Electronic Structure of Uranium Dioxide

Younsuk Yun, Kwangheon Park and Hunhwa Lim

Kyung Hee University
Suwon 449-701, Korea
hlim@khu.ac.kr

Kun Woo Song

Korea Atomic Energy Research Institute
150 Dukjin-Dong, Yusong-Gu, Taejon 305-353, Korea

Abstract

The details of the electronic structure of the perfect crystal provides a critically important foundation for understanding the various defect states in uranium dioxide. In order to understand the local defect and impurity mechanism, we carry out the calculation of electronic structure of UO_2 in the one-electron approximation, using a semi-empirical tight-binding formalism with and without f-orbitals. The local density of states for both spin are calculated from the spectral representation of Green's function. We discussed the bonding mechanism in perfect lattice of UO_2 based upon the calculations of band structure, local and total density of states.

_____

Keywords : tight-binding method, LCAO, energy band, density of states, bonding mechanism

I. Introduction

Interest in UO_2 is stimulated both by the diversity of the fundamental properties associated with the materials and by the important technical problems associated with its use as a reactor fuel. Its electronic structure has been investigated by x-ray and resonant spectroscopies[1-3] , which concern the occupied states, and by optical absorption[4], Bremsstrahlung Isochromat spectroscopy, inverse photoemission[5] and x-ray absorption spectroscopy[6-7], which concern the empty states. In spite of all these experimental results as well as theoretical ones[8-13], relatively little is still known about its electronic structure.

The details of the electronic structure provide a critically important foundation for understanding both the perfect and various defect states in uranium dioxides. We carried out electronic structure calculation of perfect lattice in the one-electron approximation, using a semiempirical tight-binding

model with the linear combination of atomic orbital (LCAO). The local and total density of states are calculated for UO_2 through the spectral representation of Green's function.

After a brief presentation of the calculation method in the next section, we present the band structure in uranium dioxide along with the local and total densities of states of each orbital from the Green's function. We discussed the chemical bonding mechanism based upon the present calculations.

II. Theoretical Formalism

1. Crystal Structure

At room temperature uranium dioxides crystallize in the fluorite structure (CaF_2), as originally proposed by Goldschmidt in 1923[14], and belong to the *Fm3m* space group. The unit cell parameter is a_0=5.47 Å[15-16]. The lattice can be described as an fcc cation lattice in which all the tetrahedral site are occupied by an oxygen atom. This leads to a cubic local symmetry around each cation. The atomic positions are those for the fluorite arrangement, with uranium at (000)+f.c. and oxygens at $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, $\frac{3}{4}\frac{3}{4}\frac{3}{4}$ +f.c. Each oxygen is tetrahedrally surrounded by four uranium atoms at a distance of 2.37 Å, and six second nearest neighbor oxygen atoms at 2.735 Å. Each uranium atom is surrounded by eight oxygen atoms at 2.37 Å and twelve second neighbor uranium atoms at 3.87 Å, as shown Fig. 1.

Above room temperature the atomic arrangement can no longer be described exactly in terms of the ideal fluorite structure with harmonic thermal vibration. Above 1800 ℃ it transforms to the sub-stoichiometric phase UO_{2-x}, whereas at lower temperature it dissolves oxygen and change into super- stoichiometric phase UO_{2+x}.

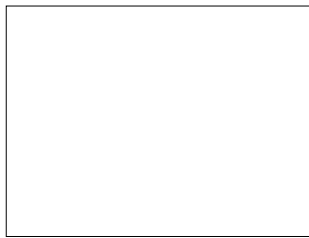Fig. 1 Unit cell of flourite
structure of UO_2.

2. Tight-binding formulation

The tight-binding approach has less predictive power than techniques that use the local-density approximation (LDA), in which the electronic states are calculated self-consistently from first principle but with electron correlation and exchange effects approximated by a local-potential. The LDA often provides a good description of ground state properties, but is less accurate in representing the excited states. However, the tight-binding model has a distinct advantage over other techniques, since one can obtain a better representation or the electronic structure by using a semiempirical fit to the experimental measurement. Also, the parameters of the model has a

strong chemical meaning, representating effective atomic energies and bond strengths. Especially the tight-binding approach gives deeper insight into the bonding picture of the sample than any other electronic structure calculations. It was for this reason that we first chose to work with LCAO approach which is less time consuming than a full-potential approach but still is able to give physically correct results.

The standard tight-binding method works by expanding eigenstates of a Hamiltonian in an orthogonalized basis of atomic-like orbitals and representing the exact many-body Hamiltonian operator with a parametrized Hamiltonian matrix, where the matrix elements are fitted to the band structure of a suitable reference system and experimental results.

The solution of the matrix form of the time-independent Schrodinger equation

$$H(\vec{k})\Psi(\vec{k},n) = E(\vec{k},n)\Psi(\vec{k},n) \tag{1}$$

gives tight-binding wave functions $\Psi(\vec{k},n)$ $(\equiv\Psi_k)$ with components representing the atomic orbital basis of the model. The host crystal energy eigenvectors are approximated with the linear combination of atomic orbital. Schematically, one writes the crystal wave function Ψ_k as a linear combination of Bloch functions $\Psi_\alpha(\vec{k})$, each of which depends on only one type of orbital. For each wave vector $\vec{k}$ characterizing a state, we construct Bloch sums

$$|\Psi_\alpha(\vec{k})\rangle = \frac{1}{\sqrt{N_p}}\sum_i \exp(i\vec{k}\cdot\vec{r_i})|a_\alpha(\vec{r}-\vec{r_i})\rangle \tag{2}$$

,where $|a_\alpha(\vec{r}-\vec{r_i})\rangle$ $(\equiv|\alpha,i\rangle)$ is the atomic orbital at the site $\vec{r_i}$, and N_p is the number of lattice sites. For each eigenstate of wave number k, the crystal wave function can be written as a linear combination of these Bloch sums;

$$|\Psi_k\rangle = \sum_\alpha C_\alpha|\Psi_\alpha(\vec{k})\rangle \tag{3}$$

The atomic and hybrid orbitals are assumed orthonormal such that

$$\sum_\alpha |\Psi_\alpha(\vec{k})|^2 = 1 \tag{4}$$

for the orbital components α.

For any wave vector in the Brillouin zone we seek the lowest energy solution by minimizing

$$\frac{\langle\Psi_k|H|\Psi_k\rangle}{\langle\Psi_k|\Psi_k\rangle} \tag{5}$$

with respect to C_α

$$\sum_\beta \langle\Psi_\alpha(\vec{k})|H|\Psi_\beta(\vec{k})\rangle C_\beta - E_k C_\alpha = 0 \tag{6}$$

or

$$\sum_{\beta} H_{\alpha\beta}(\vec{k})C_{\beta} - E_k C_{\alpha} = 0 \tag{7}$$

There is one such equation for each α corresponding to a basis state. The eigenvalue can be obtained directly from the secular equation. The lowest E corresponds to the lowest electron state; the next lowest, to the lowest electron state having a wave function orthogonal to that of the first, and so on. The solutions of these equations give the C_{α} which give the wave function of the crystal through Eq. 3. The wave functions and the energy eigenvalues are plotted as dispersion relations in k along particular symmetry lines of the Brillouin zone for the fcc structure. The tight-binding Hamiltonian matrix has elements

$$H_{\alpha i, \beta j}(\vec{k}) = \sum_{l} < \alpha i \,|\, H \,|\, \beta j, l > \, \exp[i\vec{k} \cdot (\vec{r}_i - \vec{r}_j)] \tag{8}$$

,where α and β label orbitals, and the sum is over all atoms that are equivalent to atom j in the unit cell and that neighbor atom i. The diagonal elements of the Hamiltonian are the atomic energies in Table 1. The inter-atomic matrix elements $\sum_{l} < \alpha i \,|\, H \,|\, \beta j, l >$ are determined by the primitive tight-binding matrix elements and by the relative coordinate from atom i to atom j, l as shown in Table 2. Consider a matrix element $H_{\alpha i, \beta j}(\vec{k})$, from Eq.(8), where α correspond to a cation s orbital and β to an anion s orbital. Each orbital $< S^c|$ in the sum making up the state $< \alpha, i|$ will have matrix elements $V_{ss\sigma}$ between it and the four neighboring orbitals $|S^a>$, indicated in Fig. 2; each of three neighboring orbitals enters the matrix elements $V_{ss\sigma}$ with a phase factor differing from that of $|S^a>$ orbital by $e^{i\vec{k} \cdot \vec{d}_i}$ with $\vec{d}_i$ being the vector distance to that neighbor.

$$H_{S^c S^a}(\vec{k}) = V_{ss\sigma} \sum_{i} e^{i\vec{k} \cdot \vec{d}_i} \tag{9}$$

The neighbor to the cation and there vector distance are given as

$$\vec{d}_1 = [1\ 1\ 1]\frac{a}{4}$$

$$\vec{d}_2 = [1\ \bar{1}\ \bar{1}]\frac{a}{4}$$

$$\vec{d}_3 = [\bar{1}\ 1\ \bar{1}]\frac{a}{4}$$

$$\vec{d}_4 = [\bar{1}\ \bar{1}\ 1]\frac{a}{4}$$

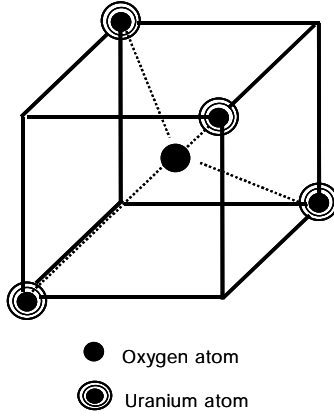For the neighbor to the anion we can get the similar eight vector distances as shown in Fig. 3.

Fig. 2 Bonding in the CaF$_2$ structure. The central oxygen atom surrounded its four nearest neighbors.

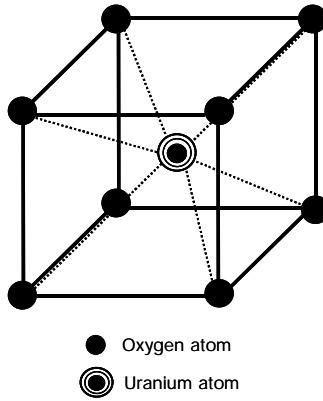Fig. 3 Bonding in the CaF2 structure. The central metal atom sits at the center of cube formed by its eight nearest neighbors(O atom in the present case).

The primitive tight-binding matrix elements between nearest neighbor atoms[17-19] are

$$V_{ll'm} = \eta_{ll'm} \frac{\hbar^2}{m_e d^2}(l,\ l' = s,\ p;\ m = \sigma,\pi,\delta)$$ (10)

$$V_{ldm} = \eta_{ldm} \hbar^2 \frac{r_d^{\frac{3}{2}}}{m_e d^{\frac{7}{2}}}(l,\ l' = s,\ p;\ m = \sigma,\pi,\delta)$$ (11)

$$V_{ddm} = \eta_{ddm} \hbar^2 \frac{r_d^3}{m_e d^5}(l,\ l' = s,\ p;\ m = \sigma,\pi,\delta)$$ (12)

$$V_{lfm} = \eta_{lfm} \hbar^2 \frac{r_f^5}{m_e d^{9/2}}(l = s,\ p;\ m = \sigma,\pi)$$ (13)

$$V_{dfm} = \eta_{dfm} \hbar^2 \frac{(r_d^3 r_f^3)^{1/2}}{m_e d^6} (m = \sigma, \pi, \delta) \tag{14}$$

$$V_{ffm} = \eta_{ffm} \hbar^2 \frac{r_f^5}{m_e d^7} (l = s, p; m = \sigma, \pi, \delta, \phi) \tag{15}$$

where m_e is the mass of the electron. The matrix elements varies with the indicated inverse power of the inter-atomic separation, d, a result from scaling in the linear combination of atomic orbital (LCAO) theory. The strength of the interaction is given by the dimensionless variables $\eta_{ll'm}$, where l refers to the angular momentum quantum number (s, p, d, or f) of the first orbital, l' is the angular momentum quantum number of the second orbital, and m describes the total angular momentum of the interaction ($\sigma, \pi,$ or δ bonding). $V_{ll'm}$ is unaffected under exchange of l and l' if the sum of the parities is even, but changes sign if the sum of the parities is odd. We have adjusted the strength parameters $\eta_{ss\sigma}$ etc. to better fit the LDA results[22,23] and experimental results[24-26].

3. f-orbitals

Actinide metals and their compounds are characterized by an incomplete 5f shell, whose radial extent is somewhat greater than for the corresponding 4f elements. The participation of 5f electrons in chemical bonding and the suitability of one-electron models for these system has been the subject of lively debate. Uranium dioxide is one of the typical examples. As mentioned above many studies have been undertaken about UO_2, not only because of its technological interest, but also for its peculiar fundamental properties often linked with its U 5f electrons[20]. Localization versus itineracy and the degree of hybridization of 5f state with orbitals of the oxygen atom (especially 2p) are central questions for the understanding of bonding in uranium oxides. Arko et al [21] have performed on band-structure calculation on this materials with treating 5f states as core states and neglected correlation effects, while Kelly and Brooks[22] treated the 5f states as filled with one seventh of an electron. Petit[23] et al studied the cohesive properties of UO_2 by means of linear combination of muffin-tin orbital(LMTO) method in the atomic sphere approximation(ASA). They treated uranium 5f states as band states and did not fill 5f states artificially. They showed that, although UO_2 is a very strongly ionic materials, the uranium-oxygen bond has a partly covalent nature due to uranium 5f and oxygen 2p hybridization. Rahman[24] has calculated the energy levels of the configuration f^2 in an eight-fold cubic crystal field approximation and the results are used to explain the experimental spectrum of UO_2. Davis et al.[25] compare the results of their calculations treating the uranium 5f states as band states, and as localized states in UGa_2. They found that the latter model gave better agreement with experimental data on the total magnetic moment and the anisotropy of magnetic susceptibility.
In spite of experimental and theoretical results the nature of f-orbital is still debating.
The strength of the O_{2p}-U_{5f} hybridization has been assumed to be zero[10], to exist[26] or to be strong[27].
Thus in this paper we performed the calculation of electronic structure with and without f-orbitals. Then we discussed the chemical bonding mechanism by the degree of hybridization of 5f states.

4. Green's Function

The Green's function, which expresses all of the necessary information about perfect crystal, is

obtain from LCAO calculation. It is given in the spectral representation[28] by

$$G^{(0)}(E) = \sum_{k,n} W_{\vec{k}} \frac{\Psi^+(\vec{k},n)\Psi(\vec{k},n)}{E - E(\vec{k},n) + i\delta}$$ (16)

,where $E(\vec{k},n)$ and $\Psi(\vec{k},n)$ are the electronic eigenvalue and the wave function in the tight-binding representation for the nth band and one of the N samples wave vectors $\vec{k}$ with weight $W_{\vec{k}}$ within the irreducible part of the Brillouin zone[29]

For these calculations, the sum is taken over N=20 sample points for the fcc structure. A finite value of δ=0.2 eV

was used, smoothing the results with a Lorentzian line shape. The total density of states is simply the sum of the local densities of states of each atom in the unit cell.

The Fermi energy is calculated by integrating the total density of states up to the number of valence electrons for each material which is consistent with a average of the highest occupied energy states across the sample wave vectors. The local density of states for both spins is calculated from[33]
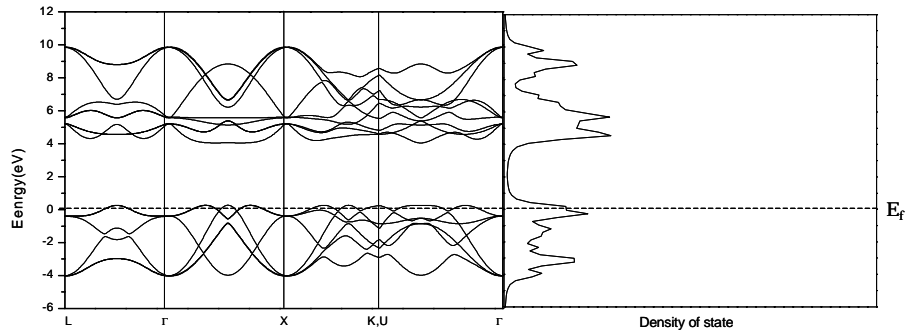
$$\rho(E) = -\frac{1}{\pi} TrIm \mid G^{(0)}(E) \mid$$ (17)

Fig. 4 Energy band of UO$_2$ without f-orbital.

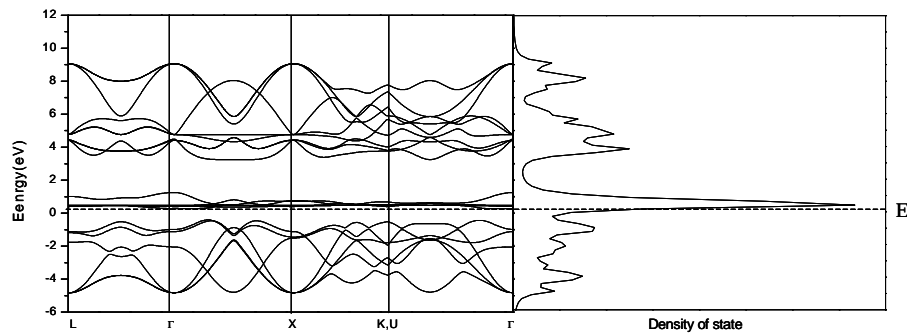Fig. 5 Energy band of UO$_2$ with f-orbital.

,where Tr indicates a trace over those orbitals associated with a given site.

III. Results and Discussion

1. Electronic Energy Bands

In tight-binding approach the effect of covalency and ionicity can be lumped together in atomic energies and strength parameters in order to reflect the characteristic chemical bonding. A common actual tight-binding calculation and its results, hence, clearly depends upon the parametrization scheme. Within the framework of standard empirical tight-binding theory, several proposals have been made to generalize the TB energies by explicitly considering inter-atomic electron interactions [17-19]. The energy bands of the uranium dioxide are calculated in the one electron approximation, using a semiempirical tight-binding model with p and s orbitals included for the oxygen ions and f, d, p and s orbitals for the uranium ions. Also, the energy bands and density of states are calculated without f-orbitals(with s,p,d only) for the uranium ions in order to understand the role of f-orbitals in the bonding picture of UO_2. However, the calculational results without f-orbitals did not satisfactorly explain the experimental results, so we stopped calculating the structure based upon the s,p,d bases.

The resulting atomic parameters are listed in Table. 1; the interatomic strengths($\eta_{sp\sigma}$ et al.) are listed in Table 2. As mentioned above the results are fitted to other theoretical calculations and experimental results. The calculated energy bands for UO_2 without f-orbitals are shown in Fig. 4, along several symmetry lines in the Brillouin zone, with the zero of the energy shift to Fermi enrgy, E_f.

The characteristic features of the band structure are conduction bands derived from U_{7p} and U_{6d} and valence bands derived from O_{2p} and U_{6d} states as indicated at the local density of states(Fig. 6). The Fermi energy is -6.57 eV and the direct band gap at the X-point is 5.5 eV. The widths of valence bands and conduction bands at the Γ-point are ~ 4 eV and ~ 5 eV respectively.

The calculated band structure with the f states is shown Fig. 7. Due to p-f hybridization the theoretical 5f bands of UO_2 are found to be delocalized and show somewhat broader dispersion of the bands. The Fermi energy level is -5.76 eV and the band gap is 3 eV, which are quite good agreement with other experimental results and theoretical calculations. The parameters of our tight-binding model are thus considered properly fitted for UO_2.

	ε_s (eV)	ε_p	ε_d	ε_f
uranium	-3.5	-2.0	-1.0	-5.3
oxygen	-29.4	-6.3		

Table. 1 Tight-binding parameters(on-site energies).

$\eta_{ss\sigma} = -1.1$	$\eta_{sp\sigma} = 0.9$	$\eta_{ps\sigma} = -0.9$
$\eta_{pp\sigma} = 0.3$	$\eta_{pp\pi} = -0.5$	$\eta_{sd\sigma} = -1.6$
$\eta_{ds\sigma} = -1.6$	$\eta_{pd\sigma} = -2.5$	$\eta_{dp\sigma} = 2.5$
$\eta_{pd\pi} = 1.4$	$\eta_{dp\pi} = -1.4$	$\eta_{dd\sigma} = -16.8$
$\eta_{dd\pi} = 8.8$	$\eta_{pf\sigma} = -10.0$	$\eta_{fp\sigma} = -2.5$
$\eta_{pf\pi} = -30$	$\eta_{fp\pi} = 5.0$	

Table 2. Strength parameters for hopping integrals.

2. Density of States

The local density of states for both spins is calculated from Eq.(17). The local density of states for uranium atom without f-orbitals are shown in Fig. 6   .

Uranium 6d and 7p bands have narrow, unoccupied peaks above Ef at ～6 eV and ～4.5 eV respectively. The occupied O_{2p} bands form broad spectra and peak near -4.8 eV, while the O_{2s} bands lie far below near -28 eV. The local density of states with f-orbitals are also shown in Fig. 7. The uranium f-bands lie around ～-5.3 eV(the zero of the energy shift to E_f.)and more tightly bound to core(atomic-like states). It has a sharp spectrum related to the ionic bond formed with oxygen atoms. U_{7p}(～3 eV), and U_{6d}(～5 eV) bands show broad feature above the Fermi energy characteristic features of covalent bonds with O_{2p} orbitals. Thus we would expect that there would be an appreciable degree of covalence in UO_2 even though it is strong ionic compound[30-32].

In summary, we find that a single tight-binding model, with fully transferable parameters, provides a good description of the electronic structure of the uranium dioxides, in the sense that the results satisfactorily agree with LDA calculations and with certain experimental details of the electronic states.

The 5f states in uranium dioxide are found to be localized and to form relatively narrow bands pinned at E_f as shown in Fig. 7. The narrow and intense peak located within 0.5 eV above E_f certainly accounts for the rather pure 5f states, which do not hybridize with other orbitals. It indicates that f-orbital localized(atomic-like) and does not participate in bonding of uranium dioxide. we find also that the ion size of uranium atom is increased about 0.03 Å after including the f-orbitals. The energy levels of f-orbitals in uranium atoms are lower than any other orbitals(5f<7s<7p<6d).

As mentioned above our results indicate that, even though UO_2 is known as highly ionic, the solid cannot be viewed electrostatically as separated ions. This fact causes to question any quantitative use for concepts as ionic radii and net charge.

We have calculated the bonding picture in some detail and will present elsewhere in the near future.
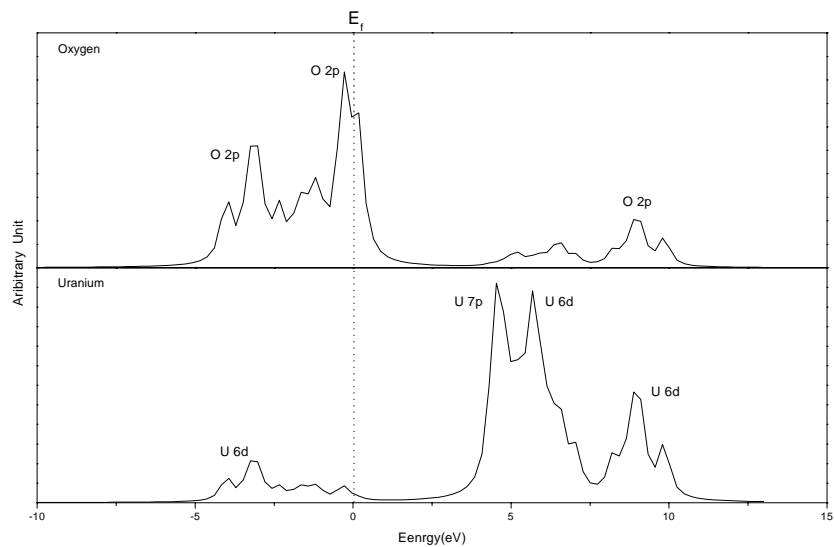
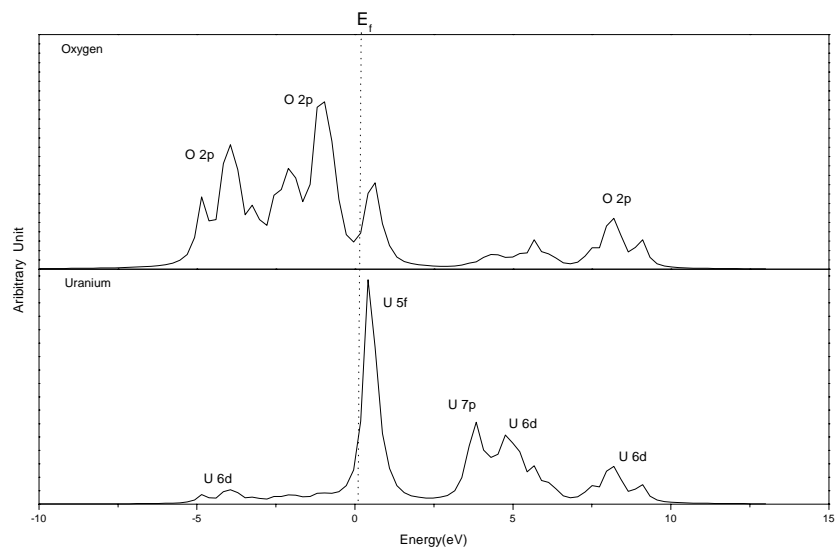Fig. 6 Local density of states without f-orbital.

Fig. 7 Local density of states with f-orbital.

References

1. Y. Baer and J. Schones, Solid State Commun. 33, 885(1980).

2. O. Gunnarsson, D. D. Sarma, T. U. Hillebrecht and K. Schonhammer, J. Appl. Phys. 63, 3676(1988).

3. L. E. Cox, W. P. Ellis, R. D. Cowan, J. W. Allen, S. J. Oh, I. Lindau, B. B. Pate and A. J. Arko Phys. Rev. B 35, 5761(1987) and references therein.

4. J. Schones, J. Physique. Coll. 41(supplement 6), C5 31(1980).

5. G. Chauvet and R. Baptist, Solid State Commun. 43, 7931(1982).

6. J. Guo, D. E. Ellis, E. Alp, L. Soderholm and G. K. Shenoy, Phys. Rev. B 39, 6125(1989).

7. E. A. Hudson, J. J. Rehr and J. J. Bucher Phys. Rev. B 52, 13 875(1995) and references therein.

8. V. A. Gubanov, A. Rosen and D. E, Ellis, Solid State Commun. 22, 219(9177).

9. T. Petit, B. Morel, C. Lemaignan, A. Pasturael and B. Biget, Phil. Mag. B 73, 893 (1996).

10. P. J. Kelly and M.S.S. Brooks, Physica B 102, 81(1980).

11. C. R. A. Catlow, Nonstoichiometric Oxides ed. O. Toft Sorensen, Academic Press (1981), Chap. 2.

12. H. L. Skriver, O. K. Andersen and B. Johanssen, Phys. Rev. Lett. 44, 1230(1980).

13. D. D. Koelling and A. J. Freeman, Solid State Commun. 9, 1369(1971); Phys. Rev. B 12, 5622(1975).

14. V. M. Goldschmidt and L. Thomassen, Videnskap. Skirift I., Mat. Nat. Klasse, p. 1(1923).

15. B. T. M. Willis, Nature, 167, 755(1963); Pro. R. Soc., London, Ser. A, 274,122(1963).

16. B. T. M. Willis, J. Chem. Soc. Faraday Trans. 2, 83, 1078(1987); Acta Cryst. A34, 88(1978).

17. W.A. Harrison , Electronic Structure and Properties of Solids, W. H. Freeman, San Francisco(1980) and references therein

18. W.A. Harrison, Phys. Rev. B 31, 2121(1985); phys. Rev. B 28, 550(1983).

19. J. A. Majewski and P. Vogel, Phys. Rev. B 35, 9666(1987).

20. M.S.S. Brooks, Structure and Bonding 59/60, Chap. F, Springer-verlag, Berin(1985)

21. J. Arko, D. D. Koelling, A. M. Ellis, W. P. Boring, and L. E. Cox, J. lesscommon metals 122, 95 (1986).

22. P. J. Kelly and M. S. S. Brooks, J. Phys. C 13, L939 (1980); J. Chem. Soc., Faraday Trans. II, 83, 1189(1987)

23. T. Petit, B. Morel, C. Lemaignan, A. Pasturel, and B. Bigot, Phil. Mag. B 73, 893(1996)

24. H. U. Rahman, Phys. lett. A, 240, 306(1998)

25. H. Eschrig, L. Steinbeck, Phys. Rev. B 53, 9658(1996)

26. L. E. Cox, J. Electron Spectrosc. Relat. Phenom. 26, 167 (1982)

27. O. Gunnarsson, D. D. Sarma, F. U. Hillebrecht and K. Schonhammer, J. Appl. Phys. 63, 3676(1988).

28. E. N. Economou, Green's Function in Quantum Mechanics, Springer-Verlag(1983), chap 1 and 4.

29. A. Baldereschi, phys. Rev. B7,(1973); D. J. Chadi and M.L. Cohen, phys. Rev. B8, 5747(1973).

30. C. R. A. Catlow and A. M. Stoneham, J. Phys. C 16, 4321(19830).

31. C. R. A. Catlow J. Chem. Soc., Faradays Trans. 2, 83, 1065(1987)

32. D. R. Jennison and A. B. Kunz, Phys. Rev. B 13, 5597(1976).