

# Electronic structure and ionicity of actinide oxides from first principles

**Leon Petit<sup>1,2</sup>, Axel Svane<sup>2</sup>, Zdzislawa Szotek<sup>1</sup>, Walter Temmerman<sup>1</sup>, Malcolm Stocks<sup>3</sup>**

<sup>1</sup> Daresbury Laboratory, Daresbury, Warrington WA4 4AD, United Kingdom, e-mail:  
leon.petit@stfc.ac.uk

<sup>2</sup> Department of Physics and Astronomy, Aarhus University, DK-8000 Aarhus C, Denmark

<sup>3</sup> Materials Science and Technology Division, and Center for Defect Physics, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

The ground state electronic structures of the actinide oxides AO,  $A_2O_3$  and  $AO_2$  ( $A=U$ , Np, Pu, Am, Cm, Bk, Cf) are determined from first-principles calculations using the self-interaction corrected local spin-density (SIC-LSD) approximation.[1] This approach gives rise to a split 5f electron manifold, describing the dual character of the electrons, represented by localized/occupied and hybridized/unoccupied subsets. Different localized/delocalized configurations are realized by assuming different numbers of localized states—here f states on actinide-atom sites, and the investigated configurations range from the LSD scenario, where the electrons, including all the f-electrons, are treated as itinerant electron states, to the fully localized scenario, where all the f-electrons are treated as localized. Since the different localization scenarios constitute distinct local minima of the same energy functional, their total energies may be compared and the global energy minimum then defines the ground-state total energy and the valence configuration of the actinide ion. This latter is defined as the integer number of electrons available for band formation,  $N_{val} = Z - N_{core} - N_{SIC}$ , where  $Z$  is the atomic number,  $N_{core}$  is the number of atomic core electrons, and  $N_{SIC}$  is the number of SIC-localized f-electrons.

The calculated groundstate valency configurations that result from our total energy calculations are summarized in Table 1. [2] For the actinide monoxides, assuming a hypothetical NaCl structure, the trivalent configuration is found energetically most favourable, except for UO and NpO that respectively prefer the  $U^{5+}(f^1)$  and  $Np^{4+}(f^3)$  configurations. The divalent (nominal ionic  $A^{2+}O^{2-}$ ) insulating picture does not become energetically favourable for any of the monoxides. According to the SIC-LSD calculations, the AO would be metallic, if they would occur naturally.

The actinide sesquioxides from Pu onwards are stable and have been synthesized, whilst bulk phases of  $U_2O_3$  and  $Np_2O_3$  do not exist. In our calculations, the trivalent ground state configuration is found to be energetically favourable for all the sesquioxides apart from  $U_2O_3$  and  $Np_2O_3$ , for which the tetravalent ground state is preferred. In the trivalent ground state the nominal  $A_2^{3+}O_3^{2-}$  picture is realized, and the sesquioxides are found to be insulators.

Table 1. Calculated ground state actinide ion valency configurations for the actinide oxides. Coloured fields indicate compounds that occur in nature.							
A	U	Np	Pu	Am	Cm	Bk	Cf
AO	5+	4+	3+	3+	3+	3+	3+
$A_2O_3$	4+	4+	3+	3+	3+	3+	3+
$AO_2$	5+/4+	4+	4+	4+	4+	4+	4+

The actinide dioxides from U to Cf have all been synthesized, crystallizing in the fluorite structure. As can be seen from Table 1, the SIC-LSD calculations predict a tetravalent ground state for all the dioxides, except  $UO_2$  where the groundstate is found to be pentavalent  $U(f^1)$  but close to degenerate with the tetravalent  $U(f^2)$  configuration. All the dioxides are

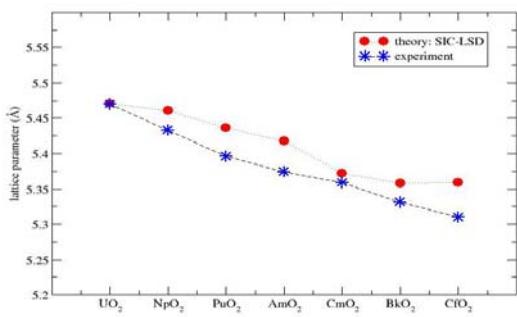


Fig. 1. Actinide dioxide lattice parameters.

unfavourable compared to the tetravalent scenario by 0.68 eV, and we predict an ionic rather than a covalent bonding for  $\text{CmO}_2$ . It should be noted that although our calculated ground state finds a localized  $f^6$  Cm ion, the system turns out to be magnetic with a total moment of  $\mu=5.21 \mu_B$  which exceeds the experimental moment of  $\mu=3.36 \mu_B$ .

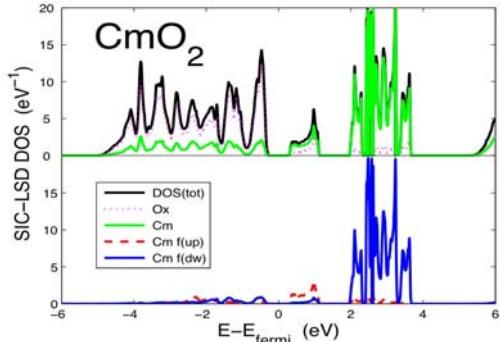


Fig. 2.  $\text{CmO}_2$  DOS in tetravalent configuration.

The actinide ions play an active role in accommodating extra O as their localized  $f$ -electrons can act as electron reservoirs for the highly electronegative O ion. In other words, whether oxidation is favoured depends on the willingness of the actinide to delocalize a further  $f$ -electron. The calculations show that the divalent monoxide is never favoured. The predicted trivalent monoxide on the other hand does not form, as the additional delocalized electron is made available for oxidation, which leads to the formation of sesquioxides. In the early actinides, where the  $f$ -electrons are less tightly bound, a fourth (and for U even a fifth) electron readily delocalizes, and the dioxides are formed at the expense of the corresponding sesquioxides. However as one progresses through the actinide series the  $f$ -electrons become increasingly bound to the actinide ion, the trivalent sesquioxide configuration becomes the groundstate, with delocalization less likely to happen, and further oxidation harder to achieve. For example the synthesis of  $\text{CfO}_2$  will only take place under powerful oxidation conditions.

predicted to be insulators. Their calculated lattice parameters are in very good agreement with experiment, within 1%, as can be seen from Fig. 1. In Fig. 2 we show the DOS of  $\text{CmO}_2$  in the  $\text{Cm}^{4+}(f^6)$  ground state configuration. The Fermi level is situated between the completely filled O  $p$ -band and the remaining delocalized empty majority  $f$ -spin state that strongly hybridizes with O  $p$ -states. The localized  $f$ -states are not shown in Fig. 2 as they occur at too low binding energies. Despite the associated half-filled shell, the trivalent Cm configuration is found to be energetically

From Table 1 a link emerges between the degree of oxidation and the degree of  $f$ -electron localization. The orange background indicates those compounds that exist in nature, and incidentally for these same compounds the calculated ground state valency agrees with the valency expected from an ideal ionic picture. On the other hand, all those compounds where the calculated groundstate valency represents an excess of charge (compared to nominal ionic charge) do not occur naturally. The bonding in the actinide oxides thus emerges to be very ionic in nature.

## References

- [1] W. M. Temmerman et al., *Lecture Notes in Physics*, edited by M. Dreyssé, (Springer Verlag, Berlin, 2000), vol. 535, p. 286.
- [2] L. Petit et al., *Phys. Rev. B* **81**, 045108 (2010).