Journal of Nuclear Materials 384 (2009) 226–230

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

First-principles study of electronic structure and insulating properties of uranium and plutonium dioxides

M.V. Ryzhkov [a],*, A.Ya. Kupryazhkin [b]

[a] Institute of Solid State Chemistry, Ural Branch of the Russian Academy of Sciences, Pervomaiskaya Str. 91, Ekaterinburg 620219, Russia
[b] Ural State Technical University, Mira Str. 19, Ekaterinburg 620219, Russia

ARTICLE INFO

Article history:
Received 25 March 2008
Accepted 18 November 2008

ABSTRACT

First-principles density functional theory calculations were carried out to investigate the electronic structure and the degree of 5f states localization of the Mott–Hubbard type insulators UO_2 and PuO_2. We used the fully relativistic cluster discrete variational method (RDV) with the local exchange-correlation potential. The energies of one-electron transition between occupied and vacant $5f^{5/2}$ states of neighboring actinide atoms were evaluated on the base of the ground state and the excited state calculations. It is found that in UO_2 and PuO_2 the energy difference between $5f^{5/2}$ levels of nearest metal sites in the lattice are close to 1.0 eV and 0.9 eV, despite the results of conventional band structure approach predicting that both oxides are good conductors.

1. Introduction

Though the electronic structure of the uranium and plutonium dioxides has been the subject of theoretical investigations over the last 30 years [1–6], some questions concerning the inclusion of all relativistic effects and correct description of their insulating properties are still unclear. It is known from experiments [7,8] that UO_2 and PuO_2 are the so-called Mott–Hubbard insulators, i.e. the occupied and vacant 5f bands are separated by the band gaps of 2.1 eV [7] and 1.8 eV [8] in UO_2 and PuO_2, respectively. However, when the electronic structure of UO_2 and PuO_2 is calculated using conventional first-principles methods such as the local density approximation (LDA) or generalized gradient approximation (GGA) these band gaps are not reproduced. Both the LDA and the GGA predict UO_2 and PuO_2 in the ground states to be good conductors. We know two approaches based on periodic boundary conditions, which appear to remedy the band gap problem. (1) The LDA + U model [9] of treating the strong correlation effects, in this method the orbital potential splits the 5f band of UO_2 into narrow occupied and broad unoccupied bands [4,5]. (2) The use of hybrid functionals for the exchange-correlation potential also predicts a non-zero band gap for uranium and plutonium oxides [6].

On the other hand, the crystallographically equivalent atomic sites become non-equivalent in the finite fragments of the lattice which are described with the use of point symmetry instead of translational symmetry in the band structure approach. Specifically, in the cluster models the absence of the band gap does not directly mean the metal conductivity because the highest occupied (HOMO) and the lowest unoccupied (LUMO) molecular orbitals could be located on the same atom. On the other hand, the energies of the occupied and vacant orbitals belonging to the nearest atomic sites could be noticeably different as in the case of semiconductors or even insulators. Furthermore, the electron transition between two atoms in the lattice could lead to the redistribution of charge density of several nearest sites and, therefore, to the additional shifts of the initial and final energy levels.

The aim of the present paper is the investigations of the properties of occupied and vacant 5f states of UO_2 and PuO_2 in the direct space approach. In this work we concentrate on a one-electron transition from the occupied to the vacant $5f^{5/2}$ molecular orbitals (MO) located on the neighboring actinide atoms. Our purpose is to evaluate the energy difference between initial and final levels of this transition in the ground state and in the excited state of these compounds.

2. Objects and methods of calculations

The ground state calculations of the electronic structure of UO_2 and PuO_2 were made for the 279-atom clusters $U_{63}O_{216}$ and $Pu_{63}O_{216}$ representing the fragments of dioxide lattices. The structure of these clusters is illustrated in Fig. 1. For the modeling of boundary conditions we used an "extended cluster" scheme described in details in Refs. [10,11]. In this model the crystal fragment under study consists of two parts: the internal main part (or the "core" of the cluster) and the outer part (or the "shell"), the latter part usually includes the atoms of 1–5 coordination spheres surrounding the "core". During the self-consistency procedure the electron densities and the potential of the ions in the "shell" are replaced by the corresponding values obtained for the

---

* Corresponding author. Tel.: +7 343 3623554; fax: +7 343 3744495.
E-mail address: ryz@ihim.uran.ru (M.V. Ryzhkov).

0022-3115/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2008.11.011

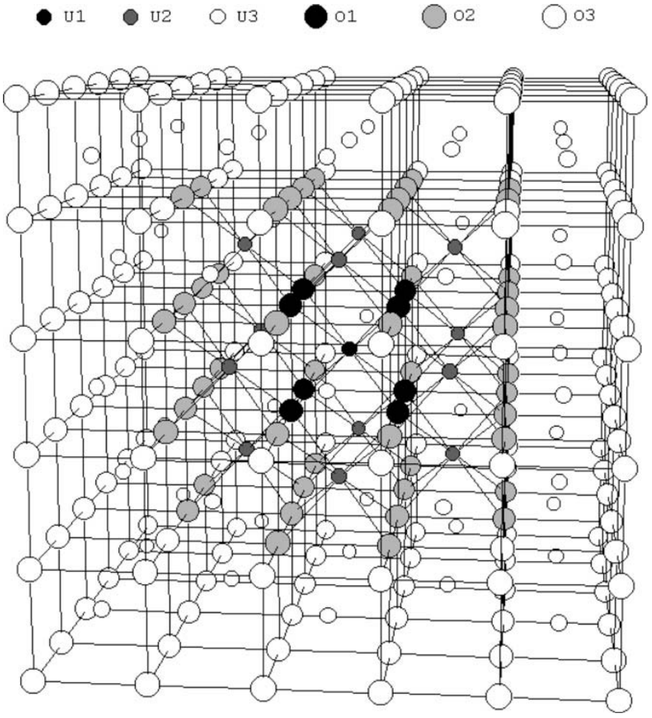

Fig. 1. The structure of $U(Pu)_{63}O_{216}$ cluster in the actinide dioxide lattice.

crystallographically equivalent centers of the cluster "core". In addition to introduce the long-range component of the surrounding crystal potential, the extended cluster is embedded in a pseudo-potential of the outer crystal lattice including 7972 centers with coulomb and exchange-correlation potentials obtained for the corresponding equivalent atoms in the internal part of the cluster [12].

In the present calculations the "core" of $Ac_{63}O_{216}$ clusters included: U(Pu) atom in the center with its eight nearest oxygen neighbors (these atoms are labeled below as U_1, Pu_1, O_1), 12 actinide sites of the next metal coordination sphere (U_2, Pu_2) with their 48 nearest ligands (O_2) forming two crystallographically non-equivalent groups (Fig. 1). The other atoms of the cluster (U_3, Pu_3, O_3) formed the "shell" and during self-consistency their electron densities and potentials were kept equivalent to those of $U_1(Pu_1)$ and O_1.

The investigation of the excited state corresponding to the electron transition between $5f^{5/2}$ molecular orbitals was performed using the Slater's "transition state procedure" [13]. In this method the population of initial occupied MO is decreased and the population of final vacant MO is increased by 0.5. The energy difference of these partially occupied levels obtained in the SCF calculation can serve as a measure of the relaxation effects which take place when 5f electron moves from one atom to another.

Since the transition state calculations for the 279-atomic clusters could not be done during reasonable time, we consider the quite small $Ac_{13}O_{56}$ clusters (the main part of $Ac_{63}O_{216}$) where 48 outer ligands (O_2) now form the "shell" around AcO_8Ac_{12} "core" and during self-consistency their density and potential were kept equivalent to those of O_1. The rest sites of $Ac_{63}O_{216}$ fragment were added to the pseudo-potential part of the boundary condition of $Ac_{13}O_{56}$. Another problem of excited state calculations concerns the fact that the transition of an electron from one individual atom (U_1 or Pu_1) to the individual atom of the next coordination sphere of Ac breaks the equivalency of $12U_2(Pu_2)$ sites. For this reason we changed the orientation of coordinate axes and reduced the symmetry of $Ac_{13}O_{56}$ clusters from D_{4h} to C_{2v}.

In this work the electronic structure was calculated in the density functional theory approximation (DFT) using the original code of the fully relativistic discrete variational cluster method (RDV) [14,15] with local exchange-correlation potential [16]. The RDV method is based on the solution of the Dirac–Slater equation for 4-component wave functions transforming according to irreducible representations of the double point groups (in the present calculations – D_{4h} and C_{2v}). For the calculation of symmetry coefficients we used the original code which realizes the projection operators technique [14] and includes the matrices of irreducible representations of double point groups obtained in Ref. [17] and the transformation matrices presented in Ref. [18]. The extended bases of 4-component numerical atomic orbitals (AO) obtained as the solution of the Dirac–Slater equation for the isolated neutral atoms also included $Ac7p^{1/2}$ and $7p^{3/2}$ functions in addition to occupied AOs. Numerical diophantine integration in matrix elements calculations was carried out for 700 000 ($Ac_{63}O_{216}$) and 178 000 ($Ac_{13}O_{56}$) sample points, that provided the convergence of valence MO energies within 0.1 eV. The effective charges on atoms (Q_{eff}) were computed as the integrals of electron density inside the domains bounded by the points of its minimum [19].

3. Results and discussion

The total and partial densities of states (DOS) obtained for the central $U_1(Pu_1)$ and O_1 atoms in $Ac_{63}O_{216}$ clusters are shown in Figs. 2 and 3. Since the partial DOS for $Ac7p^{1/2}$ and $7p^{3/2}$, $Ac6d^{3/2}$ and $6d^{5/2}$, $O2p^{1/2}$ and $O2p^{3/2}$ are close to each other, the sum of DOS for 7p, 6d and O2p MOs are presented in the figures. The comparison of our results with those obtained in conventional band structure calculations of UO_2 and PuO_2 [2,6] shows that the structure of valence and vacant states of the central part of $Ac_{63}O_{216}$ clusters are close to the positions and widths of the valence and

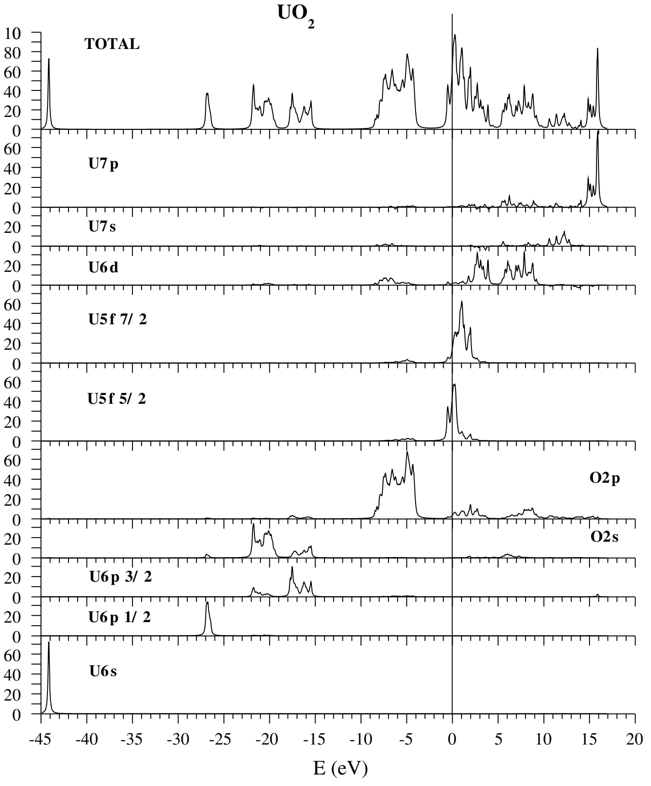

Fig. 2. Total and partial densities of states for the central part of $U_{63}O_{216}$ cluster in UO_2.

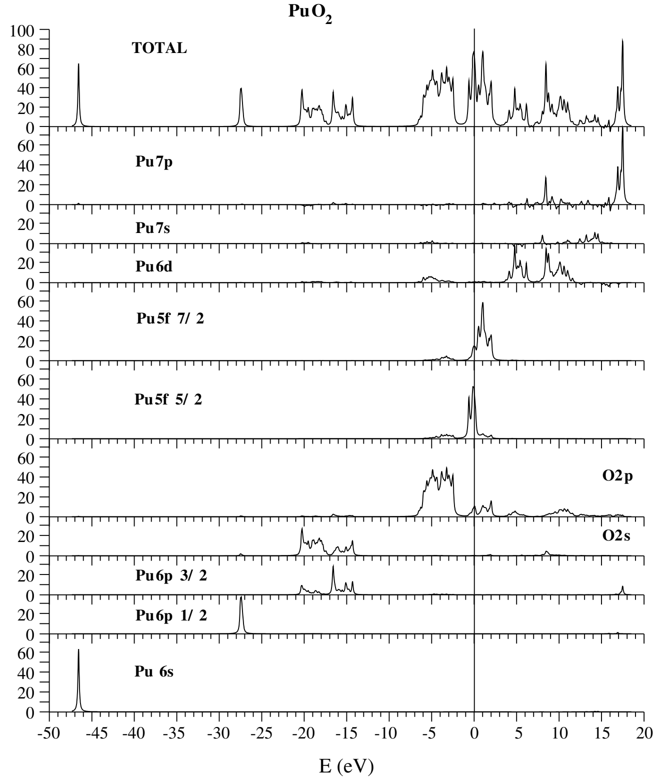

Fig. 3. Total and partial densities of states for the central part of $Pu_{63}O_{216}$ cluster in PuO_2.

conduction bands in the methods using periodic boundary conditions.

The increase of 5f states occupation on going from UO_2 to PuO_2 shifts the Pu5f levels downward to O2p band (Fig. 3). Though the energy gaps between O2p and Ac6d sates are close in both oxides, the Pu6d band position measured relative to E_F (which is used as a zero of energy scale) is shifted upward by ~2 eV. The $Pu6p^{3/2}$–O2s band gap is also reduced as compared with UO_2, this shift is accompanied by the corresponding increase of O2s–$6p^{3/2}$ covalent mixing. The spin-orbital splitting of 6p states is also larger in PuO_2.

For the evaluation of direct and indirect relativistic effects we have made the non-relativistic spin-unrestricted DV calculation of $U_{63}O_{216}$ cluster with the same computational parameters as in RDV approach. Though the detailed features of the bands in DV and RDV approaches are different, the band widths of O2p, U5f, 6d and 7p states are quite similar in both methods. The principle difference is revealed for the U6s and U6p–O2s bands. The relativistic contraction of U6s MOs decreases their energy by 17 eV. In the case of U6p–O2s states the simple non-relativistic two-band (U6p and O2s) structure transforms to the three main bands due to the spin-orbital interaction (Fig. 2). The latter result is in agreement with the experimental photoelectron spectra of UO_2 [20].

On the other hand, the considerable relativistic transformation of the core and semicore states could lead to the change in nucleus screening and, therefore, to the additional transformation of the structure of valence orbitals. In the case of UO_2 these indirect relativistic effects induce the decrease of O2p–U6d band gap by 1.5 eV and the change of the degree of U5f states delocalization. The latter could be evaluated by the values of overlap populations (n_{ij}) of various pairs of the metal and ligand atomic orbitals, which can also give the bond orders of these states [21]. The values of n_{ij} for O2p and 6d, 5f, 7s, 7p AOs of U and Pu obtained in DV and RDV calculations are listed in Table 1. Examination of Table 1 reveals that Ac5d orbitals play the main role in chemical bonding of dioxides and their contributions are nearly identical in the relativistic and non-relativistic description. On the contrary, the overlap populations of U5f–O2p states increase by 1/3 on going from DV to RDV approach. It can be seen that U5f contribution to bonding is only 2.5 times less than that of the main U6d–O2p interaction in the fully relativistic description. The Pu5f–O2p bonding in PuO_2 is even stronger, as compared with UO_2. However, the most prominent role of the indirect relativistic effects is detected for Ac7s orbitals, the corresponding relativistic values of the overlap populations are almost two times greater than those in the non-relativistic calculations. The anti-bonding character of Ac7p–O2p AOs interaction is rather unexpected result, because in the non-relativistic description their contribution to chemical bonding is usually positive, as well as those of the similar 6p states of lanthanides [22].

Table 2 lists the effective charges on atoms obtained in DV and RDV calculations for the main part of $Ac_{63}O_{216}$ clusters in UO_2 and PuO_2. A comparison of the Q_{eff} in Table 2 with the Mulliken values shows that the latter are nearly three times less than the integral charges. Though the Q_{eff} obtained by spatial integration are always more realistic than the Mulliken and Hirshfeld values [19,23], the charges on uranium, plutonium and oxygen atoms are noticeably less than their formal valencies in dioxides. The decrease of the effective charges on going from UO_2 to PuO_2 is mainly due to the increase of O2p–Ac5f covalent mixing which is the result of the smaller splitting of corresponding bands in PuO_2 (Fig. 3). The same effect is found for UO_2 where the lowering of O2p–U5f band gap by 1 eV in DV approach (with corresponding increase of covalent mixing) reduces the charges on uranium atoms by 20%, as compared with RDV calculations. In the cluster models of the periodic systems one could not simply define the so-called formula unit, and thus the effective charges obtained in this approach could not provide the electroneutrality condition for the selected group of atoms. In the case of relativistic calculation of UO_2 the total charge, $Q_{U1} + 2Q_{O1} = -0.07$ is found to be noticeably less than that in the non-relativistic approach (−0.39) and in RDV calculation of PuO_2: $Q_{Pu1} + 2Q_{O1} = -0.22$. As mentioned in Ref. [19], the charge balance is better for the compounds with wider gap between metal and

Table 1
Overlap populations of U_1, Pu_1 6d, 5f, 7s, 7p and $O_1$2p orbitals (the sum for $2p^{1/2}$ and $2p^{3/2}$ AO) in UO_2 and PuO_2 (10^{-3} e, per one ligand).

AO	UO_2		PuO_2
	DV	RDV	
$Ac6d^{3/2}$–O2p	168	67	66
$Ac6d^{5/2}$–O2p		99	97
$Ac5f^{5/2}$–O2p	48	25	18
$Ac5f^{7/2}$–O2p		39	53
Ac7s–O2p	31	55	59
$Ac7p^{1/2}$–O2p	9	9	2
$Ac7p^{3/2}$–O2p		−25	−54

Table 2
Effective charges on atoms in UO_2 and PuO_2 obtained by spatial integration [19] and Mulliken population analysis in RDV and DV calculations.

Atom	UO_2				PuO_2	
	DV		RDV			
	Integral	Mulliken	Integral	Mulliken	Integral	Mulliken
$U_1(Pu_1)$	2.45	1.25	2.97	1.04	2.46	0.77
O_1	−1.42	−0.59	−1.52	−0.51	−1.34	−0.39
$U_2(Pu_2)$	2.43	1.14	2.94	1.00	2.50	0.79
O_2	−1.42	−0.60	−1.53	−0.51	−1.34	−0.39
O_3	−1.42	−0.60	−1.52	−0.51	−1.34	−0.39

ligand valence bands (in the case of wide gap insulators CaF_2 and SrF_2 these values are within 0.02).

In $U_{63}O_{216}$ cluster the highest occupied (HOMO) and the lowest unoccupied (LUMO) molecular orbitals correspond to Γ_6^+ and Γ_6^- irreducible representations, respectively. The HOMO contains more than 50% of $5f^{5/2}$ atomic orbitals of U_3 with admixtures of $U_25f^{5/2}$ and O_12p, O_22p character; the LUMO is also of the $U_35f^{5/2}$ character. Noticeable admixtures of the $U_15f^{5/2}$ and $U_25f^{5/2}$ states appear in MOs just below E_F, however, the molecular levels with considerable $U_15f^{5/2}$ and $U_25f^{5/2}$ contributions are located ~0.5 eV and 0.45 eV below the HOMO. Unoccupied orbitals containing the main contributions of $U_15f^{5/2}$ and $U_25f^{5/2}$ AOs begin at 0.1 eV and 0.05 eV above the LUMO. Thus according to the ground state calculation of 279-atom cluster the energy difference for the $5f^{5/2}$ electron transition from U_1 to U_2 (or in the opposite direction) is equal or greater than 0.5 eV. In $Pu_{63}O_{216}$ cluster the HOMO and LUMO correspond to Γ_6^- and Γ_7^- representations and also do not contain any noticeable contributions of the $Pu_15f^{5/2}$ states. However, in this cluster the Fermi level is located just above the main peak of $Pu_15f^{5/2}$ DOS (Fig. 3) and the energy of the highest occupied level belonging to $Pu_15f^{5/2}$ orbital is only 0.03 eV less than that of the LUMO (corresponding to $Pu_35f^{5/2}$ character). Unoccupied orbitals of $Pu_25f^{5/2}$ character begin at 0.02 eV above the LUMO and therefore the energy edge for the electron transition from Pu_1 to Pu_2 is essentially lower than in $U_{63}O_{216}$.

For the investigation of the effects of electronic structure relaxation following the $5f^{5/2}$ electron transition between two individual actinide atoms in the dioxide lattice, the RDV calculations of $Ac_{13}O_{56}$ clusters with C_{2v} symmetry were carried out. The total and partial DOS obtained for the central U_1 and O_1 atoms in the ground state calculations of $U_{13}O_{56}$ cluster are shown in Fig. 4. Though some details of the valence bands shape are different for 279- and 69-atom fragments, the positions and widths of O2s–Ac6p and O2p–Ac5f, 6d states are surprisingly very close in both models. However, the Ac7s and 7p orbitals appeared to be sensitive to the cluster size, in small fragments the main peaks of U(Pu)7s and 7p DOS shift downward about 2 eV and 3 eV, respectively in both oxides. The contributions of $5f^{5/2}$ AOs of the central atom in the HOMO and LUMO are also small as in the calculations of large clusters. Note that 12 atoms of $U(Pu)_2$ type (Fig. 1) become nonequivalent in $Ac_{13}O_{56}$ model and form five types of symmetrically equivalent centers: $Ac_2^{(1)}$ and $Ac_2^{(2)}$ along the new z axis, $4Ac_2^{(3)}$, $2Ac_2^{(4)}$ and $4Ac_2^{(5)}$ in the planes which are perpendicular to this axis. The analysis of possible electron transitions between MO levels corresponding to $Ac_15f^{5/2}$ and $Ac_2^{(1)}5f^{5/2}$ character showed that in the ground state calculation of $U_{13}O_{56}$ the energy difference of such transitions is equal or greater than 0.5 eV, i.e. is close to the value obtained for the transition from U_1 to the $5f^{5/2}$ states delocalized among 12 equivalent U_2 centers in $U_{63}O_{216}$. In the case of the ground state calculation of $Pu_{13}O_{56}$ cluster the energy of the transition from occupied $Pu_15f^{5/2}$ to vacant $Pu_2^{(1)}5f^{5/2}$ levels is near 0.2 eV, i.e. this value is greater than 0.05 eV obtained for the $Pu_{63}O_{216}$ cluster.

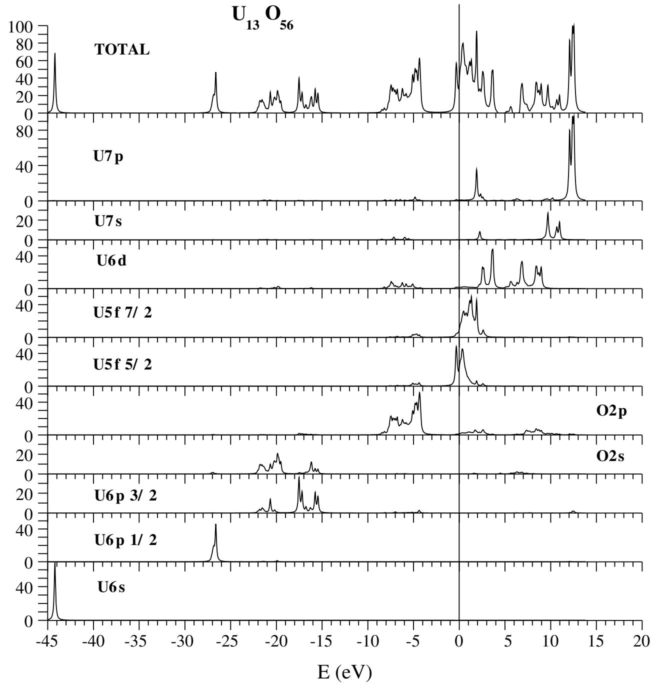

Fig. 4. Total and partial densities of states for the central part of $U_{13}O_{56}$ cluster in UO_2.

The transition state calculations were started from the direct changing of the population of $Ac_15f^{5/2}$ and $Ac_2^{(1)}5f^{5/2}$ basis atomic orbitals by −0.5 and +0.5, respectively. As a result the energy difference of the molecular orbitals of $Ac_15f^{5/2}$ and $Ac_2^{(1)}5f^{5/2}$ character achieved ~13 eV in both oxides. This result means that the electron transition between MOs with 100% contribution of $Ac_15f^{5/2}$ and $Ac_2^{(1)}5f^{5/2}$ AOs without admixtures of any other orbitals could be possible with the excitation energy near 13 eV. However, there are no such $5f^{5/2}$ molecular states "purely" located on an individual metal site in $Ac_{13}O_{56}$ clusters as well as in $Ac_{63}O_{216}$ clusters. Actually the half of the hole and the half of additional electron are partially distributed over the nearest neighbors and next nearest neighbors and during self-consistency the configurations of several atoms are modified. As a result the energy difference between initial and final molecular levels converged to the values which are near 1.0 eV and 0.9 eV in $U_{13}O_{56}$ and $Pu_{13}O_{56}$ clusters, respectively. Thus the results of our calculations show that these values are strongly connected with the covalency effects in the electronic structure and could also be considered as some indirect measure of the degree of $5f^{5/2}$ states hybridization in uranium and plutonium dioxides.

In LDA + U studies the U values are usually found empirically, however in the paper of Anisimov and Gunnarsson [24] the first-principles procedure for the calculation of U was described. In order to compute this parameter, one has to remove the transfer integrals between the f orbitals and the rest of the system and the occupancy of the f orbitals of the nearest metal sires is varied, while the other metal electrons are allowed to relax self-consistently, and it follows that the "screened" $U = E(f^{n+1}) + E(f^{n-1}) - 2E(f^n)$, where E is the LDA total energy. In the case of dioxides the hybridization of metal and oxygen orbitals noticeably decreases the band gap as compared with the value of U. For instance, Lasowski et al. [5] used $U = 0.4$ Ry to obtain the experimental gap of about 2 eV in UO_2. In our calculations the above mentioned value of 13 eV (near 1 Ry) means the energy difference without any "screening" and the final self-consistent values of 1.0 and 0.9 eV include the effects of relaxation of all metal and ligand states.

4. Conclusions

Our investigations of the uranium and plutonium dioxides confirm the earlier results that the 5f states of metal atom are strongly hybridized with 2p orbitals of nearest ligands as well as with 5f AOs of the next nearest neighbors and with even more distant sites. Due to this hybridization the energy difference for the transition between occupied and vacant $5f^{5/2}$ MOs located on different atoms is considerably less than 13 eV for the completely localized $5f^{5/2}$ states.

Though there were successful attempts to explain the experimental band gap in the ground state calculations, the excitation of conductivity in UO_2 and PuO_2 is an interesting phenomenon for the theoretical investigations. According to our transition state calculations the energy differences for the initial and final levels are two times less than experimental excitation energy for both oxides. However, two metal sites participating in this process are not nearest neighbors and the $5f^{5/2}$–$5f^{5/2}$ transition corresponds to the so-called "hoping" conductivity. There is no doubt that an additional effect of the energy barriers for the electron hoping has to be considered for such excitation. The results obtained here show that a "proper" explanation of the experimental values will have to take account of both effects.

Acknowledgments

We would like to thank V.I. Anisimov for helpful discussions.

This work was supported by the Russian Foundation for Basic Research, Grant 06-08-00808.

References

[1] V.A. Gubanov, A. Rosen, D.E. Ellis, J. Phys. Chem. Solids 40 (1978) 17.
[2] J.C. Boettger, A.K. Ray, Int. J. Quant. Chem. 80 (2000) 824.
[3] J.C. Boettger, A.K. Ray, Int. J. Quant. Chem. 90 (2002) 1470.
[4] S.L. Dudarev, D. Nguyen Manh, A.P. Sutton, Philos. Mag. B 75 (1997) 613.
[5] R. Lasowski, G.K.H. Madsen, P. Blaha, K. Schwarz, Phys. Rev. B 69 (2004) 140408R.
[6] I.D. Prodan, G.E. Scuseria, R.L. Martin, Phys. Rev. B 73 (2006) 045104.
[7] J. Shoenes, J. Appl. Phys. 49 (1978) 1463.
[8] C.E. McNeilly, J. Nucl. Mater. 11 (1964) 53.
[9] V.I. Anisimov, J. Zaanen, O.K. Andersen, Phys. Rev. B 44 (1991) 943.
[10] M.V. Ryzhkov, N.I. Medvedeva, V.A. Gubanov, J. Phys. Chem. Solids 56 (1995) 1231.
[11] M.V. Ryzhkov, T.A. Denisova, V.G. Zubkov, L.G. Maksimova, J. Struct. Chem. 41 (2000) 927.
[12] D.E. Ellis, G.A. Benesh, E. Byrom, Phys. Rev. B 20 (1979) 1198.
[13] J.C. Slater, K.H. Johnson, Phys. Rev. B 5 (1972) 844.
[14] A. Rosen, D.E. Ellis, J. Chem. Phys. 62 (1975) 3039.
[15] H. Adachi, Technol. Reports Osaka Univ. 27 (1977) 569.
[16] O. Gunnarsson, B.I. Lundqvist, Phys. Rev. B 13 (1976) 4274.
[17] P. Pyykko, H. Toivonen, Acta Acad. Aboensis, Ser. B 43 (1983) 1.
[18] D.A. Varshalovich, A.N. Moskalev, V.K. Khersonskii, Quantum Theory of Angular Momentum, World Scientific, Singapore, 1988.
[19] M.V. Ryzhkov, J. Struct. Chem. 39 (1998) 933.
[20] Yu.A. Teterin, A.Yu. Teterin, Russ. Chem. Rev. 73 (2004) 541.
[21] R.S. Mulliken, Ann. Rev. Phys. Chem. 29 (1978) 1.
[22] M.V. Ryzhkov, V.A. Gubanov, Yu.A. Teterin, A.S. Baev, Z. Phys. B 59 (1985) 7.
[23] M.V. Ryzhkov, A.L. Ivanovskii, B.T. Delley, Chem. Phys. Lett. 404 (2005) 400.
[24] V.I. Anisimov, O. Gunnarsson, Phys. Rev. B 43 (1991) 7570.