Chapter 7

Further Work

7.1 Cation Disorder $MgAl_2O_4$ Spinel

The combined monte carlo and energy minimisation technique was described in chapter 3. This technique proved capable of reproducing accurately the experimentally determined variation of lattice parameter with increasing inversion. The results obtained for the variation of the oxygen positional parameter with inversion however, showed less close correspondence. The value obtained for the oxygen positional (u) parameter is a function of the relative strength of the Mg^{2+}-O^{2-} and Al^{3+}-O^{2-} interactions, i.e. an increasing the attractiveness of the Mg^{2+}-O^{2-} interaction leads to a smaller u parameter whereas increasing the attractiveness of the Al^{3+}-O^{2-} interaction leads to a larger u parameter. In order to produce better correspondence in u parameter variation a different potential model should be investigated. As a first attempt a partial charge model might be considered as it would allow balancing of the Mg^{2+}-O^{2-} and Al^{3+}-O^{2-} interactions not just in terms of the short range forces but also in the coulombic component. An alternative would be to consider the polarization model. At the moment only dipole polarization of oxygen is allowed. It is clear from quantun mechanical simulations of oxides that the oxygen wave function would be better represented by a multiple polarisation model. Finally a charge transfer approach could be considered that allows small changes in ionic charges to occur as a function of changes in interatomic distances.

7.2 Mass Action Analysis of Defects in $MgAl_2O_4$ Spinel

The mass action analysis presented in section 4.2.2 enabled the evaluation of relative concentrations of a large number of different defects and defect clusters. The use of potentials assuming full formal charges means, however, that while these results provide a useful indication of the relative importance of different defects, the absolute values obtained for concentrations are unlikely to closely reflect the real situation. The form of the mass action equations mean that the calculated concentration is very sensitive to changes in the defect reaction energies used. While the pair potential methods used primarily throughout this thesis are generally able to accurately evaluate relative energies it is not expected that the values obtained are necessarily close to the actual energy. One reason for this is the assumption that ions have full formal charges. In reality solids are not fully ionic but only partly so (a thorough discussion of ionicity can be found in [158]). The assumption of full charges tends therefore to overestimate the coulombic contributions to the lattice and defect energies. Recent experiments find that the degree of ionicity is very high, giving Born effective charges of +1.97 for the Mg ion and +2.95 for the Al ion [159] although a series of density functional calculations predict the less ionic $Mg^{1.79+}Al_2^{2.63+}O_4^{1.76-}$ [160]. By repeating the defect calculations using a quantum mechanical techniques more accurate energies could be evaluated allowing more confident prediction of defect concentrations. Of course, such calculations are considerably more computationally demanding.

In section 4.1.1 it is explained that the system of mass action equations has been solved in this work by an implementation of Newton's method in 2D. This method was found to offer more reliable convergence than others schemes discussed by Broyden [135], however, it is very sensitive to initial conditions, such that solution of the systems at a given temperatures requires the user to manually run the minimisation many times, adjusting the starting concentrations, until a satisfactory solution is obtained. Much time would be saved if the code was modified to find reasonable starting parameters (which is possible as the form of all the mass action equations are known) and if it could be automated to run through a set of starting parameters close to the expected values.

7.3 Migration in $MgAl_2O_4$ Spinel

Chapter 5 contains a complete study of migrations of intrinsic defects in normal $MgAl_2O_4$ spinel. The results obtained in chapters 3 and 4 however, suggest that this may not be the complete story. As we have seen, the assumption of normal spinel is not wholly applicable, as even at low temperatures antisite defects are present in the lattice in sufficient concentrations that they might be expected to have some effect on migration barriers. Probably the most significant effect would be that caused by the clustering of the migrating ions with antisite species as described in section 4.2.2. If, for example, a $V_O^{\cdot\cdot}$ is locally charge compensated by two Mg'_{Al} defects then it might become trapped, i.e. the activation energy required to move from its charge compensated location to one which has less charge compensation could increase. Clearly looking at all possible cation configurations local to the migrating species would be computationally prohibitive, however, if a study was limited to considering different cation configurations on only the sites nearest to the migrating species then some measure of the effect of clustering on migration rates might be obtained. This could be facilitated by using the new temperature accelerated dynamics approach [140] which can simulate dynamic processes over much larger time scales than conventional molecular dynamics (necessary for cation migration processes in oxides which operate on time scales which are very long compared to atomic vibrations).

7.4 Pair Deconvolution

In chapter 6 it is shown that the binding energies of defect cluster formed through the inclusion of Gd_2O_3 in CeO_2 can be accurately modelled as the sum of the binding energies of the cluster's constituent pairs of defects. By assuming that these pair interactions do not depend on the local environment they could form the basis for Monte Carlo simulations on a very large defective lattice.

It is envisaged that these simulations would proceed as follows: beginning with a preselected random configuration of defects over lattice sites the total interaction (binding) energy is calculated, then a defect is moved (swapped) to a new site and the new total interaction energy calculated. This new configuration may be accepted according to its energy difference with respect to the previous configuration. Whether or not it is accepted, a new random swap is performed and the process repeated. After many transitions the system will generate a series of more stable states appropriate to a given target temperature. The problem becomes more complex because there are both cation and anion defects. How the Monte Carlo process will partition the swaps is yet to be decided.

In principle it is very attractive to perform calculations in this manner because only the defects need be considered, making it possible to simulate very large system sizes. There are some problems: as was shown in section 6.2.2 the pair deconvolution becomes less accurate if three of more defects are first neighbours, this can be countered effectively through the use of a correction in appropriate cases, however determination of such cases would significantly increase the time taken to perform an iteration. Additionally, there is a question of whether to employ periodic boundary conditions or to model a defective region in an otherwise perfect crystal.