

SIMULATION OF CERIA: BULK AND SURFACE DEFECTS

A dissertation submitted to the University of London

for the degree of

Doctor of Philosophy

By

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April 2005

Abstract

Atomistic computer simulation techniques, based on the classical pair potential model, have been used to study several inorganic materials: primarily CeO_2 , but also CaF_2 and MgO . Both bulk and surface properties have been investigated.

In bulk ceria defect clusters incorporating indium or cadmium dopants with oxygen vacancies have been modelled. The binding energies show an isolated Cd^{2+} defect prefers to be in a first nearest neighbour site with respect to an oxygen vacancy; the In^{3+} ion shows no such preference. When Cd^{2+} and In^{3+} bind to Ce^{3+} ions (small polarons present in CeO_{2-x}), at least one of the ions must be at a second neighbour site with respect to the vacancy. The same is true for small polaron clusters in undoped non-stoichiometric ceria.

The importance of defect - defect interactions has been assessed through the study of the solution of Al_2O_3 in MgO . Two defect models are examined, trimer and dimer clusters of the Al substitutional ions with the charge compensating $V_{\text{Mg}}^{\text{II}}$ species dominate. The results agree favourably with the experimental lattice parameter data.

A number of perfect CeO_2 surfaces have been modelled using the MARVIN code. The dependence of the surface structure and crystal morphology on the interionic potential was examined. The resultant morphology is dominated by (111) faces, irrespective of the potential. In addition, studies of the angular dependence of the

surface energy have been carried out. These demonstrate that the surface energies lie on a well defined curve. A physical basis for this trend is proposed.

Initial studies of non-stoichiometric surfaces of CeO_2 have been carried out. The configurations of neutral polaron clusters on a number of important faces are examined. The results suggest that for the (200) face the vacancy prefers to be at the surface; for the (331) face the opposite is true. On the remaining faces, the defects rearrange such that they reduce the defect dipole in the Z-direction.

Finally, molecular dynamics techniques have been used to study two CaF_2 nanoclusters. The results are compared with those of static surface calculations. In addition, studies of melting and solidification are carried out on the smaller cluster. In only one case was the cooling rate sufficiently slow to form an ordered structure.

Acknowledgments

The three years I have spent doing my Ph.D at the Royal Institution and latterly at Imperial College have to paraphrase Dickens been ‘... the greatest of times and the worst of times’. Thankfully, there have been more of the former than the latter. This alone is testament to the quality and character of the people I have met and known. Hence, this is my opportunity to thank them and I apologise now if I’ve left anyone out.

Firstly, I must thank my supervisor, Robin Grimes, whose encouragement and advice have proved invaluable. It would be safe to say that without him this thesis, let alone the research within it, would not have seen the light of day. I must also thank him on a personal level for the number of occasions he’s bought lunch and everything else he’s done for me. Thanks for everything man !

I am also indebted to my ‘other’ supervisors; Prof. Richard Catlow (The Royal Institution), Prof. John Kilner (Imperial College), Julian Cox and Geoff Taylor (Johnson-Matthey) for their time, help, and guidance. The codes used in the present work were all produced ‘in house’ and I am grateful for the ‘on-line’ help of Drs David Gay (The Royal Institution) and Andrew Rohl (Curtin Technical University, Perth formerly, The Royal Institution) - MARVIN, Dr Julian Gale (Imperial College) - GULP, Adrian Dornford-Smith and Dr. Vladimir Bulatov (Imperial College)

- PENICILLIN. For all their help with the wonders of UNIX, ‘sys. admin.’, making slides and the general day to day stuff I must thank (in no particular order): Dewi Lewis, Ashley George, Phil Sinclair, Jason Binks, Rob Bell, Gerdjan Busker, Peter Lee, Dan Waters, Simon Carling and Jean Conisbee. Special thanks also to John Evans for proof reading some of this thesis.

The environment at the DFRL and at Imperial have proved incredibly stimulating and very enjoyable places in which to have worked. This is due to the presence of people like Mike McCoy, Sasha Schluger, G. Sankar, Dean Sayle, Dickie Dashwood, Andy, Phil B., Yvonne, Grant, Chris, Bob, Alexei, and many, many, others with whom I have spent many hours having useful and occasionally trivial discussions. In addition, as many scientists will testify, research is not something one can stop thinking about when one leaves the lab door and is something we discuss with a number of different people. Thus, the following people have in their own unique way played a role in shaping this work: Karl, Sue, George, Elysee, Stuart, Shyama, the ‘others’ at Charing Cross Medical School, Rachel, Mark, Roger, Eliana, and Sensi Jim Lewis.

Finally, and most importantly, I am indebted to the love and support of my Mum, Dad, and sister, Neeti, and it is to them that I dedicate this thesis.

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