ELSEVIER

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Nuclear Materials 341 (2005) 25–30

journal of nuclear materials

www.elsevier.com/locate/jnucmat

Calculation of the threshold displacement energies in UO_2 using ionic potentials

C. Meis [a,*], A. Chartier [b]

[a] CEA-Saclay, INSTN, Bât 395, 91191 Gif-sur-Yvette, France
[b] CEA-Saclay, DEN/DPC/SCP, Bât 450 Sud, 91191 Gif-sur-Yvette, France

Received 14 November 2004; accepted 6 January 2005

Abstract

A set of ionic potentials matching exactly the crystallographic, elastic and dielectric properties of the uranium dioxide is established. It is further validated upon some basic thermodynamic properties as well as upon the Frenkel pairs formation energies and the activation energies for lattice migration in UO_2. The threshold displacement energies, useful to characterise the radiation resistance of the materials, are calculated for the uranium dioxide along various crystallographic directions applying the optimised force field within the sudden approximation approach.

© 2005 Elsevier B.V. All rights reserved.

PACS: 34.20.C; 71.15.D; 61.80.−x

1. Introduction

Uranium dioxide UO_2 physicochemical properties have been extensively studied both experimentally and theoretically. The crystallographic, elastic and thermodynamic properties, static and high frequency dielectric constants, point defects formation energies, activation energies for lattice migration are very well known today and can be easily found in the plethoric literature [1–16]. From a theoretical point of view, this is a fairly favorable situation since the well known properties of this material can be used for establishing reliable empirical potentials [17–25] in order to perform quite relevant microscopic scale studies. Despite the fact that numerous experimental works have been carried out in order to investigate the behavior of uranium dioxide under irradiation, the threshold displacement energies have never been measured directly and have been rather deduced by indirect considerations which were supposed to match the final irradiation state obtained by theoretical calculations with that of the experimental observations. In fact, the very first theoretical work was done by Soullard et al. [26,27] who established a computational code for studying single event displacement cascades in UO_2. They evaluated the threshold displacement energies of oxygen and uranium, to be roughly 20 eV and 40 eV respectively, since, according to their calculations, these values permitted to obtain consistent results with the experimental observations. Since then, quite a few theoretical works, mainly based on molecular dynamics MD simulations [28,29] have

---

[*] Corresponding author. Tel.: +33 169 089 162; fax: +33 169 089 221.

E-mail address: cmeis@cea.fr (C. Meis).

0022-3115/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2005.01.001

been done on this subject. Thus, the values established by Soullard et al. are still used today for evaluating radiation damage in UO_2. However, the threshold displacement energy, which is defined as the minimum energy transferred to a lattice atom along a given crystallographic direction yielding the creation of a stable Frenkel defect is considered as a parameter of high importance for quantifying the number of displaced atoms during irradiation induced displacement cascades.

Consequently, it is worthy evaluating theoretically the threshold displacement energies of uranium and oxygen in mono-crystalline uranium dioxide. For that purpose the short range interactions that may be used for the simulations should be able of reproducing the better possible both the UO_2 physical properties and the energetic pathways in the crystalline structure. Hence, we have established a new set of inter-atomic potentials for uranium dioxide imposing the requirement to reproduce not only the crystallographic, elastic and thermodynamic properties but also the Frenkel pairs formation energies as well as the activation energies for lattice migration. The threshold displacement energies for uranium and oxygen have been calculated using the sudden approximation (SA) method along various crystallographic directions.

2. Short-range interaction potentials

The force field has been established by applying an iterative method. A set of potentials is fitted upon the experimental data of crystallographic, elastic and dielectric properties of uranium dioxide and then applied to calculate the thermodynamic properties, the Frenkel pairs formation energies and finally the activation energies for lattice migration. If the last properties were not reproduced well by the established potentials then a new set was established by the fitting procedure until all the required properties are reproduced within a convenient precision. The GULP code [30] has been used throughout this work.

Potentials parameters fitting is based on a least squares refinement procedure minimizing the difference of the squares between the experimental and the calculated values of various observables f.

$$\Delta_n = \sum [w_n f_n(\mathrm{cal}) - f_n(\mathrm{exp})]^2 \rightarrow \min, \qquad (1)$$

where w_n is a weight factor for the observable f_n. For that purpose, we have used the UO_2 experimental lattice parameter a [2], the elastic matrix elements c_{ij} [13], the bulk modulus B [2] and finally the static and high frequency dielectric constants ε_0 [14] and ε_∞ [15]. Previous studies [17,21] have shown the ionic polarizability to be an important feature of uranium dioxide yielding a very large high-frequency dielectric constant $\varepsilon_\infty = 5.3$ and playing a direct influence on the defect formation and migration energies. It is well known that shell-model potentials can describe the ionic polarizability, reproducing physical values for the constant ε_∞. Hence, we have considered here both the oxygen and uranium ions to be polarized according to the Dick and Overhauser model [32]. The harmonic constants K_O and K_U characterize the interaction between the core and shell for oxygen and uranium respectively. As it is usually the case in ionic modeling of crystals, cation–cation short range interactions are put to zero while the anion–anion and anion–cation short-range interactions, complementing Coulomb ones, are expressed by Buckingham potentials composed by a Born–Mayer repulsive term and an r^{-6} attractive one: $E_{ij} = A_{ij} \exp[-r/\rho_{ij}] - C_{ij}/r^6$. We have used a fourth-order Buckingham potential to describe the O_shell–O_shell interaction. It consists of introducing polynomial expressions between the Born–Mayer and the attractive term. Thus, the potential energy, supplementing the Coulomb one within the range 1 Å–12 Å, is expressed by four different analytical expressions each one being valid within a given distance interval with the first and second derivatives continuity being ensured at the interconnection points.

The GULP code [30] permits the iteration of all the potential parameters $\{A_{ij}, \rho_{ij}, C_{ij}\}$, the polarisability constants, K_O and K_U, as well as the core and shell charges

Table 1
Short-range potential parameters for UO_2 complementing Coulomb interactions

Interactions	Analytic form	Interval (Å)	
O_shell–O_shell	$20908.03 \exp[-r/0.129629]$	$r < 1.17$	
	Fifth-order polynomial	$1.17 \leqslant r < 1.62$	
	Third-order polynomial	$1.62 \leqslant r < 2.84$	
	$229.04/r^6$	$2.84 \leqslant r < 12$	
O_shell–U_shell	$844.41 \exp[-r/0.425243]$	$r < 10$	
Polarizability charges and spring constants			
O_core: +1.186267	O_shell: −3.186267	$K_\mathrm{O} = 70.824$ eV Å^{-2}	$r < 0.8$
U_core: −2.8400	U_shell: +6.8400	$K_\mathrm{U} = 171.556$ eV Å^{-2}	$r < 0.8$

E is in eV and r in Å.

Table 2
Fitting result for the UO_2 potentials given in Table 1

UO_2 observables	Experiment [2,13–15]	Fitting results (%)
a (Å)	5.468	5.468 (0.0)
C_{11} (10^{11} dyn/cm^2)	38.93	38.93 (0.0)
C_{12} (10^{11} dyn/cm^2)	11.87	11.87 (0.0)
C_{44} (10^{11} dyn/cm^2)	5.97	5.97 (0.0)
ε_0	24.0	24.0 (0.0)
ε_∞	5.3	5.3 (0.0)
Bulk modulus (GPa)	209	208.94 (0.0)

during the fitting procedure. The potentials established are given in Table 1 while the corresponding fitting result, which matches exactly the experimental values of the observables, is given in Table 2. In order to check further the efficiency of the established potentials, we have also calculated the thermodynamic properties, the Frenkel defect formation energies, the activation energies for lattice migration as well as the super-ionic state at high temperature of uranium dioxide.

3. Thermodynamic properties, defect formation energies and lattice migration

The phonon frequencies ν_i can be calculated from the eigen-values of the dynamic matrix of the system, corresponding to the second derivatives Cartesian matrix of the energy weighted by the inverse square root of the ion masses. Thus, the partition function is obtained by:

$$Z_{\text{vib}} = \sum_{k\ \text{points}=20} g_k \sum_{i=1}^{3N} \exp[-h\nu_i/k_B T], \tag{2}$$

where k_B and h are Boltzmann's and Planck's constants respectively. The phonon frequencies are summed here over a grid covering 20 k symmetry-unique points across the Brillouin zone, excluding the three translational degrees of freedom at the gamma point, g_k being the weight number on each grid point. The vibration entropy S_{vib} at a given temperature T is obtained by the partition function Z_{vib} according to the relation:

$$S_{\text{vib}} = k_B \ln Z_{\text{vib}} + k_B T \frac{\partial}{\partial T}(\ln Z_{\text{vib}}). \tag{3}$$

The constant pressure specific heat C_P can be calculated by the well known expression:

$$C_P = T \left. \frac{\partial S_{\text{vib}}}{\partial T} \right|_P. \tag{4}$$

While the constant volume specific heat C_V is obtained directly from the phonon spectra:

$$C_V = \sum_{i=1}^{3N} k_B \left(\frac{h\nu_i}{k_B T}\right)^2 \frac{\exp\left(\frac{h\nu_i}{k_B T}\right)}{\left(\exp\left(\frac{h\nu_i}{k_B T}\right) - 1\right)^2}. \tag{5}$$

Table 3
Calculated and experimental [9,13,14] values, at 300 K, for the uranium dioxide. Vibration entropy S_{vib}, specific heats C_P, C_V and the linear thermal expansion coefficient α_{lin}

UO_2 properties at 300 K	Experiment [2–5]	Calculated
S_{vib} (J/mole K)	77.0	77.2
C_P (J/mole K)	63.5	61.8
C_V (J/mole K)	62.3[a]	60.5
α_{lin} (10^{-6} K^{-1})	9.8	10.1

[a] Deduced from the experimental values of C_P, B and α.

Finally, the linear thermal expansion coefficient α_{lin} can be obtained [2] by the specific heat difference at constant volume and constant pressure:

$$C_P - C_V = \alpha^2 BNVT, \tag{6}$$

where B is the bulk modulus, N the Avogadro number, V the primitive cell volume and α is the volume expansion coefficient corresponding to three times the linear one, $\alpha = 3\alpha_{\text{lin}}$.

Using the above formalism and the phonon spectra calculated over 20 k points of the Brillouin zone we get for the thermodynamic properties the values presented in Table 3, showing a quite satisfactory agreement, within less than 3% with the experimental data. The variation of the constant pressure specific heat $C_P(T)$ with respect to the temperature is plotted in Fig. 1 up to 1500 K. The discrepancies for $T > 1300$ K are mainly due to the electronic effects, which are very important for UO_2 and which, obviously, cannot be taken into account by the semi-empirical models.

The defects formation energies can be obtained by using the well known expression:

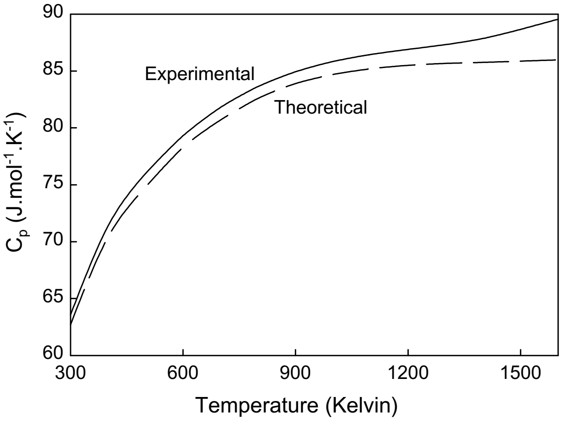

Fig. 1. Comparison between experimental [9,14] and calculated constant pressure specific heat C_P with respect to the temperature. At $T > 1300$ K the electronic effects become important for the uranium dioxide and cannot be described by the classical potentials.

Table 4
Activation energies E_{act} for oxygen vacancy and uranium lattice migration, Frenkel pairs and Schottky trio formation energies in uranium dioxide

	Calc.	Previous semi-empirical values [20,24,31,38]	Experiment	Ab-initio LMTO-ASA [39,40]	Ab-initio DFT-LDA [41]
E_{act} (V_O)	0.6	0.30–0.694	0.51[a]		
E_{act} (U^{4+})	4.9		4.4–4.8[b]		
O Frenkel	4.5	4.8–6.82	3.0–4.6[c]	6.7	3.9
U Frenkel	12.6	19.4	9.5[d]	30.6	10.7
Schottky trio	7.4	7.03–13.27	6.5 ± 0.5[d]	17.1	5.8

Note that activation energies quoted for uranium are affected by surface artifacts [1]. Matzke suggested a corrected value of 5.6 eV.

[a] Data from Refs. [7–12].

[b] [1,6,8–11].

[c] [1,16,37].

[d] From Ref. [1].

$$E(\text{defect}) = E_{\text{relaxed}}(\text{bulk} + \text{defect}) - E_{\text{relaxed}}(\text{perfect bulk}) + \Delta E_{\infty}, \qquad (7)$$

where ΔE_{∞} is a correction energy for the missing species at infinite distance from the crystal. For individual ion defects the last quantity is zero as the potentials are defined with respect to zero energy at infinity. It is also the case for Frenkel pair defects, as both the vacancy and the interstitial are present in the bulk. However, for Schottky defects ΔE_{∞} is the lattice energy corresponding to the missing molecule when it is present in the bulk.

We have calculated the energy for the oxygen and uranium Frenkel pairs formation as well as that of an UO_2 Schottky defect using super cells of 192 ions with periodic boundary conditions and applying the rational function optimization procedure (RFO) [30,33] for minimizing the energy of the system. These values are given in Table 4 and they are compared to the experimental values showing a quite good agreement. For comparison, previous semi-empirical and ab-initio calculations are also reported in the same table.

The classical Mott–Littleton approximation (MLA) [34] with the eigen vector following method [33] have been applied here to calculate the activation energies for lattice migration in uranium dioxide. We recall that the MLA method simply consists of considering two concentric spheres around the defect(s) center. In the inner one the interactions are treated explicitly and ions are allowed to relax fully. In the region between the first and the second sphere the species are weakly perturbed leading only to harmonic relaxation, while in the outer regions ions interact with any net charge in the defect as a dielectric medium. By this way, choosing sufficiently high values for the spheres radius (12 Å for the inner and 20 Å for the outer) the defect may be considered as in an infinite perfect crystal. Within the eigen vector following method, the investigation of the first order saddle point research is carried out by checking systematically the nature of the eigen-values of the hessian, the energy second derivatives matrix. The obtained values, given in Table 4, are also in good agreement with the experimental results.

As a final test of the force field efficiency to reproduce the energetic path ways in the crystal structure we have carried out shell model molecular dynamic simulations at high temperature in order to investigate whether it can reproduce the super ionic state of UO_2 characterized by the high mobility of the oxygen ions with respect to the uranium ones. We have used a super cell with 1296 ions in the NPT ensemble at $T = 2400$ K and the mean square displacements (MSD) for both uranium and oxygen ions have been obtained by the classical formalism:

$$(\text{MSD})_{\text{U,O}}(t)|_T = \frac{1}{N_{\text{U,O}}} \sum_{i=1}^{N_{\text{U,O}}} \langle r_{\text{U,O}}(t + \delta t) - r_{\text{U,O}}(t) \rangle^2. \qquad (8)$$

In order to ensure that there is no energy transfer between the shell vibrations and the real modes, according to the finite mass algorithm implemented in GULP [30],

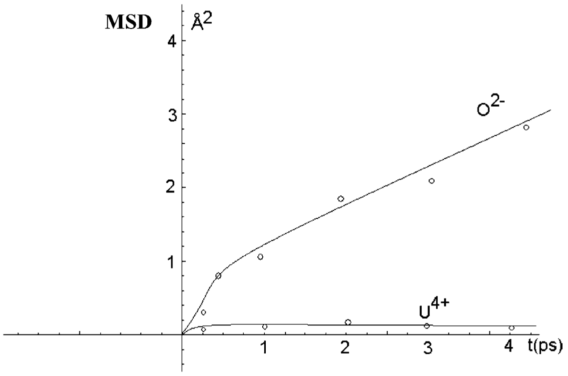

Fig. 2. Evolution of the oxygen ions mean square displacements (MSD) with respect to time calculated by molecular dynamics simulations in the (NPT) ensemble at 2400 K, showing the super-ionic conductivity of solid UO_2.

Table 5
Threshold displacement energies in UO_2 calculated using the sudden approximation method within the Mott–Littleton approach

[u v w]	[1 0 0]	[1 1 0]	[1 3 0]	[1 5 0]	[2 1 4]	[3 1 3]	[1 4 1]	[2 3 2]
E_d[O] (eV)	–	16	28	–	21	–	22	18
E_d[U] (eV)	52 (35)	85 (51)	46	44	79	43	55	74

The values in parenthesis come from Van Brutzel et al. [28]. The mean values estimated by Soullard et al. [8,49] are $E_d[O] \sim 20$ eV, $E_d[U] \sim 40$ eV.

the time step for the integration of Newton's equations of motion was set to $\delta t = 0.1$ fs. The calculated MSDs are given in Fig. 2 and compare quite satisfactorily with previous calculations of the super ionic state of uranium dioxide [21,35,36].

4. Threshold displacement energies

The threshold displacement energies E_d may give insight on the response of a material to the pka (primary knock-on atom) ballistic propagation by providing an estimation of the number of displaced atoms produced during the displacement cascades. The E_d may be calculated either by using molecular dynamics (MD) or by applying the sudden approximation (SA) [42] within the MLA [34]. In the MD method [43], a definite momentum is conferred to the sub-lattice in a given crystallographic direction [u v w]. After an evolution of a few picoseconds, 10–50 ps, the system is examined to determine whether the sub-lattice is permanently displaced or not. However, during the pka collision event such a process occurs in a time interval much shorter than that needed for phonons to relax the lattice and consequently it may be assumed that during the collision of the sub-lattice with the pka the vibration motion is frozen. This is the basis of the SA method, which does not take into account the dynamic effect of the pka. In the SA method, only static energy calculations are performed. The pka is displaced in a given crystallographic direction [u v w] calculating at each position the total energy of the un-relaxed system. The E_d is obtained by the difference between the minimum energy of the un-relaxed configuration and that of the perfect bulk provided that the ion will occupy a stable interstitial position after relaxation of the given configuration. Thus, since the SA method is considerably less computationally expensive than MD, while at the same time equally reliable [44–46], it has been applied here for the E_d calculations in uranium dioxide using the above established potentials. For avoiding complications due to eventual meta-stable states during relaxation, the RFO minimization procedure [33] in the MLA framework has been applied.

As it is well known, the E_d strongly depends on the crystallographic direction [u v w] along which the sub-lattice is displaced. Consequently, eight characteristic crystallographic directions have been considered in UO_2 and the results are given in Table 5. The results for the oxygen compare well with the value estimated previously by Soullard et al. [26,27], that is approximately $E_d[O] \sim 20$ eV. Conversely, for the uranium the calculations show that the mean threshold displacement energy is higher than the mean value estimated by Soullard et al., being rather close to $E_d[U] \sim 50$ eV.

References

[1] Hj. Matzke, J. Chemical Society, Faraday Trans. 83 (1987) 1121.
[2] A. Padel, Ch. de Novion, J. Nucl. Mater. 33 (1969) 40.
[3] C. Ronchi, M. Scheindlin, M. Musella, J. Appl. Phys. 85 (1999) 776.
[4] J.K. Fink, J. Nucl. Mater. 279 (2000) 1.
[5] C. Ronchi, J. Phys.: Condens. Matter 6 (1994) L561.
[6] Y. Iwano, J. Nucl. Mater. 209 (1994) 79.
[7] K.W. Lay, J. Am. Ceram. Soc. 53 (1970) 369.
[8] A.C.S. Sabioni, W.B. Ferraz, F. Millot, J. Nucl. Mater. 257 (1998) 180.
[9] J. Belle, J. Nucl. Mater. 30 (1969) 3.
[10] J.F. Marin, P. Contamin, J. Nucl. Mater. 30 (1969) 16.
[11] Hj. Matzke, J. Nucl. Mater. 30 (1969) 26.
[12] P. Contamin, J.J. Bacmann, J.F. Marin, J. Nucl. Mater. 42 (1972) 54.
[13] I.J. Fritz, J. Appl. Phys. 47 (1976) 4353.
[14] G. Dolling, R.A. Cowley, A.D.B. Woods, Can. J. Phys. 43 (1965) 1397.
[15] R.J. Ackermann, R.J. Thorn, G.M. Winslow, J. Opt. Soc. Am. 49 (1959) 1107.
[16] M.T. Hutchings, J. Chemical Society, Faraday Trans. 83 (1987) 1083.
[17] T. Karakasidis, P.J.D. Lindan, J. Phys.: Condens. Matter 6 (1994) 2965.
[18] M. Abramovski, R.W. Grimes, S. Owens, J. Nucl. Mater. 275 (1999) 12.
[19] J.R. Walker, C.R.A. Catlow, J. Phys. C: Solid State Phys. 14 (1981) L979.
[20] R.A. Jackson, A.D. Murray, J.H. Harding, C.R.A. Catlow, Philos. Mag. A 53 (1986) 27.
[21] P. Sindzingre, M.J. Gillan, J. Phys. C: Solid State Phys. 21 (1988) 4017.
[22] P.J. Kelly, M.S.S. Brooks, J. Chemical Society, Faraday Trans. 83 (1987) 1189.

[23] G. Busker, R.W. Grimes, M.R. Bradford, J. Nucl. Mater. 279 (2000) 46.
[24] S. Nicoll, Hj. Matzke, R.W. Grimes, C.R.A. Catlow, J. Nucl. Mater. 240 (1997) 185.
[25] C.B. Busak, A.K. Sengupta, H.S. Kamath, J. Alloys Compd. 360 (2003) 210.
[26] J. Soullard, A. Alamo, Radiat. Eff. 38 (1978) 113.
[27] J. Soullard, J. Nucl. Mater. 135 (1985) 190.
[28] L. Van Brutzel, J.-M. Delaye, D. Ghaleb, M. Rarivomanantsoa, Philos. Mag. 83 (2003) 4083.
[29] N.D. Morelon, D. Ghaleb, J.-M. Delaye, L. Van Brutzel, Philos. Mag. 83 (2003) 1533.
[30] J.D. Gale, J. Chemical Society, Faraday Trans. 93 (1997) 629.
[31] C.R.A. Catlow, Proc. R. Soc. Lond. A 333 (1977) 533.
[32] B.G. Dick, A.W. Overhauser, Phys. Rev. 112 (1958) 90.
[33] A. Barnajee, N. Adams, J. Simos, R. Shepard, J. Phys. Chem. 89 (1985) 52.
[34] N. Mott, M. Littleton, Trans. Faraday Soc. 34 (1938) 485.
[35] S. Motoyama, Y. Ichikawa, Y. Hiwatari, A. Oe, Phys. Rev. B 60 (1999) 1.
[36] K. Yamada, K. Kurosaki, M. Uno, S. Yamanaka, J. Alloys Compd 307 (2000) 10.
[37] K. Clausen, W. Hayes, J.E. Macdonald, R. Osborn, Phys. Rev. Lett. 52 (1984) 1238.
[38] C.R.A. Catlow, J. Chemical Society, Faraday Trans. 74 (1978) 1901.
[39] T. Petit, B. Morel, C. Lemaignan, A. Pasturel, B. Bigot, Philos. Mag. B 73 (1996) 893.
[40] T. Petit, C. Lemaignan, F. Jollet, B. Bigot, A. Pasturel, Philos. Mag. B 77 (1998) 779.
[41] J.P. Crocombette, F. Jollet, L. Thien Nga, T. Petit, Phys. Rev. B 64 (2001) 104107.
[42] R.D. Levine, R.B. Bernstein, Molecular Reaction Dynamic, Oxford University, New York, 1974.
[43] H.O. Kitchner, L.P. Kubin, V. Pontikis, Computer Simulation in Materials Science, 308, NATO ASI series, 1995.
[44] R.E. Williford, R. Devanathan, W.J. Weber, Nucl. Instrum. and Meth. B 141 (1998) 94.
[45] C. Meis, J. Nucl. Mater. 289 (2001) 167.
[46] A. Chartier, C. Meis, J.-P. Crocombette, L.R. Corrales, W.J. Weber, Phys. Rev. B 67 (2003) 174102.