Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Journal of Nuclear Materials 344 (2005) 213–218
journal of nuclear materials
www.elsevier.com/locate/jnucmat

Defects and oxygen diffusion in PuO_{2-x}

M. Stan *, P. Cristea

Los Alamos National Laboratory, P.O. Box 1663, MS-G755, Los Alamos, NM 87544, United States

---

Abstract

A thermochemical model of defects formation is proposed. Using this model, defect species concentrations are determined. The model allows for the calculation of the non-stoichiometry of PuO_{2-x}, as functions of temperature and oxygen pressure. A model of oxygen diffusion is proposed and the oxygen self and chemical diffusivities are calculated for temperatures in the (900–1400 °C) range and partial pressure of oxygen $P_{O_2} \in (1\text{–}10^{-25}\ \text{atm})$. This work shows that, given appropriate parameters, the model is able to describe the non-stoichiometry and oxygen diffusivity in a reasonable way.

---

1. Introduction

Accurate models and simulations can guide the development and optimization of fuel processing parameters, such as particle size, sintering atmosphere, and temperature regime [1]. In particular, modeling the kinetics of oxygen diffusion in non-stoichiometric oxides is a critical component of the combined experimental and theoretical effort aimed at predicting properties and phenomena in nuclear fuel materials [2]. Bulk diffusivity is the controlling parameter in designing 'low' temperature processes to retain volatile constituents while developing a microstructure that will be stable in-pile [3]. Together with phase stability, diffusion governs the formation of homogeneous solid solutions in otherwise heterogeneous powder blends [4]. Modeling the thermochemistry of defects opens a path to modeling of more complex phenomena, such as fission products diffusion.

The work on mixed oxide fuels generated thermodynamic properties of various non-stoichiometric compounds in the U–Pu–O system [5–11]. Plutonia (PuO_2) has four Pu and eight O atoms per unit cell, and the fluorite type of structure with space group $Fm-3m$. The lattice parameter is $a_0 = 5.396 \times 10^{-10}$ m. Many similarities have been found between the thermochemical properties of various oxides of the type MO_2 (M = metal, O = oxygen) [12], especially PuO_{2-x} and CeO_{2-x} [13]. When heated at high temperatures in a reducing atmosphere, both oxides lose oxygen and form iso-structural compounds [13,14]. These similarities have been already used for investigating the existence of ternary phases in the Pu–Ga–O system, using the Ce–Ga–O as a surrogate [14]. Although the Pu–O phase diagram is still controversial at the high temperature [15–19], there is a consensus regarding the existence of the fluorite type phase in the region $x < 0.3$ and $1000 < T < 2000$ K, where x is the non-stoichiometry. Recent models of CeO_{2-x} [20,21] account for the change in entropy due to Coulombic defect interactions and predict the concentration of various defect species as function of temperature and partial pressure of oxygen. In this work we propose a similar treatment of PuO_{2-x}.

---

* Corresponding author.
E-mail address: mastan@lanl.gov (M. Stan).

0022-3115/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2005.04.044

2. Thermochemical model

Defect species contributions to the non-stoichiometry depend on temperature T, partial pressure of oxygen P_{O_2}, and the presence of impurities. The classical mass-action law is widely used to calculate the concentration of lattice defects. However, such an approach is only valid at very low defect concentration ($x < 0.01$). At higher non-stoichiometry, significant interactions (Coulomb and via lattice distortion) between defects occur and more complex methods were introduced to determine the distribution of the defects [20].

The model proposed in this paper is based on the observed similarities between CeO_{2-x} and PuO_{2-x}. Five types of point defects are considered as major contributors to the thermochemical properties of PuO_{2-x}: Singly positively charged oxygen vacancies $V_O^{\bullet}$, doubly positively charged oxygen vacancies, $V_O^{\bullet\bullet}$, singly positively charged metal–oxygen vacancy pairs $(PuV_O)^{\bullet}$ neutral metal–oxygen vacancy pairs $(PuV_O)^{\times}$, and reduced plutonium ions (Pu^{3+} ions, or *small polarons*) Pu'_{Pu}. The defect species are described using the Kroger–Vink [22] notation. The small polarons are often described as electronic states trapped at some atomic sites and surrounded by the lattice polarization that they induce. As pointed by Tuller and Nowick [23] this seems to be a reasonable description of CeO_{2-x}. It was recently revealed by quantum mechanics calculations [24] that a similar behavior exists in plutonia.

The following equations describe the formation of the above-mentioned point defects and also involve the perfect sites, $Pu_{Pu}^{\times}$, $O_O^{\times}$, as well as O_2 (gas, from atmosphere).

$$O_O^{\times} + 2Pu_{Pu}^{\times} \leftrightarrow \frac{1}{2}O_2 + V_O^{\bullet\bullet} + 2Pu'_{Pu}, \tag{1}$$

$$V_O^{\bullet\bullet} + Pu'_{Pu} \leftrightarrow V_O^{\bullet} + Pu_{Pu}^{\times}, \tag{2}$$

$$Pu'_{Pu} + V_O^{\bullet\bullet} \leftrightarrow (PuV_O)^{\bullet}, \tag{3}$$

$$Pu'_{Pu} + V_O^{\bullet} \leftrightarrow (PuV_O)^{\times}. \tag{4}$$

The interaction with oxygen leads to the formation of $V_O^{\bullet\bullet}$ and reduced Pu^{3+} ions (Eq. (1)). Eqs. (2)–(4) describe the formation of $V_O^{\bullet}$, $(PuV_O)^{\bullet}$, and $(PuV_O)^{\times}$, respectively.

Defects induce a change in the lattice Gibbs free energy. The free energy of a defective crystal, G is given by the free energy of the perfect crystal G_p, plus a contribution, G_d, due to defects: $G = G_p + G_d$. The contribution G_d can be written as [20]:

$$G_d = G_f - TS_{conf}. \tag{5}$$

G_f is related to the formation energy that accounts for both the short-range and the long-range (i.e. Coulombic) interactions of defect species, and S_{conf} is the configurational entropy associated with the presence of defects. S_{conf} is calculated using the classical Boltzmann relation, $S_{conf} = k_B T \sum_i \ln \Omega_i$ where Ω_i is the number of ways of arranging the defect species of type i in a lattice already containing all other $j \neq i$ species, and k_B is the Boltzmann constant. For each defect species i, the virtual chemical potential is defined as:

$$\mu_i = \frac{\partial G_d}{\partial N_i}, \tag{6}$$

where N_i represents the total number of i type defects in the lattice. These potentials contain contributions from both defect formation, $\mu_{f,i}$ and the defect configurational entropy. Therefore:

$$\mu_i = \mu_{f,i} - k_B T \sum_j \Gamma_{i,j}, \tag{7}$$

where $\mu_{f,i} = \partial G_f/\partial N_i$, and $\Gamma_{i,j} = \partial(\ln \Omega_j)/\partial N_i$. The Ω_i functions include the generalized exclusion effect and the spatially correlated defect distribution [20]:

$$\Omega_i = \frac{\left[B_i + \Lambda_{i,i}N_i - \sum_j \Lambda_{i,j}N_j\right]!}{N_i!\left[B_i + (\Lambda_{i,i} - 1)N_i - \sum_j \Lambda_{i,j}N_j\right]!}. \tag{8}$$

Here, B_i is the total number of ways that an i defect may be arranged in a perfect lattice, and $\Lambda_{i,j}$ are the exclusion factors representing the number of excluded configurations for the i defect species, due to the presence of j defect species. If the atmosphere is an ideal gas, the partial oxygen excess chemical potential can be written as $\mu_{O_2} = k_B T \ln(P_{O_2})$ According to Eqs. (1)–(4), at thermodynamic equilibrium:

$$\mu_{O_O^{\times}} + 2\mu_{Pu_{Pu}^{\times}} = (1/2)\mu_{0_2} + \mu_{V_O^{\bullet\bullet}} + 2\mu_{Pu'_{Pu}}, \tag{9a}$$

$$\mu_{V_O^{\bullet\bullet}} + \mu_{Pu_{Pu}^{\times}} = \mu_{V_O^{\bullet}} + \mu_{Pu_{Pu}^{\times}}, \tag{9b}$$

$$\mu_{V_O^{\bullet\bullet}} + \mu_{Pu'_{Pu}} = \mu_{(PuV_O)^{\bullet}}, \tag{9c}$$

$$\mu_{V_O^{\bullet}} + \mu_{Pu'_{Pu}} = \mu_{(PuV_O)^{\times}}. \tag{9d}$$

If Q_i denotes the charge carried by the i defect species and, $X_i = N_i/N_c$, where N_c is the number of cationic sites in the perfect lattice, the charge conservation requires. $\sum_i Q_i X_i = 0$.

In the absence of phase transitions, due to the lattice structure conservation, two additional constraints are taken into account:

$$N_c(P_{O_2}, T) + N_{c,d}(P_{O_2}, T) = N_c, \tag{10a}$$

$$N_a(P_{O_2}, T) + N_{a,d}(P_{O_2}, T) = N_a. \tag{10b}$$

Here, N_a is the number of anionic sites in the perfect lattice, $N_{c(a)}$ is the number of non-defective cationic (anionic) sites, and $N_{c(a),d}$ is the number of defect cationic (anionic) sites. The Madelung constants of the PuO_{2-x} fluorite structure were used to determine the interaction energies, as described in [20]. The values are:

$M_c = -2.572 \times 10^{-9}$ C m^{-1} for cationic (Pu^{4+}) sites, and $M_a = 4.197 \times 10^{-9}$ for anionic (O^{2-}) sites. To account for polarization effects, we used a linear dependence of the dielectric permittivity on non-stoichiometry, $\varepsilon_r = \varepsilon_{r,0}(1 - \xi x)$ where, $\xi = 0.12$, and $\varepsilon_{r,0} = 25$ is the relative dielectric permittivity of PuO_2.

3. Oxygen diffusivity model

The model of oxygen diffusivity proposed in this work uses an average correlation factor $f_{av}(x)$, defined as $f_{av}(x) = (1/x)\sum_\alpha P(x_\alpha, x)$ where $P(x_\alpha, x) = x_\alpha/x$ is the relative probability for the i-type defect to occur, $f(x_\alpha)$ is the correlation factor for the diffusion of α defect species, and α runs over the oxygen defect types only. The partial correlation factors $f(x_\alpha)$ are calculated using a formula derived in the literature [25–27]:

$$f(x_\alpha) = \frac{1}{1 + \frac{[1-(x_\alpha/2)](1-f_0)}{[1+(x_\alpha/2)]f_0}}, \qquad (11)$$

where $f_0 = 0.653$ is the correlation factor of a simple cubic lattice [28]. The correlation factor $f_{av}(x)$ is positive and increases with the lattice non-stoichiometry. The average energy associated with the formation of defective oxygen sites is defined by

$$E_f(x, T) = k_B T \sum_\alpha P(x_\alpha, x) \ln(2/x_\alpha). \qquad (12)$$

The frequency associated with the jump of an oxygen atom into a defective oxygen site is

$$v(x, t) = v_0 \exp\left(-\frac{E_m}{k_B T}\right) \exp\left[-\frac{E_f(x, T)}{k_B T}\right], \qquad (13)$$

where E_m is the average migration energy for an oxygen jump in PuO_{2-x}, and v_0 is a constant. Therefore, the oxygen self-diffusivity, $D_s(x, T)$, can be calculated using the equation:

$$D_s(x, T) = \frac{a_0^2}{24} f_{av}(x) v(x, T) \qquad (14)$$

and further related to the chemical diffusivity $D_c(x, T)$ by the thermodynamic factor $F(x, T)$:

$$D_c(x, T) = \frac{D_s(x, T)}{f_{av}(x)} F(x, T). \qquad (15)$$

The thermodynamic factor itself is given by

$$F(x, T) = \frac{\Psi(x)}{2RT} \left| \frac{\mathrm{d}(\Delta G_{O_2}(x, T))}{\mathrm{d}x} \right|. \qquad (16)$$

In $MO_{2\pm x}$ oxides, if O is the mobile atom, $\Psi(x) = (2 - x)(3 - x)$ [29]. For small x, $\Psi(x) \cong 6$.

4. Results and discussion

The model was incorporated in a Mathcad program. Given the free energy of reaction between various types of defects, the program is able to calculate the concentration of defects and oxygen diffusivity as function of T and P_{O_2}. Conversely, the program is able to optimize the values of the free energy of the defect reactions, Eqs. (1)–(4), that are consistent with a given set of experimental measured properties. In this work, we used as target function for the optimization process the experimental correlation between the PuO_{2-x} non-stoichiometry and the partial pressure of oxygen at 1373 K. The optimization involved solving for the balance of the chemical potential and charge neutrality, as described in Eqs. (9) and (10). Table 1 shows the optimized parameters. Even though the optimized enthalpies and the entropies are not temperature dependent, the model was able to predict well the correlation between the non-stoichiometry of PuO_{2-x} and the partial pressure of oxygen at 1173 K and 1773 K. The results are compared (Fig. 1) with other theoretical results [13], and a compilation of experimental data [30–34]. The model describes the oxygen deficiency in PuO_{2-x}, in a broad interval of temperature (900–1500 °C) and partial pressure of oxygen (1–10^{-30} atm). Fig. 2 shows the relative contribution of each type of defects at 1373 K. In the very low non-stoichiometry region ($x < 0.01$), the small polarons and the doubly charged oxygen vacancies are the dominating species. The intermediate region is controlled by $V_O^{\bullet}$,

Table 1
The enthalpy and the entropy of defect reactions

Reaction	Enthalpy (eV/atom)	Entropy (eV/atom K)
(1)	4.8	0.55×10^{-3}
(2)	0.2	-2.5×10^{-4}
(3)	−0.1	0
(4)	−0.3	6.83×10^{-5}

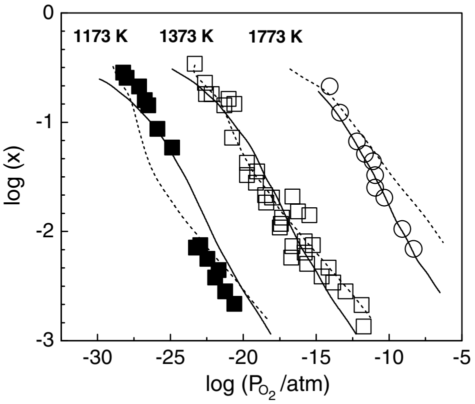

Fig. 1. Oxygen deficiency of PuO_{2-x}, as a function of oxygen partial pressure P_{O_2} and temperature (T). Solid line – this work; Dotted line – Nakamura [13]; Squares and circles – data compiled from experimental data reported in [30–34].

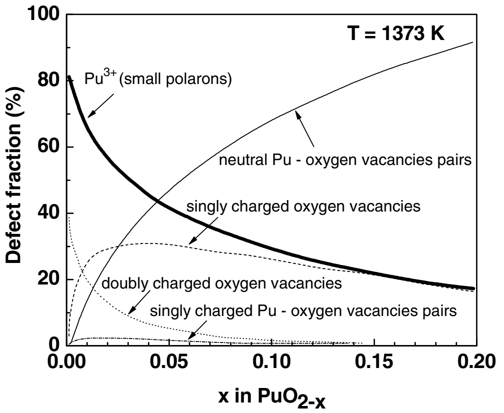

Fig. 2. Percentage contribution of various types of defect species (number of defects of i type/total number of defects) at $T = 1373$ K. Thick solid line – polarons, thin solid line – $V_O^{\bullet\bullet}$, dot line – $V_O^{\bullet}$, dash-dot line – $(PuV_O)^{\bullet}$ (+ singly-charged pairs), dashed line – $(PuV_O)^{\times}$ (neutral pairs).

and the high non-stoichiometry region by the neutral $(PuV_O)^{\times}$ pairs, similar to the situation in CeO_{2-x}. Calculation at 1173 K and 1773 K produced a pattern similar to Fig. 2, with all peaks shifted towards lower or higher partial oxygen pressures, respectively.

Fig. 3 shows the calculated partial free energy, $\Delta G_{O_2}(x,T) = RT\ln(P_{O_2})$ as a function of oxygen deficiency at several temperatures. The comparison with previous models [7,8] shows a good agreement, mainly at low temperature and low non-stoichiometry.

The knowledge of the partial Gibbs free energy $\Delta G_{O_2}(x,T)$ allowed for the calculation of the thermodynamic factor, further used to determine the chemical diffusivity (Eq. (15)). Using the results from the thermochemical calculations, the correlation factor $f_{av}(P_{O_2},T)$ was calculated as a function of P_{O_2} at different temperatures. Fig. 4 shows that the average defect formation energy, as defined by Eq. (12), considerably decreases with the increase in the non-stoichiometry. This behavior is responsible for the registered trend in the self-diffusivity with non-stoichiometry. The self and the chemical diffusivities have been calculated using parameters similar to those resulted from atomistic calculations for ceria [35]: $E_m = 0.45$ (eV), $\nu_0 = 3 \times 10^{13}\ s^{-1}$. Figs. 5 and 6 show the calculated oxygen self and chemical diffusivity of PuO_{2-x} as a function of oxygen pressure at several temperatures, and comparisons with various data extracted from literature. The discrepancy in the chemical diffusivity predictions (Fig. 6) may be due to the simplified diffusivity model employed in

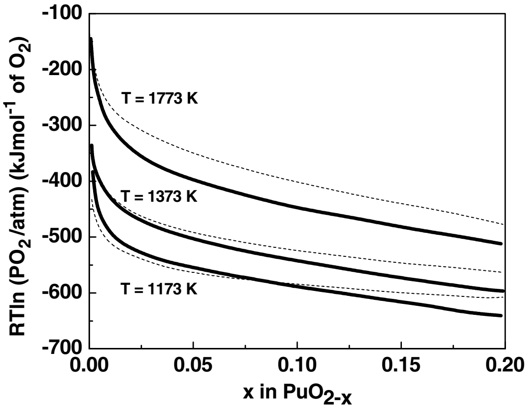

Fig. 3. The oxygen partial free energy in PuO_{2-x} as a function of non-stoichiometry. Solid lines – this work, dashed lines – data from literature [7,8].

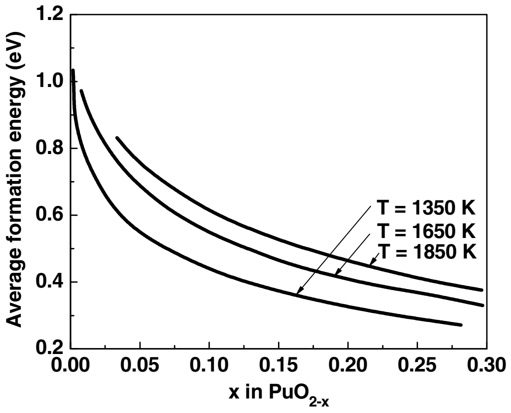

Fig. 4. The average formation energy $E_f(x,T)$ associated with the formation of defective oxygen sites, calculated using Eq. (12), as a function of oxygen deficiency (x in PuO_{2-x}) and temperature.

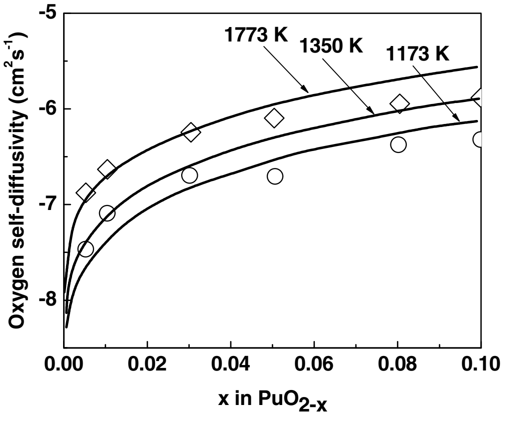

Fig. 5. Oxygen self diffusivity in PuO_{2-x}, as a function of non-stoichiometry. Full line: calculated with Eq. (14) using $E_m = 0.45$ eV and $w_0 = 3 \times 10^{13}\ s^{-1}$. Symbols: data for $T = 1350$ K [36]; diamonds evaluated using the dilatometry method; circles evaluated using the thermogravimetric method.

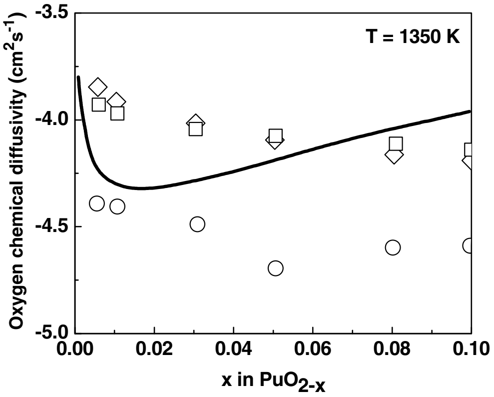

Fig. 6. Oxygen chemical diffusivity in PuO_{2-x}, as a function of non-stoichiometry. Full line: calculated with Eq. (15). Squares: experimental data [37]. Diamonds: from dilatometric measurements, extrapolated to 1350 K [36]. Circles: from thermogravimetric measurements, extrapolated to 1350 K [36].

[36], as well as to the extrapolation of the experimental results from 800 to 1350 °C.

5. Conclusions

An optimization procedure was used to determine the free energy of formation of five defect species: small polarons, singly charged vacancies, doubly charged vacancies, neutral pairs, and singly charged pairs. The model predicts that in the very low non-stoichiometry region, the small polarons and doubly charged oxygen vacancies are dominating species. The intermediate region is controlled by singly charged vacancies, and the deep non-stoichiometry region by the neutral pairs. This behavior is similar to the one occurring in CeO_{2-x} and consistent with previous calculations. This works shows that the average defect formation energy considerably decreases with the increase in the non-stoichiometry. This implies that the classical Arrhenius behavior is not a good description of oxygen self-diffusivity in PuO_{2-x}. Using average migration energy $E_m = 0.45$ (eV) and pre-exponential factor of jumping frequency $\nu_0 = 3 \times 10^{13}\ s^{-1}$, the model predicted self and chemical diffusivity for temperatures in the (900–1500 °C) range and $P_{O_2} \in (1\text{–}10^{-25}$ atm). The predictions are in good agreement with reported data. More experimental and theoretical studies are needed before deciding about the nature of the defect species and about their formation energies in this material.

Acknowledgements

This work was performed under the auspices of DOE-NE, Advanced Fuel Cycle Initiative at Los Alamos National Laboratory. We thank B.P. Uberuaga (Los Alamos National Laboratory) for useful comments and discussions regarding this work.

References

[1] T. Ogawa, M. Akabori, F. Kobayashi, R.G. Haire, J. Nucl. Mater. 247 (1997) 215.
[2] M. Stan, Trans. Amer. Nucl. Soc. 91 (2004) 131.
[3] E.K. Storms, J. Nucl. Mater. 132 (1985) 231.
[4] M. Beaivy, J. Nucl. Mater. 188 (1992) 232.
[5] T.M. Besmann, T.B. Lindemer, J. Amer. Ceram. Soc. 66 (1983) 782.
[6] T.M. Besmann, T.B. Lindemer, Trans. Amer. Nucl. Soc. 47 (1984) 198.
[7] T.M. Besmann, T.B. Lindemer, J. Nucl. Mater. 130 (1985) 489.
[8] T.M. Besmann, T.B. Lindemer, J. Nucl. Mater. 137 (1986) 292.
[9] T.D. Chikalla, J. Amer. Ceram. Soc. 46 (1963) 323.
[10] T.D. Chikalla, J. Amer. Ceram. Soc. 47 (1964) 309.
[11] M. Stan, P. Cristea, Trans. Amer. Nucl. Soc. 91 (2004) 491.
[12] D.J.M. Bevan, J. Kordis, J. Inorg. Nucl. Chem. 26 (1964) 1509.
[13] A. Nakamura, J. Nucl. Mater. 201 (1993) 17.
[14] M. Stan, T.J. Armstrong, D.P. Butt, T.C. Wallace, Y.S. Park, C.L. Haertling, T. Hartmann, R.J. Hanrahan, J. Amer. Ceram. Soc. 85 (2002) 2811.
[15] H.A. Wriedt, Bull. Alloy Phase Diagr. 11 (1990) 184.
[16] T.D. Chikalla, C.E. McNeilly, R.E. Skavdahl, J. Nucl. Mater. 12 (1964) 131.
[17] H. Kinoshita, D. Setoyama, Y. Saito, A. Hirota, K. Kurosaki, M. Uno, S. Yamanaka, J. Chem. Thermodyn. 35 (2003) 719.
[18] T.M. Besmann, J. Nucl. Mater. 144 (1987) 1.
[19] E.H.P. Cordfunke, R.J.M. Konings, in: Thermochemical Data for Reactor Materials and Fission Products, North-Holland, Amsterdam, 1993.
[20] S. Ling, Phys. Rev. B 49 (1994) 864.
[21] P. Cristea, M. Stan, Phys. Rev. B, submitted for publication.
[22] F.A. Kröger, H.J. Vink, in: F. Seitz, D. Turnbull (Eds.), Solid State Physics: Advances in Research and Applications, Academic Press, New York, 1956.
[23] H.L. Tuller, A.S. Nowick, J. Phys. Chem. Solids 38 (1977) 859.
[24] L. Petit, A. Svane, Z. Szotek, W.M. Temmerman, Science 301 (2003) 498.
[25] K. Nakazato, K. Kitahara, Prog. Theor. Phys. 64 (1980) 2261.
[26] R.A. Tahirkheli, R.J. Elliott, Phys. Rev. B 27 (1983) 844.
[27] R.A. Tahirkheli, Phys. Rev. B 28 (1983) 3049.
[28] J.R. Manning, Diffusion Kinetics for Atoms in Crystals, D. Van Nostrand Company, Inc, 1968, p. 95.
[29] D.S. Tannhauser, in: G. Simkovich, V.S. Stubican (Eds.), Transport in Nonstoichiometric Compounds, Plenum, New York, 1985, p. 139.
[30] L.M. Atlas, G.J. Schlehman, in: A.E. Kay, M.B. Waldron (Eds.), Plutonium 1965, Chapman and Hall, London, 1965, p. 838.

[31] T.L. Markin, M.H. Rand, in: Thermodynamics; Proceedings of the Symposium on Thermodynamics with Emphasis on Nuclear Materials and Atomic Transport in Solids, International Atomic Energy Agency, Vienna, 1966, p. 145.
[32] G.C. Swanson, Los Alamos National Laboratory Report (LA-6063-T), 1975.
[33] R.E. Woodley, J. Nucl. Mater. 96 (1981) 5.
[34] O.T. Sorensen, in: Proceedings of the Conference in Baden, 10–13 September 1975, North-Holland, Amsterdam, 1976.
[35] B.P. Uberuaga, Los Alamos National Laboratory Report (LA-UR-04-8157), 2004.
[36] A.S. Bayoglu, R. Lorenzelli, J. Nucl. Mater. 82 (1979) 403.
[37] P. Chereau, J.F. Wadier, J. Nucl. Mater. 46 (1973) 1.