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Letter to the Editors

Comment on ‘Location of krypton atoms in uranium dioxide’ by T. Petit, G. Jomard, C. Lemaignan, B. Bigot and A. Pasturel

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Abstract

Following the explanation of a previous confusion, the agreement between recent ab initio quantum mechanical calculations [T. Petit, G. Jomard, C. Lemaignan, B. Bigot, A. Pasturel, J. Nucl. Mater. 275 (1999) 119] and pair potential calculations is demonstrated. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

In a recent paper, Petit et al. [1] discussed their results concerning an ab initio computer modelling study of the location of krypton in UO_2. The results from this study were compared to experimental studies [2,3], which were cited as being based upon Rutherford backscattering spectroscopy. Another related reference is [4], which discusses the release of Xe in doped UO_2. The ab initio results were also compared to a previous theoretical study [5], which is based on energy minimisation using pair potentials. The Petit et al. paper concludes that their result (of the neutral tri-vacancy trap site providing the lowest solution energy for Kr) is in agreement with experiment, but in contradiction with previous theoretical studies. Petit et al. suggest that the ‘crude approximation made in semi-empirical (pair potential) schemes can explain some of the discrepancies with the results obtained in the present study’. It is our understanding that it is not the approximations inherent to pair potentials, but rather a misinterpretation of terms which has led to the discrepancy and in fact the two sets of results agree remarkably well.

2. Discussion

In the previous work by Grimes and Catlow [5], two definitions were given for the energy associated with placing fission products in the UO_2 lattice. The first was the incorporation energy, i.e., the energy to place a fission product at a pre-existing trap site. The energies of two atomic configurations must be calculated: the empty trap site and the fission product at the trap site. Then, the incorporation energy is given by

$$\text{incorp. energy} = \text{energy of fission product in trap site} - \text{energy of empty trap site.}$$

Inherent in this definition is the assumption that there are more trap sites than fission products. Given the large defect energy of trap sites, such as the neutral tri-vacancy, this is unlikely to be the case. Therefore, a second definition was made, the solution energy. This assumes that for the fission product to be accommodated in the lattice, the energy to form the trap site in equilibrium with the majority Frenkel intrinsic defects must be accounted for. The solution energy is then

$$\text{solution energy} = \text{incorporation energy} - \text{equilibrium trap formation energy.}$$

Of course the equilibrium trap formation energy is a strong function of stoichiometry. The energies for equilibrium trap formation are given in Appendix B of Grimes

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Table 1
Comparison of calculated solution energies of a krypton atom in uranium dioxide (in eV)

Krypton location	Grimes (pair potential)			Petit (hybrid ab initio/pair potential)		
	UO_{2-x}	UO_2	UO_{2+x}	UO_{2-x}	UO_2	UO_{2+x}
Interstitial	13.3	13.3	13.3	14.2	14.2	14.2
Oxygen vacancy	9.9	13.3	16.8	8.0	11.4	14.8
Uranium vacancy	17.2	10.3	3.5	16.3	9.5	2.7
Di-vacancy	12.5	9.0	5.7	12.5	9.0	5.7
Neutral tri-vacancy	9.5	9.5	9.5	9.8	9.8	9.8
Charged tetra-vacancy	19.1	12.3	5.5	–	–	–

and Catlow [5]. We are now in a position to understand the confusion. Petit et al. [1] calculated incorporation energies which were then erroneously compared to the solution energies of Grimes and Catlow [5].

Petit et al. [1] found the discrepancy puzzling since the agreement between the two sets of calculations is correct for simple point defects (interstitial, oxygen and uranium vacancies) but very poor for more complex structures (divacancy and neutral tri-vacancy). This discrepancy can easily be explained. The trap site formation energy for simple point defects is either negligible or zero, whereas for the more complex defect structures there is a more substantial trap site formation energy [5]. To rectify the discrepancy, the pair potential trap site formation energies of Grimes and Catlow [5] are added to the ab initio incorporation energies of Petit et al. [1], resulting in hybrid ab initio/pair potential values, see Table 1. Unfortunately, there is insufficient past data from which to formulate ab initio trap site formation energies [6–8].

3. Conclusion

When corrected for trap site formation energy, the hybrid ab initio results agree remarkably well with the pair potential results, especially for those complex defect structures which provide the most stable solution sites. However, what should also be noted from these studies is the predicted preference for Kr solution at di-vacancies in stoichiometric UO_2. Furthermore, that these two studies agree does not invalidate the agreement with experiment. The experimental work was conducted on Xe, which is a considerably larger atom than Kr and consequently, solution is expected at the larger neutral tri-vacancy trap, despite the chemical similarity of Kr and Xe. Of course, a hybrid ab initio/pair potential calculation is not entirely satisfactory. Therefore, it would be beneficial to calculate the equilibrium solution site energies ab initio. We accept that good quality ab initio simulations are inherently more reliable than pair potential calculations. However, in the event of a more complete comparison between the techniques, attention should also be paid to the difference between large unit cell simulations [1] and isolated defect cluster calculations that relate to the infinite dilute limit.

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