ONSET OF THE LOCAL MAGNETIC MOMENT ON Nb IN ZIRCONIA

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Abstract

The CASTEP *ab initio* quantum mechanical program, employing density functional theory and ultrasoft pseudopotentials, is used to study crystal and electronic structure of zirconium, zirconia and Zr_3NbO_8 compound. It has been found that it is essential to perform spin polarized calculations for these compounds since zirconium niobium compound becomes magnetic when oxidized. Although only theoretical studies are described, it is suggested that the onset of magnetic moment on Nb when Zr-Nb alloy oxidizes may be potentially used in non-destructive testing of the corrosion.

1. Introduction

The CASTEP *ab initio* quantum mechanical program, employing density functional theory [1], is commonly used to study the structure of materials. The CASTEP code uses pseudopotentials, and it has been demonstrated that plane wave ultrasoft pseudopotentials predict structural properties and elastic properties of cubic zirconia in good agreement with experiment [2].

Using the minimization of total energy method [1], the equilibrium lattice constants and the positions of atoms of zirconium, cubic zirconia and Zr_3NbO_8 can be calculated.

The current calculations are performed for a temperature of 0 K and idealized structures, where small unit cells can be used and therefore the computational time is reduced. The spin non-restricted calculations allow for prediction of existence of a non-zero value of local spin. The exchange-correlation potential is approximated within the Generalized Gradient Approximation (GGA) framework [3,4].

2. Structural and energetic properties

Preliminary research on the application of CASTEP *ab initio* [1] calculations, to assess changes in material properties of zirconia (ZrO_2) that have been doped with niobium, are described here.

Pure zirconia has a monoclinic structure at low temperatures, but above 1400°C or when stabilized by adding impurities of Ca or Y, the cubic fluorite structure becomes stable (e.g. [5]). Extensive studies of Zr-O-H (with fluorite structure) systems have been presented at the 9th International CANDU Fuel Conference [2]. The calculated values for binding energies and lattice constants, along with the elastic constants of zirconia are in good agreement with the experimental values.

It is of interest to investigate how physical properties of Zr and Zr-Nb compounds change when oxidized. Spin polarized calculations performed in this work are of special interest since the onset of magnetism in oxidized compounds may be estimated.

In Table 1, CASTEP calculations are shown for Zr. The default cutoff energy of 400 eV (with 12 empty bands) was used. The structures and energies per atom are shown; also it is evident that the calculated lattice constants agree very well with the experimental values [5].

Table 1

The Structures, Energies per Atom and Lattice Constants of Zr

Compound	Structure	Energy per atom [eV]	Lattice constants [nm]	Lattice constants [nm]
	Calculated using CASTEP			Experimental [5]
Zr	P63/mC	-7.414	0.323(a) 0.516(c)	0.323 (a) 0.515 (c) (25ºC)

In Table 2, the results of CASTEP calculations are presented for cubic zirconia, Zr_3NbO_8 and Zr_3NbO_7. The energies per atom, lattice constants, spins and charges on selected atoms (Nb and O) in these compounds are calculated. In contrast to our earlier calculations [2], in the current work the unit cell (lattice constants and positions of atoms) of zirconia was optimised, and the calculated zero temperature equilibrium lattice constant (0.510 nm) is only slightly larger than the experimental value for the cubic phase of zirconia (0.507 nm) [5]. The larger, previously used [2] value of cutoff energy, 495 eV (with 8 empty bands) was used.

The equilibrium lattice constants were also calculated for Zr_3NbO_8 and Zr_3NbO_7 to examine the effect of Nb substitution for Zr and the presence of oxygen vacancies. The default cutoff energy of 380 eV (with 8 empty bands) was used. It can be seen in Table 2 that the lattice constants are almost the same in all compounds. The binding energy per non oxygen atom also stays the same, except in the presence of oxygen vacancies, when it is reduced. The charge transfer to oxygen (last column in Table 2) is also almost the same and its value, (much lower than 2 e), indicates that these compounds are not purely ionic.

The calculated spin on the Nb atom in Zr_3NbO_8 has non-zero value equal to 0.52. The spin value on Nb is reduced to 0.40 in the presence of one oxygen vacancy per unit cell (Zr_3NbO_7). The CASTEP calculations also confirmed that Nb is not magnetic in Zr-Nb alloy. The Nb atom becomes magnetic in Zr_3NbO_8 compound since it's charge is 1.29 e due to transfer of electrons to oxygen. However the calculations also predict that Nb is non magnetic in NbO ($Pm\bar{3}m$) and NbO_2 (rutile P42/mnm structure) compounds, where charge transfer from Nb to O is equal 0.66 e and 1.34 e respectively. Zr whose charge in Zr_3NbO_8 compound is 1.53 e, is non magnetic, since its atomic configuration contains $5s^2$ electrons while Nb has only one 5s electron (see Section 3 for details). The phenomenon that Nb in oxidised zirconia becomes magnetic can be used in non-destructive testing of corrosion of Zr-Nb alloys.

Table 2
Lattice constants, spins, electronic charges and energies of ZrO_2, Zr_3NbO_8 and Zr_3NbO_7 calculated using CASTEP [2].

Compound	Structure	Energy per non O atom [eV]	Spin (Zr)	Spin (Nb)	Lattice constants [nm]	Charge (O) [electron]
ZrO_2	$Fm\bar{3}m$	-27.950			0.510	-0.74
Zr_3NbO_8	$Pm\bar{3}m$	-27.872	0	0.52	0.507	-0.74
Zr_3NbO_7	R3m	-25.150	0	0.40	0.509	-0.72

3. Electron density of states

Electrons densities of states, calculated using CASTEP [1], are shown in Figures 1-3 for pure Zr and its compounds: ZrO_2 and Zr_3NbO_8. The electrons that contribute to the density of states are respectively: for Zr: $4s^2$, $4p^6$, $4d^2$, $5s^2$, Nb: $4s^2$, $4p^6$, $4d^4$, $5s^1$ and for O atoms $2s^2$ and $2p^4$.

In Figure 1 electron density of states per Zr (2 atoms) unit cell is shown. The d, p and s electron density of states are shown by black solid line, thick blue solid line and red broken lines respectively. The 4s electron density is located around –50 eV and just above –30 eV the density of states of 4p electrons is situated. The Fermi Energy is indicated by vertical, broken black line. The main contribution to the states around Fermi energy originates from 4d electrons. At the Fermi energy the electron density of states is low therefore Zr is not magnetic as expected from Stoner criterion of band ferromagnetism [6].

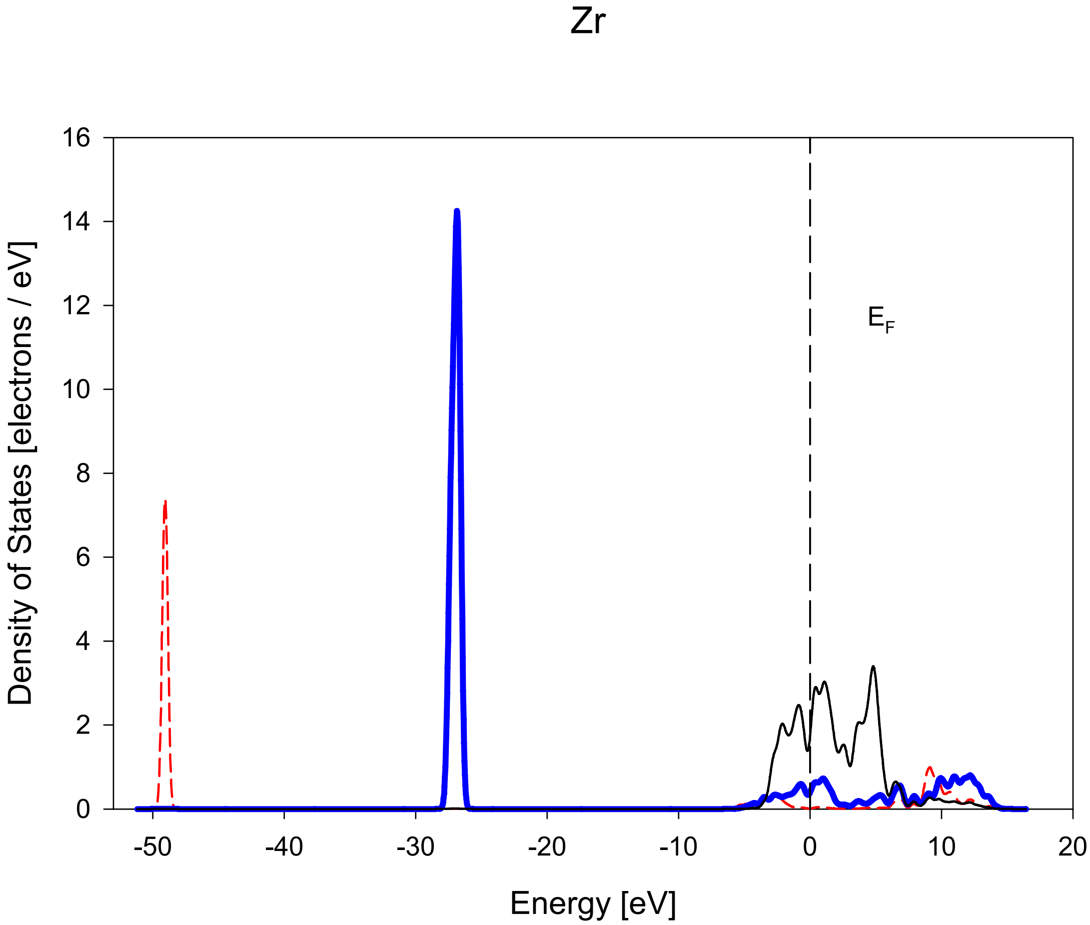

Figure 1. Electron density of states per Zr (2 atoms) unit cell. The d, p and s electron density of states is shown respectively by black solid line, thick blue solid line and red broken line. Fermi Energy is indicated by vertical, broken black line.

Electron density of states changes dramatically when oxygen is added to Zr or Zr-Nb compound. In Figures 2 and 3 the electron density of states, calculated using CASTEP [1], are shown for ZrO_2 and Zr_3NbO_8 respectively. The spin unrestricted calculations were performed for all compounds. The density of states of electrons with opposite direction of spins (up and down) are shown above and below horizontal axis, respectively. As it will be discussed below only Nb doped compound is magnetic but the density of states of ZrO_2 is shown for both spins for easy comparison with magnetic compound of Zr_3NbO_8.

The ZrO_2 density of states around Fermi Energy originates predominantly from 2p electrons of oxygen atoms, and they are indicated by the thick blue line. The two peaks around –50 eV and –25 eV correspond to the density of states of 4s and 4p electrons of the zirconium atom, respectively. The maximum value of the density of states of 2s electrons of oxygen is located close to –15 eV.

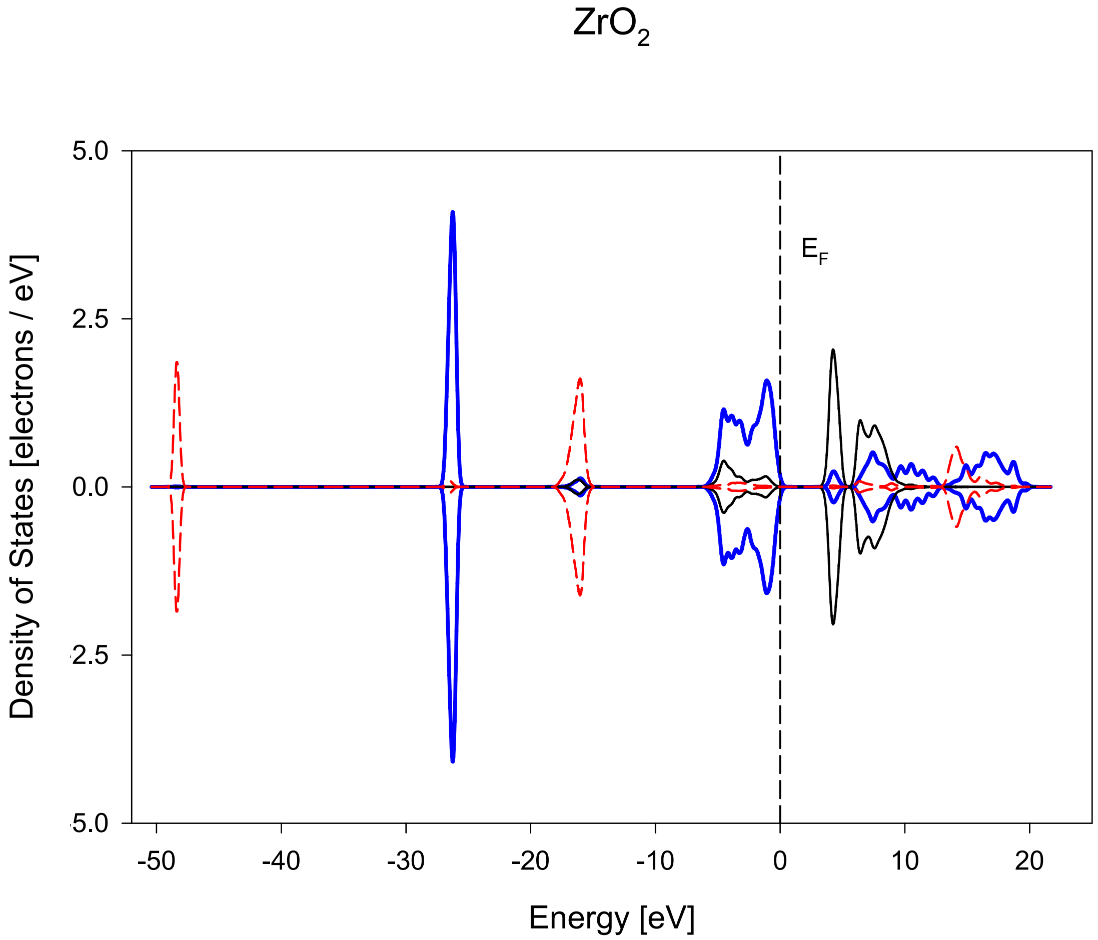

Figure 2. Electron density of states per ZrO_2 unit cell. The d, p and s electron density of states is shown respectively by black solid line, thick, blue solid line and red broken line, respectively. The density of states of electrons with opposite direction of spins (up and down) are shown above and below horizontal axis, respectively.

In Figure 3, electron density of states per Zr_3NbO_8 unit cell is shown. As described in Section 2, both Zr and Nb transfer electrons to oxygen (Nb transfers 1.29 e from it's higher energy electrons: $4d^4$ and $5s^1$), therefore besides the 2s electrons density of states of oxygen (around -20 eV), a significant contribution of 2p electrons density of states of oxygen is visible just below Fermi energy. As a result Nb atom becomes magnetic and therefore one can see splitting of spin up and spin down states of 4s, 4p and 4d electrons of Nb.

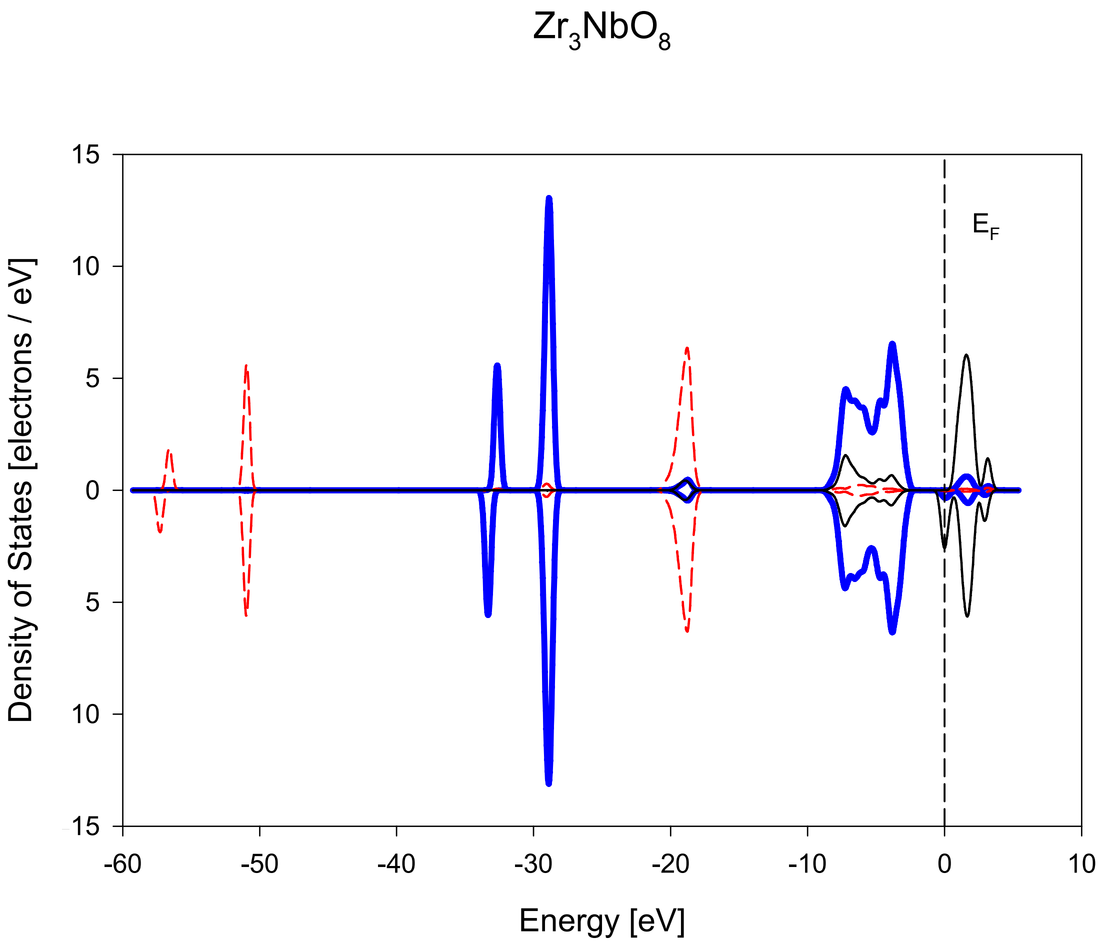

Figure 3 Electron density of states per Zr_3NbO_8 unit cell. The d, p and s electron density of states is shown by black solid line, thick, blue solid line and red broken line, respectively. The density of states of electrons with opposite direction of spins (up and down) are shown above and below horizontal axis, respectively.

5. Conclusion

Crystal structure and magnetic properties are calculated using CASTEP, *ab initio* method for zirconium, zirconia and Zr_3NbO_8. Detailed calculations of the lattice structure of pure and doped zirconia are complementary to experimental measurements, and they enhance understanding of the structural properties of materials used in nuclear reactors.

Electron density of states changes dramatically when oxygen is added to Zr-Nb compound. The Nb atom becomes magnetic resulting in splitting of spin up and spin down states of Nb electrons. Although only theoretical studies are described, it is suggested that the onset of magnetic moment on Nb when Zr-Nb alloy oxidizes may be potentially used in non-destructive testing of the corrosion.

Even though the simplified structures were used in this work, the presented calculations give a good understanding of the interplay between structural and magnetic properties in Zr and pure and Nb doped zirconia.

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