urania doped with dysprosium are studied using *ab initio* calculations. The CASTEP *ab initio* quantum mechanical program, employing density functional theory and ultrasoft pseudopotentials, is used. The calculations agree well with available experimental data. Furthermore the calculations predict that Dy does not affect significantly the crystal structure and elastic properties of the host urania. This finding is important for Low Void Reactivity Fuel (LVRF) that is made from Dy doped urania to enhance safety of CANDU reactors.

1. Introduction

The paper presents some preliminary results on the application of *ab initio* calculations to assess changes in properties of urania (UO_2) that has been doped with dysprosium. Dy doped urania is used as a key ingredient in Low Void Reactivity Fuel (LVRF) fuel [1].

The CASTEP *ab initio* quantum mechanical program, employing density functional theory [2], is commonly used to study the structure of materials. The CASTEP code uses pseudopotentials, and it has been already demonstrated [3] that plane wave ultrasoft pseudopotentials predict structural properties of various compounds, containing lanthanides and actinides, in agreement with experiments.

Using the total energy minimization method [2], the equilibrium lattice constants and the positions of atoms of pure and doped urania are calculated. The results presented here, include calculations for urania doped with dysprosium.

The current calculations were performed for temperatures of 0 K and for idealized structures and small unit cells. Such small unit cells are convenient to use in *ab initio* methods simulations since the demand on computational resources is reduced.

2. Gadolinia- and dysprosia-doped urania

In the design of CANDU low void reactivity fuel, the central element contains urania with a neutron absorber (dysprosium) [1]. Considerable information is available on the properties and test irradiations of $(U,Gd)O_2$ fuel, since it is in use as a burnable-poison fuel for light-water reactors. Gd and Dy are both lanthanide elements with atomic numbers 64 and 66 and

atomic weights 157.25 and 162.50, respectively. One can expect that the Dy_2O_3 additions to UO_2 will affect physical properties in ways that are similar to those of Gd_2O_3 additions. In the following section, experimental studies of the effect of Gd and Dy doping on the density of urania are summarized. The calculated, relative densities are compared against the experimental data to demonstrate the suitability of the CASTEP *ab initio* quantum mechanical program.

2.1 Density of Gd and Dy doped urania

Some of the results discussed in this section for Gd doped urania were presented before [4]. The calculations for Dy doped urania are new, and they will be compared with the results obtained for Gd doped urania.

The UO_2 fluorite crystal structure was observed for all Gd_2O_3 concentrations (up to 12 wt.% Gd_2O_3) of the stoichiometric fuel (UO_2) studied by Chotard et al. [5]. The lattice parameter (a) for the "g" wt. fraction of Gd_2O_3 at room temperature was:

$$a(g) = 0.5470 - 0.0251\ g\ (nm) \quad (1)$$

and the density (100% theoretical density in kg/m^3) was:

$$\rho = 0.1096\times10^5 - 0.2041\times10^4\ g - 0.27075\times10^5\ g^2 + 0.15355\times10^6\ g^3 \quad (2a)$$

In contrast, Hirai and Ishimoto [6] proposed that the density is linearly dependent on the wt.% Gd_2O_3 (for up to 10 wt% Gd_2O_3 and the same units as above):

$$\rho = (0.1096 - 0.034\ g) \times10^5 \quad (2b)$$

X-Ray diffraction (XRD) measurements of lattice parameters by Hirai and Ishimoto [6] agree well with those of Amaya et al. [7], who used XRD to determine the crystal structure of 10 wt% Gd_2O_3-doped UO_{2+x} and to measure how the lattice parameter changed with a change of stoichiometry, x, in UO_{2+x}. The crystal structure of the solid for all measured deviations from stoichiometry ($0 \le x \le 0.15$) had the same UO_2 fluorite structure, and a decrease in the lattice constant, a, as a function of the deviation in stoichiometry, x, was observed*:

$$a_x = 0.5446 - 0.01186\ x\ (nm) \quad (3)$$

While there were no diffraction peaks of the M_4O_9 (M=U+Gd) phase for 10 wt% Gd_2O_3-doped UO_{2+x}, the U_4O_9 phase was observed for pure UO_{2+x} [7].

We were not able to find in the literature any correlation for the variation of density of $(Dy,U)O_2$ alloys with Dy concentration. Ploetz et al. [8] investigated dysprosia-diluted urania alloys and found that, for up to 70 wt% Dy_2O_3 the compounds had a UO_2 fluorite crystal structure, but values for the stoichiometry deviation (x) were not provided. Their measurements of density as a function of dysprosia weight percent will be used in this paper to derive a correlation for the change in density of urania alloyed with dysprosia.

* 0.01186 was incorrectly printed as 0.001186 in Reference [7]

One can assume that the change of the lattice constants of stoichiometric urania (described by Equation 1), is the same when doping with the same atomic fraction ($y = y_{Gd} = y_{Dy,}$ where y is the fraction of U atoms substituted respectively by Gd or Dy) of Dy or Gd. Therefore using Equation 1 lattice shrinkage can be calculated for both Gd and Dy doped urania (the same for the same atomic fraction substitution, y), and it is equal to a(y)/a(0). This shrinkage of the lattice constants is implemented and the formulas 4a ad 4b are derived for the relative density of dysprosium-doped or gadolinium-doped stoichiometric urania (y is the atomic fraction of dysprosium or gadolinium) respectively. In the following derivation it is assumed that atomic masses of U, Dy, Gd and O are: 238.029, 162.5, 157.25 and 15.999 respectively. The relative density of dysprosium-doped stoichiometric urania is expressed by the following equation:

$$\rho_y^{Dy} \Big/ \rho_o = \frac{y \times 162.5 + (1-y) \times 238.029 + 2 \times 15.999}{238.029 + 2 \times 15.999} \times (a(0)/a(y))^3 \quad \text{(4a)}$$

The related formula for gadolinium doping is:

$$\rho_y^{Gd} \Big/ \rho_o = \frac{y \times 157.25 + (1-y) \times 238.029 + 2 \times 15.999}{238.029 + 2 \times 15.999} \times (a(0)/a(y))^3 \quad \text{(4b)}$$

and to show the effect of shrinkage on the relative density, the relative density of gadolinium-doped stoichiometric urania (y is the atomic fraction of gadolinium) without the shrinkage correction is calculated by dropping last cubic term in Equation 4b:

$$\rho_y^{Gd} \Big/ \rho_o = \frac{y \times 157.25 + (1-y) \times 238.029 + 2 \times 15.999}{238.029 + 2 \times 15.999} \quad \text{(4c)}$$

It is common in the reactor physics community to use weight percent of diluted metal as the unit to characterize urania alloys therefore it is shown below how these weight percents are related to the used above atomic fractions (y) and the weight fraction of Gd_2O_3 (g). The Dy or Gd wt% ($w_{Dy\ or\ Gd}$) percents are defined as:

$$w_{DyorGd} = DyorGdwt\% = \frac{100\,\% \times \text{weight of DyorGd}}{\text{weight of U}} = 100\% \times h_{DyorGd} \quad (5)$$

where h of Dy or Gd is weight fraction respectively of Dy or Gd. The atomic fraction of gadolinium (y_{Gd}) is calculated from the weight fraction using the following expression:

$$y_{Gd} = \frac{238.029 \times h_{Gd}}{157.25 + h_{Gd} \times 238.029} \quad (6)$$

and the corresponding weight percent of dysprosium (w_{Dy}), calculated for the atomic fraction of Dy that is equal to the atomic fraction of Gd ($y = y_{Dy} = y_{Gd}$), is:

$$w_{Dy} = \frac{100\% \times 162.5 \times y}{238.029 \times (1 - y)} \quad (7)$$

In order to express densities, proposed by Chotard (Equation 2a) [5], Hirai and Ishimoto (Equation 2b) [6], in weight percent of Gd the relation between the weight fraction of Gd_2O_3 (g) in doped urania fuel and the weight fraction of Gd (h_{Gd}) is needed:

$$g = \frac{h_{Gd}}{0.984 + 1.044 \times h_{Gd}} \quad (8)$$

In Figure 1, the relative density of $(Dy,U)O_2$ calculated using Equation 4a (dotted line), the relative density of $(Gd,U)O_2$ using Equation (2a) of Chotard et al. [5] (solid line) and Equation 2b of Hirai et al. [6] (broken line) are shown. The Hirai et al. Equation 2b predicts slightly lower densities than those obtained by Chotard et al. (Equation 2a). Correlation 4b (triangles) predicts relative densities of gadolinia-diluted urania in good agreement with those predicted by Equations 2a, b. One can also see in Figure 1 that the relative density calculated from Equation 4c (circles) is significantly lower than the relative density calculated using Equation 4b, where the shrinkage effect (when alloying urania with gadolinium) was taken into account. The assumption that the shrinkage due to alloying urania with Gd or Dy is the same (for the same atomic fraction) is probably not completely valid, since the dotted curve predicts higher relative density than the relative density (squares) obtained by Ploetz [8]. The relative density for gadolinia-doped urania, which is predicted by the Hirai et al. correlation, agrees well with the measured by Ploetz relative density of dysprosia-doped urania [8]. In contrast, Equation 2a of Chotard et al. predicts far too high densities (indicated by crosses in Figure 1) when extrapolated to higher Gd doping.

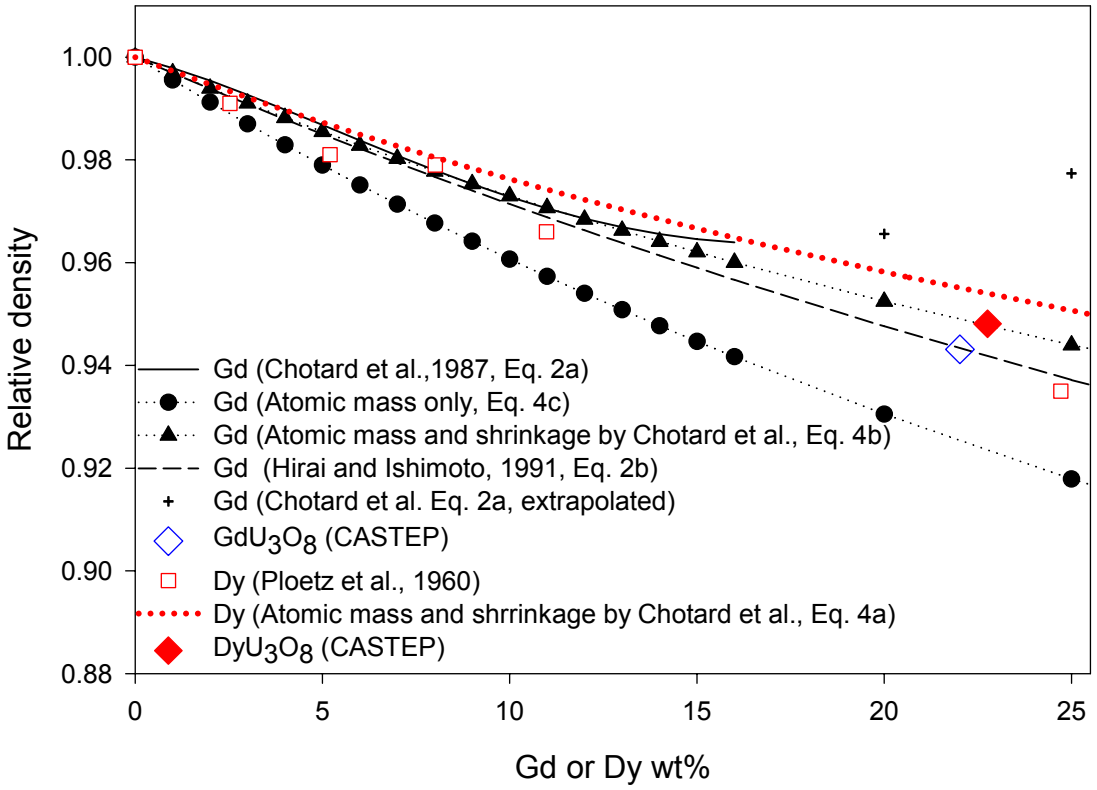

Figure 1 Relative density of $(Dy,U)O_2$ (dotted red line) calculated using equation 4a and relative density of $(Gd,U)O_2$ calculated using equations 2a (solid black line and black crosses for Gd wt% > 15), 2b (broken black line), 4b (black triangles) and 4c (black spheres) as a function of the corresponding weight percentage of dysprosium and gadolinium. The relative density of $(Dy,U)O_2$ obtained from Reference [8] is represented by open red squares. CASTEP calculations for 25% atomic substitution by Dy or Gd atoms are indicated by solid, red diamond and open, blue diamond respectively.

Ab initio calculations for 25% atomic substitution by Dy (indicated by solid, red diamonds and corresponding to 22.76 wt% Dy and 18.72 wt% Dy_2O_3) and Gd (open, blue diamonds and corresponding to 22.02 wt% Gd and 18.29 wt% Gd_2O_3) also predict lower density at this higher concentration (Figure 1). Calculations, for 25% atomic substitution, for Gd agrees very well with Hirai et al. Equation (2b) (broken line) even though this equation was developed for lower Gd concentration. The details of the method of calculations will be presented in the next Section.

The gadolinia and dysprosia doped structures are usually created with oxygen vacancies (e.g. $Dy_2U_2O_7$, created by mixing Dy_2O_3 with UO_2) but vacancies are not desirable in LVRF fuel since they may decrease thermal conductivity.

3. Crystal structure of urania and dysprosia-doped urania

The CASTEP *ab initio* calculations of lattice constants for various uranium oxides and gadolinium compounds were presented in Reference [4]. In the previous calculations [3,4] the electronic exchange-correlation potential was approximated within the Generalized Gradient Approximation (GGA) framework [9,10].

In this section we present a comparison of the previous calculations [3, 4] of lattice constant of urania with the new calculations where local exchange-correlation functional (LDA) is used [11]. The calculated lattice constant of Dy doped urania, obtained using both GGA and LDA, are shown in Table 1. The LDA calculations were performed since the available ultrasoft pseudopotential for Dy was derived using LDA. The structure of urania and Dy doped urania are shown in Figure 3.

Table 1
Lattice constants, spins, electronic charges (on oxygen atoms) and energies (per non-oxygen atom) calculated using CASTEP [2].

Compound	Structure	Energy per non-O atom [eV]	Method	Spin (U)	Spin (Dy)	Lattice constants [nm]	Charge (O) [electron]
UO_2	$Fm\bar{3}m$	-30.709	GGA	1.18		0.545	-0.65
UO_2	$Fm\bar{3}m$	-30.709	LDA	1.15		0.533	-0.60
DyU_3O_8	$Pm\bar{3}m$	-31.520	GGA	1.11	2.69	0.538	-0.65
DyU_3O_8	$Pm\bar{3}m$	-33.518	LDA	1.03	2.53	0.529	-0.60

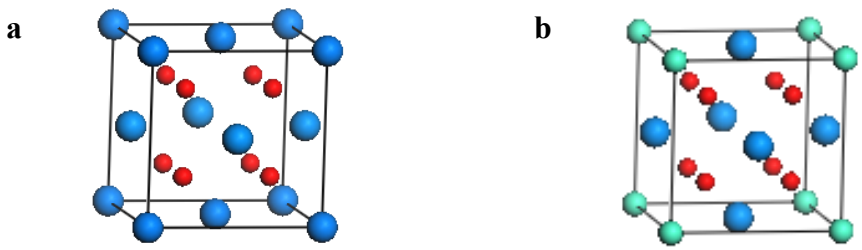

Figure 3 Lattice structure of urania (a) and dysprosium-doped urania (25% atomic substitution of U). Uranium, dysprosium and oxygen atoms are indicated by spheres, with the radius ranging from the largest for U atoms to the smallest for O atoms.

The experimentally measured lattice constant of pure urania: 0.54582 nm [12], at 399 K temperature and the value used by Amaya: 0.5446 nm in Eq. 3, for 10 wt% Gd_2O_3 doped

urania) should be reduced by about 0.002 nm due to thermal expansion before they are compared with the value calculated at 0 K. The presented in Table 1 lattice constants for pure urania agree well with experimental measurements and the value calculated previously, 0.5458 nm [3], with the earlier version of the same software when GGA is used. While GGA calculations predict slightly larger lattice constant, the value predicted by LDA underestimate it. Both framework predict lattice shrinkage when uranium is substituted by Dy.

The magnetic properties of uranium oxides were discussed in details in Reference [4]. Present calculations (Table 1) show that calculated spin values of U and Dy are slightly lower when LDA is used. The spin moment on Dy is larger than on U due to the larger number of unpaired f electrons. The moment on Dy is oriented in the opposite direction to the alignment of the moment of U. The charge transfer to oxygen, which is shown in the last column of Table 1 is slightly lower when LDA is used and it is not much affected by Dy substitution.

4. Elastic properties of UO_2, DyU_3O_8

The experimental values of elastic moduli pertain to a grain aggregate (where grains have randomly orientated crystallographic directions) rather than to single crystals. A completely random orientation of the grains is assumed in the computation. The formulas of Reuss [13] and Voigt [14] are employed in these computations, which provide least upper-bound and greatest lower-bound values for the aggregate. In particular, the approach by Voigt corresponds to an averaging over the elastic constants (stiffness), and the following formulas for bulk modulus (B_V) and shear modulus (G_V) are obtained [14]:

$$B_V = (A + 2B)/3,\ G_V = (A - B + 3C)/5 \tag{9}$$

where

$$\begin{aligned} 3A &= c_{11} + c_{22} + c_{33} \\ 3B &= c_{23} + c_{31} + c_{12} \\ 3C &= c_{44} + c_{55} + c_{66} \end{aligned} \tag{10}$$

and c_{ij} are elastic constants. The Reuss approach pertains to averages over the elastic moduli (compliances), where the formula for the bulk modulus (B_R) and shear modulus (G_R) is [13]:

$$B_R = 1/(3a + 6b),\ G_R = 5/(4a - 4b + 3c) \tag{11}$$

in which,

$$\begin{aligned} 3a &= s_{11} + s_{22} + s_{33} \\ 3b &= s_{23} + s_{31} + s_{12} \\ 3c &= s_{44} + s_{55} + s_{66} \end{aligned} \tag{12}$$

Here s_{ij} are the elastic moduli (they are the elements of the inverse matrix of the elastic constants matrix with elements: c_{ij}). The final values of B and G (shown in Table 2) are calculated as an average of Voigt and Reuss (known as Hill approach):

$$B = (B_V + B_R)/2,\ \ G = (G_V + G_R)/2 \tag{13}$$

Having calculated the bulk and shear modulus, the Young's modulus (Y) can be evaluated for an isotropic material as:

$$Y = 9BG/(3B + G) \quad (14)$$

Additionally Young modulus is calculated in [100] direction from the relation:

$$Y_{[100]} = 1/ s_{11} \quad (15)$$

The elastic constants of UO_2 were previously calculated using CASTEP [3] and they are shown in Table 2 together with experimental data from Reference [15]. The calculations demonstrate that CASTEP *ab initio* calculations reproduce reliably elastic properties of UO_2. The results are consistent with experimental data [15]. In this work we repeated calculations of the elastic constants for urania using more recent version of CASTEP and using LDA since, as described in Section 4, the ultrasoft pseudopotential for Dy was derived using LDA.

The calculations of elastic properties of UO_2, DyU_3O_8 using LDA are shown in Table 2. The cutoff energy for elastic constants calculations of UO_2 using CASTEP was 420 eV (with 14 empty bands) and the Monkhorst-Pack special wave-vectors [16], based on the 8x8x8 grid, was used. The cutoff energy for elastic constants calculations of DyU_3O_8 using CASTEP was 420 eV (with 23 empty bands) and the Monkhorst-Pack special wave-vectors [16], based on the 6x6x6 grid was used. Four (default) values of strain were applied: $\pm$ 0.3 %, $\pm$ 0.1%.

The calculated elastic moduli within LDA framework are slightly larger than calculated using GGW and some of them are in better agreement with the experimental data (e.g. c_{11} ad bulk modulus). The calculations demonstrate that addition of Dy does not influence much elastic properties of urania.

Since in Reference [3] only elastic constants are presented, the derived moduli G, Y and G/B are calculated using Voigt approach. As discussed in Section 1.3 and in Reference [17] the G/B ratio, can be considered as a measure of intrinsic brittleness and values calculated (Table 2) are within the border between brittle (less than 0.4) and ductile (more than 0.5) values found for cubic metals. The values for intrinsic brittleness for pure and doped urania are very close and when Dy is added urania becomes slightly more brittle.

Table 2
Elastic Properties of UO_2, DyU_3O_8 and U_3O_8

Property (in GPa)	UO_2	UO_2	UO_2	DyU_3O_8
	Calculated using CASTEP [3]	Calculated using CASTEP (LDA)	Experimental [15]	Calculated using CASTEP (LDA)
B	170.1	229.1	208.9	229.5
G	70.3 (G_V)	104.9		110.0
G/B	0.41 (G_V/B_V)	0.46		0.48
Y ($Y_{[100]}$)	185.4 (Y_V)	273.0 (342.9)		284.6 (366.1)
c_{11}	318.2	411.9 (± 1.7)	389.3	427.3 (± 4.0)
c_{12}	96.0	137.7 (± 0.4)	118.7	130.7 (± 2.8)
c_{44}	43.1	87.6 (± 1.2)	59.7	90.0 (± 3.5)
n		0.25		0.23

5. Conclusion

The CASTEP *ab initio* quantum mechanical program, employing density functional theory, is used to calculate elastic, magnetic and structural properties of pure and dysprosium-doped urania. The calculated values for pure urania are in good agreement with experiment.

The total energy technique is used to investigate changes in the lattice constants of gadolinium- and dysprosium-doped urania. In agreement with the experiment, the calculations predict shrinkage of the lattice constant of urania when doped with gadolinium or dysprosium.

The calculations predict that the elastic properties are not much affected when 25 % of uranium atoms are replaced by dysprosium and therefore one can expect that up to 18.72 wt% Dy_2O_3 additions to UO_2 have little impact on the elastic properties. The values for intrinsic brittleness for pure and doped urania are very close, however, when Dy is added urania becomes slightly more brittle.

Detailed *ab initio* calculations of the structure and elastic properties of pure and Dy doped urania enhance understanding of the properties of pure and doped urania, predict structure and properties in agreement with available experiments and may be developed as an important tool for modeling LVRF fuel.

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