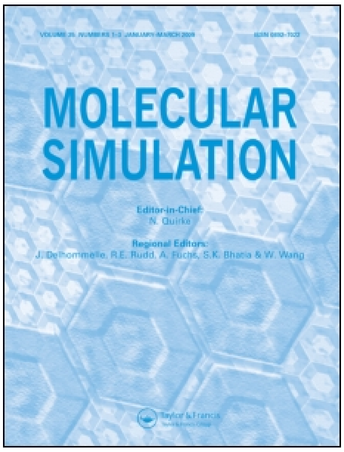

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SIMULATION STUDIES OF OXIDE MATERIALS

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In spite of numerous severe difficulties specific to metal-oxygen systems, computer simulation of oxides has developed rapidly in recent years. In this paper, we discuss its successes and some of its limitations with a particular emphasis on silica and on non stoichiometric oxides.

Keywords: Oxide materials; silica

1. INTRODUCTION

Simulation of oxides has been a major area of development in recent decades. Much of the original impetus came from the necessity to predict the properties of materials used in the nuclear industry under extreme conditions (for example, the prediction of radiation damage). Thus the first general code to predict the energies of point defects was developed at Harwell over twenty years ago. This code used a strategy based on the Mott-Littleton [1] approximation. The original code, HADES2, was developed by Norgett [2] for defects in cubic ionic systems; later codes, HADES3 [3,4], CASCADE [5], and GULP [6] extended the method to general symmetry and more covalent materials. These methods were also extended to interfaces. Other methods, notably molecular dynamics and *ab initio* calculations, have also given great insight into oxide behaviour. The goal of the present paper is not to review the whole field of simulation in oxides but rather to discuss two typical fields, silica and non stoichiometric compounds. In the present paper electronic structure calculations will be discussed only when they are relevant to classical Monte Carlo or molecular dynamics calculations; through calculating defect formation energies or validating effective potentials.

2. FEATURES OF OXIDE MATERIALS

Compared to other materials such as halides, oxides have some distinctive characteristics, which makes their study rather difficult for simulations using effective potentials as well as for quantum calculations.

2.1. Diversity

Oxides have a wide spectrum of behaviour: for example, if we consider electrical properties, we find in Table I:

TABLE I Electrical properties of oxide materials

insulators		Al_2O_3
semi-conductors	classical	SnO_2
	polaronic	CeO_{2-x}, UO_2
semi-metals		TiO
metallic conductors		ReO_3
superconductors		$YBa_2Cu_3O_{7-x}$

2.2. Partially Ionic Behaviour

The assumption of the classic ionic model that ions in a crystal are rigid spheres having the integral charges corresponding to their chemical oxidation state has numerous advantages. For example: it provides a clear picture of the crystal, and using simple notions such as the ionic radius, it is able to explain the stability domains of a number of compounds.

In so naïve a form, the ionic model is not realistic for oxides and a number of amendments have been proposed, some of them intended to address the case of iono-covalent compounds:

- *Ions have been considered as rigid charged shells bound to cores by harmonic restoring forces.* This is the shell model proposed by Dick and Overhauser, forty years ago [7], which describes polarizability. The shell model couples the ionic polarizability to the short-range forces in a simple, physically appealing way but it lacks fundamental theoretical justification and does not always correctly describe the variation of ionic polarizability with change of environment [8].

- *Dipole-dipole dispersion terms and, more recently, higher order dispersion contributions.* The use of improved dipole-quadrupole dispersion coefficients has been shown to be essential to get the correct value of cohesive energy for oxides such as ThO_2 or UO_2 [9]. These terms may be calculated from various approximations, which tends to soften the distinction between calculated and fitted potentials [10].
- *Non integer charges.* This amendment has some drawbacks. As pointed out by Cochran [11], and by Catlow and Stoneham [12], unique, universal charges cannot be assigned except in trivial cases. Moreover,these potentials cannot be expected to be transferable as partial charges are expected to be strongly coordination dependent, which casts some doubt on the reliability of these potentials to deal with defective oxides.
- *Representation of the bonding electron density by a charge midway between the bonded atoms* [13]. In practice, this method has only been used to simulate the lattice dynamics of covalent homopolar materials [14]. The specific difficulty here, in addition to the general problems encountered when non-integral charges are used, is how to describe the forces between the bond-charges and the ions.
- *Three-body terms have been included,* to correct the inadequacy of central force pair potentials for the directional bonding seen in iono-covalent compounds [10]. In a general way, pair potentials have difficulties in reproducing the tetrahedral coordination associated with sp^3 hybridization. A radical but efficient way to force it is to put a bond-bending term of the form $V_{ijk} = K \cdot (\theta_{ijk} - \theta^0_{ijk})^2$ or $V_{ijk} = (\cos\theta_{ijk} - \cos\theta^0_{ijk})^2$ where θ_{ijk} is the instantaneous angle subtended at ion j by the bonds ij and jk. A number of authors have included such a device [15–18].

2.3. Electronic Structure and Localized Density of Charge

The electronic structure of oxides of transition metals is known to be complicated. For instance the existence of a gap for NiO or CoO is not easy to understand using local density functional theory [19]. Quantum Monte Carlo [20] cannot yet attain sufficient accuracy to resolve the problem. The most successful method has been Hartree-Fock, where recent work has successfully predicted the band gap [21].

The localized character of the wave functions implies that a large number of plane waves are needed when Car-Parinello calculations are performed. This is accentuated by the necessity to use non-local pseudo-potentials. A full discussion is given in [22, 23].

3. STOICHIOMETRIC OXIDES; THE CASE OF SILICA

3.1. Effective Potentials

It is not our intention to attempt to review the whole field of silica simulations. Rather, we propose to use the case of silica as an example of what classical models can, and cannot, accomplish.

Classical potential models have often been used for silica. It has usually been found necessary to include three-body terms. Examples of their success include the simulation of the vitreous state (static structure factor, first sharp diffraction peak) [18] and studies of molten silica at high pressure [24]. Moreover, such terms have usually been considered necessary to describe silica. Despite this, Tsuneyuki *et al.* [25] have designed a *pair* potential with a simple analytical expression. This potential has been extracted from *ab initio* cluster calculations. This calculated potential is a Buckingham potential with non-integral charges on the ions:

$$U_{ij}(r) = U_{ij}^{\text{Coulomb}} + f_0(b_i + b_j)\exp\left(\frac{a_i + a_j - r}{b_i + b_j}\right) - \frac{c_i c_j}{r^6} \tag{1}$$

As stated by Tsuneyuki [26], this pair-wise potential works surprisingly well for silica in spite of several unusual features:

- Small number of parameters.
- The last term refines the details of the repulsion and does not represent the dispersion interaction which is not included in the HF-SCF method.
- In spite of the size of the charges used, (2.4 on silicon and -1.2 on oxygen atoms), Tsuneyuki *et al.* indicate that silica is essentially covalent and their potential includes a term to maintain strong repulsion between the oxygen atoms, leading to tetrahedral units.

The potential has been extremely successful in a number of applications:

- the α to β structural phase transition of quartz [27]
- the lattice dynamical properties of α-quartz [28]
- the structural properties of SiO_2 in the stishovite structure [29]. This

example is particularly interesting as it concerns sixfold coordinated structures.
- the liquid-vapour coexistence curve [30].
- the high-pressure densification of silica glass [31].
- the behaviour of α-quartz under hydrostatic and nonhydrostatic high-pressure conditions [32].

Not too surprisingly, this potential has shortcomings; for example its failure to predict the enthalpy of the quartz-coesite transition [33].

3.2. *ab initio* Studies

As mentioned above, the localized nature of the oxygen wave functions requires the use of a separable nonlocal pseudopotential in Car-Parinello molecular dynamical calculations [34]. Ten years ago, those authors performed an *ab initio* total-energy minimization of the structure and bonding of α-cristobalite. The more difficult case of β-cristobalite (with a primitive cell containing eight SiO_2 units) has been studied more recently [35]. Later still, Sarnthein *et al.* [36] performed a first-principles molecular dynamics simulation of liquid silica followed by a rapid quench to 300 K and obtained the partial structure factors of amorphous SiO_2. As pointed out by Huang and Ching [37], quenched structures obtained from high temperature molecular dynamics are not representative of the continuous random-network model which is a good description of the structure of amorphous silica.

4. POINT DEFECTS AND THE REDUCTION OF OXIDES

The calculation of the properties of point defects in oxides has been discussed at length; [38, 39] discuss ionic oxides, [40] discusses defects in silica. For purposes of illustration, we shall consider the problem of calculating the heat of reduction of oxides which is often equivalent to the problem of calculating the energy of formation of an oxide vacancy.

In the limiting case of a purely ionic compound, the strategy based on Mott and Littleton [1] is straightforward. To obtain an oxygen vacancy, an oxygen atom must be removed from the system. This is normally considered in terms of a Born-Haber cycle: the oxide ion is removed to infinity, creating the vacancy. Then the oxide ion is reduced to oxygen gas. Finally the two electrons produced by this reduction are re-injected in the oxide. This process contains two problems. First, there is the question of what value to use for the second electron affinity of oxygen. The oxide di-anion is unstable in vacuum and sensitive to the local environment when in the crystal. This question is discussed in detail in [41]. Second, there is the question of the re-injection process. A strict interpretation of the ionic model would suggest that the electrons should be added to an ion to alter its charge state. This is to adopt the small polaron approximation which may not be appropriate (small polaron theory is discussed in detail in [42]). An alternative is to assume that the electrons go into the conduction band. In this case a value for the electron affinity of the oxide is required. These are often only poorly known. This may explain some of the problems obtained in reconciling heats of reduction calculated with this approach with the experimental values obtained by [43]. Furthermore, this strategy clearly makes no sense if non-integral charges are used on the ions, as is often the case in potentials used for silica. Even when the small polaron theory is appropriate, there remain questions about the adequacy of the simple pair-potential models that are often used.

For largely ionic oxides, which are both simpler and stoichiometric, it is instructive to calculate the Schottky formation energy. These energies are often so high that reliable experimental values (normally obtained from the analysis of diffusion data) are not available. However, it is possible to compare with the results of *ab initio* calculations. This has been done for the case of MgO [44]. However, this does not directly address the problems found in non-stoichiometric oxides.

The recent ASA-LMTO calculations of Petit *et al.* [45] on UO_{2-x} is a step in that direction. Using a supercell with 4 uranium atoms, these authors have calculated the cohesive energy of UO_2 and $UO_{1.75}$. This provides a value for

$$\frac{1}{2.(2-1.75)}\int_{1.75}^{2} \Delta H(O_2)\,dx \tag{2}$$

which is the average value of the formation of an oxygen vacancy in the composition range $1.75 \leqslant \frac{O}{U} \leqslant 2.00$. Their value is consistent with the experimental determination of Javed [46].

Now let us consider the case of oxygen vacancies in silica. As shown recently by Boureau and Carniato [47], using purely thermodynamic arguments, the formation energy of an oxygen vacancy in silica is expected to be more than 7.3 eV. This quantity is somewhat larger than the one computed by Sulimov *et al.* [48] using an embedding technique based on a Hartree-

Fock program (about 5 eV). Recent calculations done using local density functional theory give a larger value (6.6. eV) which seems to be a better estimate. A very recent cluster calculation [49, 50] using Hartree-Fock with a large basis set (including d orbitals) and taking correlation into account gives a still larger value of about 8.5 eV. The variation between these numbers is a reminder that the term '*ab initio*' is not synonymous with 'accurate'. Furthermore, the necessity to choose a limited basis set and cluster size introduces an empirical element into even '*ab initio*' calculations. The last evaluation is consistent with the thermodynamic analysis of Boureau and Carniato, and in our opinion, this value may be used as a way to devise an effective potential aimed to study defects.

5. HETERO-INTERFACES

The earliest calculations on oxide interfaces were for grain boundaries. This work is summarized in [51], [38]. More recent work has extended this to problems of hetero-interfaces. A brief discussion is given in [39]. We consider here the example of the Si(100)–SiO_2 interface. This is one of the most studied interfaces because of its importance in MOS technology [52]. Of particular interest are XPS studies [53, 54] which have shown the existence of Si atoms in intermediate oxidation states (between one and four) in the vicinity of the interface. This interpretation has been confirmed by a Car-Parinello calculation of Pasquarello *et al.* [55, 56] who have shown that Si 2p core-level shifts at the Si(100)–SiO_2 boundary depend linearly on nearest neighbour oxygen atoms. These authors have also shown that the strain is localized to a transition region at the interface and does not persist in the full oxide, in agreement with an earlier simple model of Ohdomari *et al.* [57]. Here we see a limitation of static-lattice simulation studies: they are able to explore *local* minima of energy and relaxed structures. Even dynamic calculations can encounter this problem if the energy barriers are high. Neither crude nor sophisticated studies have yet been able to arrive at definite conclusions on the nature of the epitaxial oxide. (tridymite or cristobalite or continuous random network). A choice has to be made before any calculation is done.

Electrostatic effects are expected to play an essential part in interface behaviour [58]. To investigate this, the use of semi-empirical potentials appears to be the best strategy. Using a simple effective potential [16], Carniato *et al.* [59, 60] have shown that, in spite of the large value of the energy formation of an oxygen vacancy [47], the formation of such vacancies at the interface is possible due to electrostatic effects and to the low value of the chemical potential of oxygen at the interface.

6. NONSTOICHIOMETRIC OXIDES

We have already discussed the problems encountered in simulating nonstoichiometric compounds. Let us consider alternative approaches.

Kofstad's approach [61] is not a simulation method but it still plays such an important rôle in the treatment of experimental results that it is necessary to present its essential idea. The interactions between defects are handled by the introduction of a large variety of defects. For example, instead of attractive interactions between vacancies, we may consider both mono and divacancies. The populations of these defects are connected by the mass action law. In this way, we get a simple formalism which is able to describe such properties as the departure from stoichiometry, the electrical conductivity, the chemical diffusion coefficient of oxygen and the thermoelectric power as a function of the chemical potential of oxygen.

However, this approach has important limitations [62]. For nearly stoichiometric solutions, the slope of the plot of the partial molar enthalpy of oxygen as a function of the oxygen content should go to infinity (from Debye-Hückel theory) and not to zero as predicted by the Kofstad formalism. The same problem is met in methods derived from spacing statistics [63, 64].

In a general way, the plot of the partial free energy of oxygen as a function of the departure of stoichiometry is easier to fit with models based on the Kofstad approach than the separate contributions (partial molar enthalpy and partial molar entropy of oxygen). A typical example is tungsten trioxide WO_{3-x} [65]. In this oxide, the partial enthalpy and entropy have been shown to be inconsistent with a purely point defect model, which led the authors to propose a model including crystallographic shear planes in equilibrium with point defects. As shown by Tétot and Boureau [66, 67, 62, 68], using Monte Carlo simulations on rigid lattices, these models can be improved by considering only one variety of defect and the coulombic interactions between these charged defects. The only adjustable parameter is now the dielectric constant, which is equivalent to attributing partial charges to the defective sites. This approach has been used to evaluate both thermodynamic and transport quantities. For example, the electronic conductivity in CeO_{2-x} [69] and in $Co_{1-x}O$ [70] has been computed as a function of the departure from stoichiometry in this way. In a general way, it has been shown [62] that the mass action law formalism can be retained for moderate departures from stoichiometry provided that care is taken in in the choice of equilibrium constants.

Promising attempts have been made to calculate effective cluster interactions from *ab initio* calculations. Two methods formerly developed in the physics of alloys have been applied to oxides: the generalized perturbation method [71] and the inversion method due to Connolly and Williams [72]. In the case of the well studied oxide $YBa_2Cu_3O_{7-x}$, the generalized perturbation method has been used by Upward *et al.* [73] whereas the Connolly-Williams inversion method has been used by Sterne *et al.* [74]. Although the two sets of parameters are in qualitative agreement, they are rather different. The question of whether *ab initio* calculations can provide accurate pair interactions remains open.

A different way of obtaining effective cluster interactions fits tight binding parameters from *ab initio* calculations [75]. It is clear that all these methods show promise for the future.

7. CONCLUSIONS

If we try to evaluate the rôle of simulation in the complex area of oxides, the balance is rather encouraging. On the positive side, a lot of progress has been made in the understanding of simple ionic oxides such as MgO but also for more covalent oxides like SiO_2. Effective potentials can now be obtained using electronic structure calculations. This reduces the level of empiricism in the simulation method. A promising direction is the building of a code able to generate organic molecules that can serve as templates for making microporous solids with pores of a specific size and shape [76].

On the negative side, numerical simulation has still not been able to answer one of the complex questions with which it began: the evolution of defects created by radiation in nuclear oxides such as UO_2 or PuO_2. The simulation method has sometimes been over-sold. Simulation does not (usually) provide exact results but rather numbers within a given set of approximations. Words such as 'first principles' or '*ab initio*' are freely used and can be misleading.

There is no one ideal method of simulation for all problems; all have their strengths and weaknesses. Quantum calculations represent the most determined effort to remove the empirical element from simulation. Some problems, such as electronic states, can be tackled in no other way. The remarkable progress of *ab initio* molecular dynamics, now more than ten years old, bodes well for the future. However, these methods are still expensive in terms of computer resources and cannot yet tackle complex materials problems. Simulations based on effective potentials are of great interest for the study of complex systems such as interfaces or large systems. The problem is, and will remain, that of validation. Simple models still have their uses in understanding complex experimental data, particularly for nonstoichiometric oxides. Indeed, that is not a bad way to look at any simulation method. At root, they are not a source of numbers, but a source of ideas.

References

[1] Mott, N. F. and Littleton, M. J. (1938). Conduction in polar crystals. electrolytic conduction in solid salts. *Trans. Faraday Soc*, **34**, 485–499.

[2] Norgett, M. J. (1974). A general formulation of the problem of calculating the energies of lattice defects in ionic crystals. UKAEA Report, AERE-R. 7650.

[3] Mackrodt, W. C., Catlow, C. R. A., James, R. and Stewart, R. F. (1982). Defect energies in α-Al_2O_3 and rutile TiO_2. *Phys. Rev. B*, **25**, 1006–1026.

[4] Catlow, C. R. A. and Mackrodt, W. C. (1982). *Computer Simulation of Solids (Lecture Notes in Physics 166)*, Springer, Berlin.

[5] Leslie, M. (1982). Program CASCADE: Description of datasets for use in crystal defect calculations. SERC Daresbury Laboratory Report, DL-SCI-TM31T.

[6] Gale, J. (1993). General Utility Lattice Program, Imperial College London.

[7] Dick, B. G. and Overhauser, A. W. (1958). Theory of the dielectric constants of alkali halide crystals. *Phys. Rev.*, **112**, 90–93.

[8] Madden, P. A. and Wilson, M. (1991). Polarisation effects in ionic crystals. *J. Phys. Cond. Matter*, **5**, 2687–2706.

[9] Pyper, N. C. and Popelier, P. (1995). The influence of improved dipole-quadrupole dispersion coefficients on the predicted cohesion of ionic oxides. *J. Phys. Cond. Matter*, **7**, 5013–5024.

[10] Hardling, J. H. (1991). Interatomic potentials. A users guide. In Meyer, M. and Pontikis, V. editors, *Computer Simulations in Materials Science*, volume **205** of *NATO ASI E*, pages 159–182.

[11] Cochran, W. (1961). 'Effective' ionic charges in cystals. *Nature*, **191**, 60–61.

[12] Catlow, C. R. A. and Stoneham, A. M. (1983). Ionicity in solids. *J. Phys. C*, **15**, 4321–4338.

[13] Phillips, J. C. (1960). *Covalent bonding in crystals, molecules and polymers*. Chicago University Press.

[14] Weber, W. (1974). New bond-charge model for the lattice dynamics of diamond-type semi-conductors. *Phys. Rev. Lett.*, **33**, 371–374.

[15] Feuston, B. P. and Garofalini, S. H. (1988). Empirical three-body potential for vitreous silica. *J. Chem. Phys.*, **89**, 5818–5824.

[16] Stixrude, L. and Bukowinski, M. S. T. (1988). Simple covalent potential models of tetrahedral SiO_2: Applications to α-quartz and coesite at pressure. *Phys. Chem. Minerals*, **16**, 199–206.

[17] Vessal, B., Amini, M., Fincham, D. and Catlow, C. R. A. (1989). Water-like melting behaviour of SiO_2 investigated by the molecular dynamics simulation technique. *Phil. Mag.*, **60**, 753–775.

[18] Vashishta, P., Kalia, R. K., Rino, J. P. and Ebbsjo, I. (1990). Interaction potential for SiO_2: A molecular-dynamic study of structural correlations. *Phys. Rev. B*, **42**, 12197–12209.

[19] Leung, T. C., Chan, C. T. and Harmon, B. N. (1991). Ground-state properties of Fe, Co, Ni, and their monoxides: Results of the generalized gradient approximation. *Phys. Rev. B*, **44**, 2923–2927.

[20] Tanaka, S. (1995). Variational quantum Monte Carlo approach to the electronic structure of NiO. *J. Phys. Soc. Japan*, **64**, 4270–4277.

[21] Towler, M. D., Allan, N. L., Harrison, N. M., Saunders, V. R., Mackrodt, W. C. and Aprà, E. (1994). *ab initio* study of MnO and NiO. *Phys. Rev. B*, **50**, 5041–5054.

[22] Gillan, M. J. (1991). Calculating the properties of materials from scratch. In Meyer, M. and Pontikis, V. editors, *Computer Simulations in Materials Science*, volume **205** of *NATO ASI E*, pages 257–281.

[23] Galli, G. and Pasquarello, A. (1993). First-principles molecular dynamics. In Allen, M. P. and Tildesley, D. J. editors. *Computers Simulations in Chemical Physics*, volume **397** of *NATO ASI C*, pages 261–313.

[24] Vessal, B., Amini, M. and Akbarzadeh, H. (1994). Molecular dynamics simulation of molten silica at high pressure. *J. Chem. Phys*, **101**, 7823–7827.

[25] Tsuneyuki, S., Tsukada, M., Aoki, H. and Matsui, Y. (1988). First-principles interatomic potential of silica applied to molecular dynamics. *Phys. Rev. Lett*, **61**, 869–872.

[26] Tsuneyuki, S. (1996). Molecular-dynamics simulation of silica with a first-principles interatomic potential. *Molecular Engineering*, **6**, 157–182.

[27] Tsuneyuki, S., Aoki, H., Tsukada, M. and Matsui, Y. (1990). Molecular-dynamics of the α to β structural phase transition of quartz. *Phys. Rev. Lett*, **64**, 776–779.

[28] Cowley, E. R. and Gross, J. (1991). Lattice dynamics of a pair-potential model of α-quartz. *J. Chem. Phys*, **95**, 8357–8361.

[29] Keskar, N. R., Troullier, N., Martins, J. L. and Chelikowsky, J. R. (1991). Structural properties of SiO_2 in the stishovite structure. *Phys. Rev. B*, **44**, 4081–4088.

[30] Guissani, Y. and Guillot, B. (1996). A numerical investigation of the liquid-vapor coexistence curve of silica. *J. Chem. Phys.*, **104**, 7633–7644.

[31] Della Velle, R. G. and Venuti, E. (1996). High-pressure densification of silica glass: A molecular-dynamics simulation. *Phys. Rev. B*, **54**, 3809–3816.

[32] Badro, J., Barrat, J. L. and Gillet, P. (1996). Numerical simulation of α-quartz under nonhydrostatic compression-memory glass and five-coordinated crystalline phases. *Phys. Rev. Lett*, **76**, 772–775.

[33] Chelikowsky, J. R., Keskar, N. R. and Bingeli, N. (1996). The structural properties of silica using classical and quantum interatomic forces. *Molecular Engineering*, **6**, 1–37.

[34] Allan, D. C. and Teter, M. P. (1987). Nonlocal Pseudopotentials in Molecular-Dynamical Density-Functional Theory: Application to SiO_2. *Phys. Rev. Lett*, **59**, 1136–1139.

[35] Liu, F., Garofalini, S. H., King-Smith, R. D. and Vanderbilt, D. (1993). First-principles studies on structural properties of β-cristobalite, *Phys. Rev. Lett*, **70**, 2750–2753.

[36] Sarnthein, J., Pasquarello, A. and Car, R. (1995). Structural and electronic properties of liquid and amorphous SiO_2. An *ab initio* molecular dynamics study. *Phys. Rev. Lett*, **74**, 4682–4685.

[37] Huang, M. H. and Ching, W. Y. (1996). Electron states in a nearly ideal random-network model of amorphous SiO_2 glass. *Phys. Rev. B*, **54**, 5299–5308.

[38] Harding, J. H. (1990). Computer simulation of defects in ionic solids. *Rep. Prog. Phys*, **53**, 1403–1466.

[39] Harding, J. H. (1997). Defects, surfaces and interfaces. In Catlow, C. R. A. editor, *Computer Modelling in Inorganic Crystallography*, Chapter 7, Academic.

[40] Helms, R. and Pointdexter, E. H. (1994). The silicon-silicon dioxide system; its microstructure and imperfections. *Rep. Prog. Phys*, **57**, 791–852.

[41] Harding, J. H. and Pyper, N. C. (1995). The meaning of the oxygen second-electron affinity and oxide potential models. *Phil. Mag. Lett*, **71**, 113–121.

[42] Shluger, A. L. and Stoneham, A. M. (1993). Small polarons in real crystals: concepts and problems. *J. Phys. Cond. Mater*, **5**, 3049–3086.

[43] Tétot, R. and Gerdanian, P. (1985). Thermodynamic test of defect formation energies calculated by simulation techniques for nonstoichiometric oxides. Application to CeO_{2-x}, UO_{2+x}, UO_{2-x}, TiO_{2-x}, $Mn_{1-x}O$, $Fe_{1-x}O$. *J. Phys. Chem. Solids*, **46**, 1131–1139.

[44] DeVita, A., Gillan, M. J., Lin, J.-S., Payne, M. C., Stich, I. and Clarke, L. J. (1992). Defect energetics in MgO treated by first principles methods. *Phys. Rev. B*, **46**, 12964–12973.

[45] Petit, T., Morel, B., Lemaignan, C., Pasturel, A. and Bigot, B. (1996). Cohesive properties of UO_2. *Phil. Mag. B*, **73**, 893–904.

[46] Javed, N. A. (1972). Thermodynamic study of hypostoichiometric urania. *J. Nucl. Mater*, **43**, 219-240.

[47] Boureau, G. and Carniato, S. (1996). Discrepancies between thermodynamic data and theoretical calculations of the formation energy of an oxygen vacancy in silica. *Solid State Comm*, **99**, i-iv.

[48] Sulimov, V. B., Pisani, C., Cora, F. and Sokolov, V. O. (1994). Isolated and embedded cluster modelling of the oxygen vacancy in α-quartz. *Solid State Comm.*, **90**, 511-514.

[49] Pacchioni, G. and Ierano, G. (1996). Electronic and optical properties of defects in amorphous silica from first principle calculations. In Devine, R. A. B., Autran, J. L., Spinolo, G. and Vedda, A. editors, *French-Italian symposium. Structure and defects in SiO_2. Fundamentals and applications: Abstracts*, pages 3-4.

[50] Pacchioni, G., Ferrari, A. M. and Leranò, G. (1997). Cluster model calculations of oxygen vacancies in SiO_2 and mgO: Formation energies, optical transitions and EPR spectra. Farad. Disc. **106** (in press). (See also Allan, D. C. and Teter, M. P. (1990). *J. Amer. Ceram. Soc.*, **73**, 3247 who give a value of 7.9eV).

[51] Duffy, D. M. (1986). Grain boundaries in ionic crystals. *J. Phys. C*, **19**, 4393-4412.

[52] Pointdexter, E. H. (1989). MOS interface states: overview and physico-chemical perspective. *Semicon. Sci. Technol.*, **4**, 961-969.

[53] Himpsel, F. J., McFeely, F. R., Taleb-Ibrahimi, A., Yarmoff, J. A. and Hollinger, G. (1988). Microscopic structure of the SiO_2-Si interface. *Phys. Rev. B*, **38**, 6084-6096.

[54] Rochet, F., Roulet, H., Dufour, G., Carniato, S., Guillot, C., Barrett, N. and Froment, M. (1992). Si(001) vicinal surface oxidation in O_2: angle-resolved Si 2p core-level study using synchrotron radiation. *Applied Surface Science*, **59**, 117-134.

[55] Pasquarello, A., Hybertsen, M. S. and Car, R. (1995). Si 2p Core-Level shifts at the Si(001)-SiO_2 interface: A first-principles study. *Phys. Rev. Lett*, **74**, 1024-1027.

[56] Pasquarello, A., Hybertsen, M. S. and Car, R. (1996). Structurally relaxed models of the Si(001)-SiO_2 interface. *Appl. Phys. Lett.*, **68**, 625-627.

[57] Ohdomari, I., Akatsu, H., Yamakoshi, Y. and Kishimoto, K. (1987). The structural models of the Si-SiO_2 interface. *J. of non-crystalline solids*, **89**, 239-248.

[58] Tasker, P. W. (1990). Modelling oxide-oxide and oxide-metal interfaces. *J. Chem. Soc. Faraday Trans*, **86**, 1311-1315.

[59] Carniato, S., Boureau, G. and Harding, J. H. (1995). Simulation of oxygen vacancies at the Si-SiO_2 interface. *Radiation Effects and Defects in Solids*, **134**, 179-183.

[60] Carniato, S., Boureau, G. and Harding, J. H. (1997). Modelling oxygen vacancies at the (100) Si-SiO_2 interface, *Phil. Mag. B*, in press.

[61] Kofstad, P. (1972). *Nonstoichiometry, Diffusion and Electrical Conductivity in Binary Metal Oxides*. John Wiley. Interscience, New York.

[62] Tétot, R. and Boureau, G. (1994). On the reliability of the ideal mass action law formalism for the analysis of nonstoichiometry and related properties in ionic compounds. *J. Phys. Chem. Solids*, **55**, 357-365.

[63] Atlas, L. M. (1968). Statistical model of partially ordered defects in a hypostoichiometric metal oxide. *J. Phys. Chem. Solids*, **29**, 91.

[64] Ling, S. (1994). High-concentration point chemistry. Statistical-thermodynamic approach applied to nonstoichiometric cerium dioxides. *Phys. Rev. B*, **49**, 864.

[65] Boureau, G. and Marucco, J. F. (1983). Equilibrium between point defects and crystallographic shear planes. *Radiation Effects*, **74**, 247.

[66] Tétot, R., Benzakour, M. and Boureau, G. (1990). Thermodynamic treatment of coulomb interactions in nonstoichiometric oxides. *J. Phys. Chem. Solids*, **51**, 545.

[67] Tétot, R., Nacer, B. and Boureau, G. (1994). A Monte-Carlo investigation of the rôle of Coulomb interactions on thermodynamic properties and defect structure of $M_{1-x}O$ cubic oxides. *J. Phys. Chem. Solids*, **54**, 517.

[68] Tétot, R. and Boureau, G. (1995). Defect interactions, statistical thermodynamics and electronic transport in ionic nonstoichiometric oxides. *Radiation effects and defects in solids*, **137**, 239-246.

[69] Boureau, G., Masmoudi, O. and Tétot, R. (1991). Electrical conductivity in nonstoichiometric cerium dioxide. *Solid State Comm*, **79**, 299-302.

[70] Boureau, G., Masmoudi, O. and Tétot, R. (1993). Electrical conductivity in non stoichiometric cobalt monoxide. A Monte Carlo simulation. *Solid State Comm*, **87**, 417.

[71] Ducastelle, F. and Gautier, F. (1976). Generalized perturbation theory in disordered transitional alloys. Applications to the calculation of ordering energies. *J. Phys. F: Metal Physics*, **6**, 2039–2062.

[72] Connolly, J. W. D. and Williams, A. R. (1983). Density-functional theory applied to phase transformations in transition-metal alloys. *Phys. Rev. B*, **27**, 5169–5172.

[73] Udvardi, L., Szunyogh, L., Redinger, J., Weinberger, P. and Pasturel, A. (1994). Order-disorder phase transitions in $YBa_2Cu_3O_{7-x}$: The asymmetric next-nearest-neighbour interaction model revised from a first principles point of view. *Phil. Mag. B*, **69**, 583–696.

[74] Sterne, P. A. and Wille, L. T. (1989). Oxygen vacancy ordering in $YBa_2Cu_3O_{7-x}$. *Physica C*, **162**, 223–224.

[75] Kohan, A. F. and Ceder, G. (1996). Tight-binding calculation of formation energies in multicomponent oxides: Application to the MgO–CaO phase diagram. *Phys. Rev. B*, **54**, 805–811.

[76] Lewis, D. W., Willock, D. J., Catlow, C. R. A., Thomas, J. M. and Hutchings, G. J. (1996). *De novo* design of structure-directing agents for the synthesis of microporous solids. *Nature*, **382**, 604–606.