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Modeling self-diffusion in NpO_2 by connecting point defect parameters with bulk properties

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The energetics of oxygen self-diffusion in NpO_2 over a range of temperatures is important for nuclear fuel applications. This can be realized using the cBΩ thermodynamic model where the defect Gibbs energy is proportional to the isothermal bulk modulus (B) and the mean volume per atom (Ω). In the present study we employ elastic and expansivity data in the framework of the cBΩ model to derive the oxygen self-diffusion coefficient in NpO_2 in the temperature range 2000 K to 2900 K. The predicted results are in agreement with the available experimental and theoretical data.

Keywords: NpO_2; self-diffusion; thermodynamic model

Моделювання самодифузії в NpO2 шляхом зв'язку параметрів точкових дефектів з об'ємними властивостями Alexander Chroneos, Ioannis L. Goulatis, Lefteri H. Tsoukalas, Ruslan V. Vovk

Енергетика самодифузії кисню в NpO_2 в діапазоні температур є важливою для застосування в ядерному паливі. Це можна реалізувати за допомогою термодинамічної моделі с BΩ, де енергія Гіббса дефекту пропорційна ізотермічному модулю об'ємної пружності (B) та середньому об'єму на атом (Ω). У цьому дослідженні ми використовуємо дані про пружність та розширення в рамках моделі cBΩ для визначення коефіцієнта самодифузії кисню в NpO_2 в діапазоні температур від 2000 K до 2900 K. Передбачені результати узгоджуються з наявними експериментальними та теоретичними даними.

1. Introduction

A very active field of research is the understanding of the physical, chemical and mechanical properties of materials as these are important in order to optimise them for semiconductor, superconductor, battery and quantum computing applications [1-10]. Experimental work in conjunction with theoretical modelling and thermodynamic approaches can offer a more complete perspective accelerating technological advancement [11-20].

With ever increasing energy demand pumped by the need to power datacentres and artificial intelligence focus on nuclear energy has resurfaced. Nuclear energy is economic, sustainable, and generates insignificant amounts of greenhouse gases as compared to the use of fossil fuels. Presently, the main component of conventional nuclear fuel is UO_2. This

can be blended with actinide oxides (for example PUO_2 or ThO_2) to form mixed oxide (MOX) fuel [21-23]. At any rate there is a need for further understanding of nuclear materials and this is further enhanced by the consideration of alternative nuclear fuel cycles. For example, thoria has a high corrosion resistance, high melting point, higher thermal conductivity, and abundance compared to UO_2 and is therefore considered as a mainstream nuclear fuel candidate [24-26]. It is notable also that the Th-U fuel cycle results in lower concentrations of long-lived transuranic elements and can be considered to be more proliferation-resistant but there are numerous issues that need to be determined [27-30].

Spent fuel generated in light water reactors (LWR) contains uranium, short lived fission products and about 1 wt% of minor actinide isotopes [31]. Minor actinides are a significant part of long-term radiotoxicity and heat generation of spent nuclear fuels [31,32]. The aim is to reduce minor actinides to deposit in repositories and this requires advanced fuel cycles strategies and increased fuel cycle efficiency [31,33]. It is important to develop advanced techniques to reprocess spent fuel with minor actinides [34]. Mixed oxide (MOX) fuels with minor actinides loaded in Generation IV fast nuclear reactors will lead to the transmutation of the minor actinides in the fuel [35].

Considering heavy water reactors, there is no intend to reprocess spent fuel, as the content of fissile material is considerably lower than in the LWR. There are investigations to apply heavy water reactors for the partial transmutation of actinides generated by the LWR [36]. At any rate it is important to characterize the physical and thermodynamic properties of MOX fuels containing minor actinides. From an experimental viewpoint this is difficult and expensive due to the handling of highly radioactive samples [37-39].

Numerous theoretical models attempted to relate the defect Gibbs energy (g^i) and the bulk properties in solids [40]. Importantly, Varotsos and Alexopoulos [41-43] proposed that g^i is proportional to the isothermal bulk modulus B and the mean volume per atom Ω (to be referred from now on as the cBΩ model). Thereafter, the cBΩ model has been used to describe the diffusion and point defect processes in a wide range of materials [44-49], including self-diffusion in UO_2, PUO_2, ThO_2. and MOX fuel [50-54]. To our knowledge there are no cBΩ model studies for oxygen self-diffusion NpO_2, which is also a fluorite-related oxide.

In NpO_2 oxygen self-diffusion is mediated by oxygen vacancies (vacancy mechanism of diffusion) and this is appropriate for the cBΩ model given that the model works particularly well in systems with a single diffusion mechanism. In the present theoretical study, we apply the cBΩ model to investigate oxygen self-diffusion coefficients in NpO_2 in the temperature range 2000-2900 K.

2. Methodology

In a crystal with a single diffusion mechanism the diffusion phenomenon can be described using the activation Gibbs energy (g^{act}). g^{act} is the sum of the Gibbs formation (g^f) and the Gibbs migration (g^m) energies. The activation entropy s^{act} and the activation enthalpy h^{act} are defined using [44,45]:

$$s^{act} = -\left.\frac{dg^{act}}{dT}\right|_P \quad (1)$$

$$h^{act} = g^{act} + Ts^{act} \quad (2)$$

The diffusivity D is given by:

$$D = D_0 e^{-\frac{g^{act}}{k_B T}} = f a_0^2 \nu e^{-\frac{g^{act}}{k_B T}} \quad (3)$$

Where D_0 is the pre-exponential factor, f is the diffusion correlation factor, a_0 is the lattice constant, ν is the attempt frequency and k_B is Boltzmann's constant. f depends on the diffusion mechanism and the geometry of the crystal structure.

A key aspect of the cBΩ model is the link of the defect Gibbs energy g^i to the bulk properties of the solid via the relation [41-43]:

$$g^i = c^i B\Omega \quad (4)$$

Through the combination of Eqs. (3) and (4) we obtain:

$$D = f a_0^2 \nu e^{-\frac{c^{act} B\Omega}{k_B T}} \quad (5)$$

The pre-exponential factor (i.e. $f a_0^2 \nu$) can be calculated using either information from molecular dynamics or experiment. This will then require one experimental (or theoretical) diffusivity value at one temperature to calculate the c^{act} using Eq. 5. Alternatively, we can employ Eq. 5 using two experimental (or theoretical) diffusivity values at two corresponding temperatures to derive both the pre-exponential factor and c^{act}. Using this c^{act} the diffusivity D_i at any temperature T_i can be calculated using Eq. 5 assuming that the elastic data and expan-

Table 1. MD derived and calculated self-diffusion coefficients in NpO_2 alongside the elastic and expansivity data used in the cBΩ model.

T /K	B/10^9 Nm^{-2}	Ω /10^{-30}m^3	$D_{MD}^{NpO_2}$ /m^{2}s^{-1}	$D_{cB\Omega}^{NpO_2}$ / m^{2}s^{-1}
2000	131.54	14.14	$8.02 \cdot 10^{-14}$	$2.01 \cdot 10^{-13}$
2100	126.97	14.20	$7.51 \cdot 10^{-13}$	$7.53 \cdot 10^{-13}$
2200	124.77	14.26	$1.26 \cdot 10^{-12}$	$1.91 \cdot 10^{-12}$
2300	120.34	14.32	$6.64 \cdot 10^{-12}$	$5.73 \cdot 10^{-12}$
2400	115.64	14.40	$1.57 \cdot 10^{-11}$	$1.61 \cdot 10^{-11}$
2500	108.93	14.46	$4.83 \cdot 10^{-11}$	$5.23 \cdot 10^{-11}$
2600	103.42	14.55	$1.34 \cdot 10^{-10}$	$1.35 \cdot 10^{-10}$
2700	96.44	14.66	$3.86 \cdot 10^{-10}$	$3.79 \cdot 10^{-10}$
2800	95.73	14.75	$8.59 \cdot 10^{-10}$	$5.42 \cdot 10^{-10}$
2900	98.07	14.85	$1.52 \cdot 10^{-9}$	$5.59 \cdot 10^{-10}$

sivity can be derived or are known for T_i. c^{act} is considered to be constant and can be assumed to be temperature and pressure independent [41-45]. It is also important to note that the cBΩ model can capture anharmonic effects that can appear by the temperature decrease in B and by the thermal expansivity. In the present study, we only compare with molecular dynamics results as to our knowledge there is no solid experimental data on the oxygen self-diffusion coefficient in NpO_2 in the temperature range 2000 K to 2900 K.

3. Results and discussion

The expansivity and the isothermal bulk modulus data were derived using MD by Bellino *et al.* [31,32]. These values are reported in Tables 1 alongside the MD derived oxygen self-diffusion coefficients in NpO_2 [32]. The latter are compared with those calculated from Eq. 5 using the cBΩ model. To calculate the c^{act} parameter the single experimental measurement method [43,44] can be used or other methods such as the compensation law and the "mean value" method [45-48]. The advantage of the single experimental measurement method is its simplicity, however, the calculated value of c^{act} will depend upon the experimental error in the B, Ω and the diffusivity value. In more complicated diffusion mechanisms, there will be errors in the pre-exponential factor and this makes its derivation difficult.

Here we do not depend on the MD uncertainties to calculate c^{act} as we employed the mean value method. In this approach the linear behavior of lnD versus $\frac{B\Omega}{k_B T}$ further indicates the validity of the cBΩ model with the slope being c^{act} (refer to Eq. 5). As it can be seen from Figure 1 there is an almost linear relation, which can be represented by:

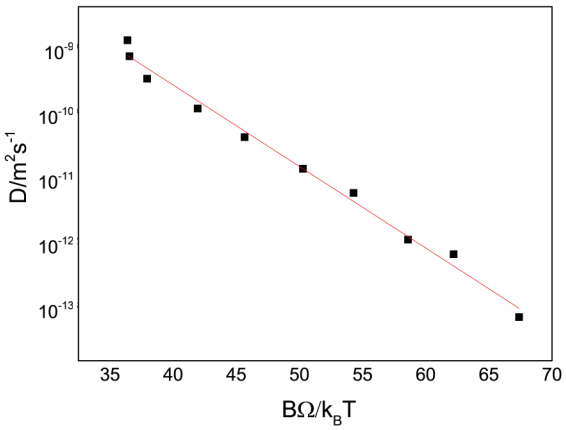

Figure 1. The Arrhenius plot of oxygen self-diffusion in NpO_2 as derived by the cBΩ model.

$$D = 6.24e^{-\frac{0.256B\Omega}{k_B T}} \cdot 10^{-6} m^2 s^{-1} \qquad (6)$$

Using Eq. 6 we can now derive the self-diffusion coefficients in NpO_2 using cBΩ model and complete the table. As it can be seen from Table 1 the self-diffusion coefficients in NpO_2 calculated by the cBΩ model are in good agreement with the MD values over the temperature range considered. There are some differences that can be explained by the calculation of B and Ω through MD. Given the nature of the material, it is hard to find appropriate experimental data. At higher temperatures there is the superionic transition in these materials [55] that may be modeled within the cBΩ model but will require a different c^{act}. Whenever there is a change of phase in the host material, different composition, or different diffusion mechanism there will be the need to derive a further c^{act}

to describe the process. The present study can serve as a paradigm to investigate the properties of other binary or ternary materials for energy applications [56-58].

4. Conclusions

In the present study we employed the cBΩ model to describe self-diffusion in NpO_2. There is a relatively good agreement between the cBΩ model derived and MD oxygen self-diffusion coefficients in both NpO_2 in the temperature range considered. It is expected that due to the superionic transition in NpO_2 the oxygen self-diffusion coefficients for very high temperatures (above 2800-2900 K) cannot be described by the cBΩ model with the derived c^{act}. The efficient description of NpO_2 motivates the investigation of other technologically important actinide oxides. In particular, it is expected that thermodynamic modelling will play an increasing role to model MOX fuel and bridge the gap in data at a range of temperatures and pressures.

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