

Solution and Migration of Impurity Ions in UO_2 ,
 U_3O_8 and Y_2O_3

*A dissertation submitted to the University of London for the
degree of Doctor of Philosophy*

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May 2002



Abstract

Atomic scale computer simulation techniques based on the Born description of forces between ions, have been used to predict the solution and migration behaviour of impurities in ceramic materials.

Static defect simulation techniques based on the Mott-Littleton approximation are shown to be particularly effective models for the study of the radiologically important fission products iodine, ruthenium and caesium. The accommodation mechanisms of these species are predicted in both $\text{UO}_{2\pm x}$ and U_3O_{8-z} , as a function of stoichiometry. In U_3O_{8-z} many of the fission products occupy large complex traps, which can exist in several different configurations. Migration often relies on a complex mechanism whereby the fission product moves through a number of different defect cluster configurations. Essentially two types of mechanisms have been found. In one, migration of the fission product is controlled by slow uranium self-diffusion. In the other, fission product migration is mediated by oxygen vacancies. In the latter case, it is the fission product association with a trap site or its migration across a trap site which is the rate determining step.

As static defect simulations can only predict migration enthalpies but not absolute diffusion coefficients or pre-exponential terms, molecular dynamics techniques are also used to study the self-diffusion of intrinsic defects in UO_2 . Unfortunately this technique is only effective for fast diffusing species with activation energies which are smaller than approximately 1 eV. As such only oxygen migration could be considered.

Finally the effects of defect-defect interactions and defect clustering are studied in Y_2O_3 . In particular, the dependence of solution behaviour upon defect ion radius has been considered. A large reduction of the solution energy can be observed as impurities form clusters with intrinsic defects and with each other via co-doping mechanisms.

Acknowledgements

It is with pleasure that I think of my time in the Materials Department. I am greatly in debt to my supervisor Robin Grimes and have fond memories of painting the walls and window ledges of our offices when the Atomistic Simulation Group was started.

Maybe not so successful at painting but more so at introducing me to the wonders of London and the simulation codes is Shyam Vyas without whom the group would have been much less colourful.

I am in debt to Volodya Bulatov who taught me how to code properly and without whom the Molecular Dynamics section of this thesis would not have existed.

Many thanks to John Evans, for bringing me to Britain in the first place, and for sharing his knowledge of nuclear materials and diffusion theory. The help with the production of manuscripts is greatly appreciated.

Dr. Mark Bradford of British Energy Plc. represented the Health and Safety Executive, who sponsored the latter half of this project. The first half of the project was sponsored by Nuclear Electric. Dr. Bradford provided most background information on experimental work on U_3O_8 and I am grateful for his contribution to the published (and to-be-published) work contained in this thesis.

The work presented in this thesis was funded under contract IMC/FC/AGR/5017

by the Industry Management Committee on behalf of the Health and Safety Executive and by the Health and Safety Committee under contract FC/GNSR/48. The contents of this thesis, including any opinions and/or conclusions expressed, are those of the author alone and do not necessarily reflect HSE policy.

Alex ChronEOS was instrumental in the yttria work and for the supply of strange brews from far away countries.

My colleagues, Matt Z., Licia, Kurt and Michael. I shall never forget the ice cream you brought me when I was in pain.

Jane, Kate, Ed, Rob, Peter, Dicky, Richard, thanks for making being alone in London a bit easier.

I wish to thank John, Doug, Matt and all the residents for a wonderful time in Beit hall. It was a magical experience.

This thesis is dedicated to my parents.

Symbols and Conventions

0.1 Symbols used in this study

a, b, c	Principal axes lengths of unit cell	[Å]
A	First parameter in Buckingham potential form	[eV]
c	Concentration of impurities	[m ⁻³]
C	Third parameter in the Buckingham potential form	[eV Å ⁶]
C_{ij}	Elements of the elastic tensor	[GNm ⁻²]
D	Diffusion coefficient	[m ² s ⁻¹]
D_0	Pre-exponential in Arrhenius equation	[m ² s ⁻¹]
ϵ^0	Static relative dielectric constant	1
ϵ^∞	High freq. relative dielectric constant	1
ΔH_m	Migration enthalpy	[eV]
H_L	Lattice energy	[eV]
k	Spring constant in shell model	[eV Å ⁻²]
k_B	Boltzmann constant	[JK ⁻¹]
ϕ	Component of an electrostatic potential	J or eV
ρ	Second parameter in Buckingham potential form	[Å]
Q_Y	Shell charge for charge model	[C]
ν	Debye frequency, vibration frequency of an ion	[s ⁻¹]

0.2 Conventions used in this study

In defect reactions the Kröger-Vink notation is used. For example, $V_O^{\bullet\bullet}$ and $V_U^{''''}$ are an oxygen vacancy with an effective charge of +2e and a uranium vacancy with a -4e charge respectively. For models which rely on partial charges, the usual notation for defect charges is replaced with numerals, e.g. $V_{MG}^{-1.6}$. Where ions can exist in a number of charge states, Kröger-Vink notation is used in combination with ion charges, for example $Ru_U^{3+'}$ may be used where an ion may exist in other charge states than the 3+ state shown here.

Since the Kröger-Vink notation is somewhat unreadable when large defects are concerned, a notation used in metals is employed to improve clarity. In this notation the subscript denotes the vacant positions in the cluster. E.g. V_{UO} is a vacancy cluster consisting of a U and a O ion. The subscript uses the normal chemical convention where more than one ion position of one type are vacant: V_{O_2} . Similarly, for e.g. a caesium ion trapped at an oxygen vacancy the notation Cs_O is used.

SI units are used as much as possible, except in those cases where tradition or clarity require a different representation. Examples of places where SI units are not used are interionic potential parameters and enthalpies of atomic processes.

The Ångstrom (0.1 nm) unit is used throughout for atomic distances and some derived units as this is customary in this research area.