

Influence of Th, Zr, and Ti Dopants on solution property of Xe in Uranium Dioxide with Defects: A DFT + U Study

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Determination of U_{eff} of Th, Zr, and Ti impurity atoms

Th, Zr, and Ti atoms contain d-orbital electrons, which have a strong correlation effect. The traditional LDA or GGA cannot describe the strong correlation effect well, so the DFT + U method is used for calculation. Impurity atoms occupy the position of U atoms in crystalline UO_2 and combine with the surrounding oxygen atoms to form +4 valence ions. To better describe the influence of impurity atoms on the dissolution and nucleation behavior of Xe atoms in UO_2 , we evaluated the ground state properties of ThO_2 , ZrO_2 , and TiO_2 under different U_{eff} , compared the calculated lattice constants, band gaps, and elastic constants with the experimental values, and finally determined the most suitable U_{eff} value of impurity atoms.

The band gap of ThO_2 can be increased using the DFT + U method. When the U_{eff} value is larger than 7.0 eV, the calculated band gap can be close to the experimental value of 5.9 eV[1], but at this time, the lattice is seriously distorted, as shown in Table S1. Shields et al. [2] studied Th and believed that adding the U_{eff} parameter would not increase structural accuracy. Therefore, for Th, we used $U_{\text{eff}} = 0$ eV for calculation. Table S1 shows the ground state properties of ThO_2 . It can be seen that the calculated results are in good agreement with the experimental values except for the band gap.

For ZrO_2 , we found that the band gap of ZrO_2 can reach the experimental value of 5.25 eV only when the U_{eff} value is 9.5 eV, but the lattice distortion is serious, as shown in Table S2. Delamelina et al. [3] found that the values of U_{eff} larger than 4 eV should be avoided in these calculations due to the deterioration observed in the description of the structural parameter, relative energies, and dielectric constants. When $U_{\text{eff}} = 4$ eV, although there is a certain deviation between the lattice parameters and the experimental values, the deviations of elastic constant, dielectric constant, and energy band gap from the experimental values are significantly reduced, and the calculated phonon dispersion curve is also improved considerably. Therefore, when $U_{\text{eff}} = 4.0$ eV, the properties of ZrO_2 can be better described.

In TiO_2 , due to the existence of the 3d electron orbital of the Ti atom, it is necessary to use DFT + U method. The calculation results show that the band gap can only reach the experimental value of 3.2 eV when $U_{\text{eff}} = 8.5$ eV, as shown in Table S3. Stausholm et al. [4] believe that since TiO_2 is more of a charge-transfer type semiconductor than a Mott–Hubbard insulator, we do not expect to be able to open up the band gap to its experimental value using any reasonable value of U_{eff} . Combined with the literature research [5–8], we finally determined $U_{\text{eff}} = 4.0$ eV, which is enough to describe the properties of TiO_2 well. In Table S3, the lattice constant and bulk modulus of TiO_2 calculated theoretically have only about a 2% error with the experimental value, which shows that the calculation method in this paper is reasonable.

Table S1. Ground state properties of ThO₂ under different U_{eff} values. Lattice parameter (a, b, c), band gap (E_{gap}), bulk modulus (B), shear modulus (G), Young's modulus (E), and elastic constant (C_{11} , C_{12} , C_{44}), compared to the reported experimental values (Exp.).

Lattice constant								
U _{eff} (eV)	E _{gap} (eV)	(Å)	C ₁₁ (GPa)	C ₁₂ (GPa)	C ₄₄ (GPa)	B (GPa)	G (GPa)	E (GPa)
a=b=c								
0.0	4.464	5.617	355.6	106.3	71.7	189.4	89.6	232.3
1.0	4.552	5.632	353.1	106.4	74.4	188.6	91.2	235.7
2.0	4.626	5.646	349.0	103.4	74.8	185.3	91.3	235.3
2.5	4.764	5.652	352.6	107.9	75.3	189.5	91.5	236.5
3.0	4.683	5.658	357.4	113.8	74.8	195.0	91.0	236.3
3.5	4.820	5.664	351.5	108.1	74.7	189.2	91.0	235.2
4.0	4.725	5.672	352.2	109.3	74.6	190.3	90.7	234.9
4.5	4.741	5.678	357.2	116.1	75.2	196.4	91.0	236.4
5.0	4.753	5.684	350.1	111.5	75.8	191.1	91.0	235.5
5.5	4.878	5.690	347.9	110.2	75.8	189.4	90.8	234.9
6.0	4.770	5.696	347.4	110.7	76.0	189.6	90.8	235.0
6.5	4.873	5.701	334.6	98.8	75.7	177.4	90.5	232.0
7.0	4.782	5.707	340.8	107.2	75.0	185.1	89.6	231.5
7.5	4.831	5.712	339.4	106.8	75.7	184.3	90.0	232.2
Exp.	5-6[1,9]	5.600[10] 5.598[9]	367[11]	106[11]	79[11]	198±2[10] 195±2[9]	97[11]	249[11]

Table S2. Ground state properties of ZrO₂ under different U_{eff} values. Lattice parameter (a, b, c), band gap (E_{gap}), bulk modulus (B), shear modulus (G), Young's modulus (E), and elastic constant (C_{11} , C_{12} , C_{33} , C_{44} , C_{66}), compared to the reported experimental values (Exp.).

U ^{eff} (eV)	E _{gap} (eV)	Lattice constant (Å)			C ₁₁ (GPa)	C ₁₂ (GPa)	C ₃₃ (GPa)	C ₄₄ (GPa)	C ₆₆ (GPa)	B (GPa)	G (GPa)	E (GPa)
		a	b	c								
1.0	3.708	5.209	5.263	5.383	312.8	157.6	271.2	80.3	119.8	190.0	89.6	232.2
2.0	3.812	5.231	5.274	5.396	313.9	158.7	276.1	84.2	119.1	192.4	90.5	234.7
2.5	3.868	5.241	5.281	5.403	313.6	159.1	276.8	85.8	119.6	192.6	90.8	235.4
3.0	3.923	5.252	5.286	5.410	315.3	158.3	284.2	87.4	119.5	194.7	91.8	238.1
3.5	3.981	5.264	5.292	5.418	316.6	158.0	282.0	88.7	119.3	195.0	91.8	238.1
4.0	4.039	5.274	5.298	5.425	314.7	158.5	283.4	89.9	119.1	194.8	92.0	238.4
4.5	4.172	5.285	5.303	5.433	315.8	159.2	281.4	90.6	119.2	194.8	91.8	237.9
5.0	4.164	5.300	5.303	5.449	316.4	163.8	275.4	90.7	117.5	194.7	87.2	227.5
5.5	4.222	5.310	5.310	5.455	316.4	162.2	277.2	91.5	117.6	194.5	88.1	229.7
6.0	4.284	5.320	5.314	5.464	319.8	160.1	290.6	92.4	117.8	197.2	89.7	233.6
6.5	4.346	5.332	5.318	5.474	323.0	155.9	303.1	93.3	116.9	198.7	91.5	238.0
7.0	4.408	5.341	5.323	5.481	323.4	154.0	308.4	94.1	116.5	198.8	92.8	241.0
7.5	4.468	5.352	5.329	5.489	323.5	153.3	305.2	94.7	116.1	198.0	92.3	239.6
8.5	4.592	5.372	5.338	5.506	326.3	148.3	311.4	95.5	115.6	197.0	92.5	239.9
9.5	4.712	5.391	5.349	5.521	325.9	145.9	313.4	96.8	114.9	195.9	93.9	243.0
Exp.	5.25	5.151[5.212[5.317[361[13]	142[13]	258[13]	99.9[13]	126[13]	187[13]	94[13]	241[13]
	[12]	12]	12]	12]	358[14]	144[14]	240[14]	99.1[14]	130[14]	177.5[14]	98.1[14]	248.6[14]

Table S3. Ground state properties of TiO₂ under different U_{eff} values. Lattice parameter (a, b, c), band gap (E_{gap}), bulk modulus (B), shear modulus (G), Young's modulus ϵ , and elastic constant (C_{11} , C_{12} , C_{13} , C_{33} , C_{44} , C_{66}), compared to the reported experimental values (Exp.).

U _{eff} (eV)	E _{gap} (eV)	Lattice constant		C ₁₁ (GPa)	C ₁₂ (GPa)	C ₁₃ (GPa)	C ₃₃ (GPa)	C ₄₄ (GPa)	C ₆₆ (GPa)	B (GPa)	G (GPa)	E (GPa)
		(Å)										
		a=b	c									
2.0	2.364	3.831	9.714	346.4	129.7	137.9	210.6	25.3	59.5	185.2	47.8	132.1

