

The enumeration of structures for γ -alumina based on a defective spinel structure

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Atomistic potential calculations of the relative energies of γ -alumina structures as a function of tetrahedral Al distribution give an exhaustive list of configurations which is used to estimate thermodynamic probabilities, subsequent relaxations allow the influence of configurational entropy on structure to be assessed.

γ -Alumina finds widespread use as a stable, highly porous medium for the support of active catalysts such as particulate transition metals. The material is formed on dehydration of the hydroxide boehmite and is the stable form of alumina from this route between 750 and 1025 K.¹ The structure is generally regarded as amorphous although it is known that the oxygen anions form an fcc lattice with Al ions occupying both octahedral and tetrahedral sites. The cubic structure resembles a defective spinel in which both tetrahedral and octahedral cation positions are occupied. In the proper spinel structure, MgAl_2O_4 , Al^{3+} ions appear in half the octahedral holes and Mg^{2+} in 1/8 of the tetrahedral holes. Various experiments have attempted to apportion the Al cations in γ -alumina between the two possible sites. In 1991 X-ray and neutron diffraction were combined to give lattice parameters for the cubic cell.² The line widths of specific reflections were used to suggest that the Al tetrahedral sub-lattice is extremely disordered and that the distribution of Al between tetrahedral and octahedral sites was roughly 50:50, although the assignment of the occupancy ratio was difficult as no reflections from the octahedral sub-lattice alone are present in the diffraction pattern. More recently, ²⁷Al MAS NMR has been used to show that $70 \pm 2\%$ of Al ions occupy octahedral sites.³ This is close to the proportion that would be expected for a spinel structure in which all octahedral Al are in place and the tetrahedral sites are partially occupied to give 75% of cations in an octahedral environment. Here, we show that this simplified model of the structure allows the calculation of the lattice energy for all possible arrangements of tetrahedral Al in the simplest stoichiometric unit cell using atomistic potentials. Furthermore the structures of the most thermodynamically stable lattices can be geometry optimised to allow thermally averaged structural data such as the lattice constants to be estimated.

Aluminas in general are based around close packed arrangements of O^{2-} anions with Al^{3+} occupying octahedral and/or tetrahedral holes. α -Alumina has the corundum structure with a hexagonal close packed arrangement of anions and exclusively octahedral cations. The α -polymorph has been widely studied using both atomistic potential and periodic quantum chemical approaches. The θ -alumina structure is based on a face centred cubic packing of anions similar to the γ -phase⁴ and contains both octahedral and tetrahedral aluminium ions. Based on these two ordered structures new potentials for octahedral and tetrahedral aluminium were fitted using the GULP program⁵ starting from the shell model potentials derived for α -alumina by Lewis and Catlow.⁶ The full procedure used in fitting and the resulting parameter set will appear at a later date. We note here that the new potentials are able to reproduce the experimental lattice constants of the two phases used in fitting to within 0.15 Å.

A unit cell of overall stoichiometry Al_2O_3 in the spinel form requires a supercell of at least three basic spinel cells ($\text{Al}_{64}\text{O}_{96}$) which we produce by extension of the c -vector. Recently Allan *et al.*⁷ have used a sampling technique to consider the configurational entropy for the mixed oxide MnO/MgO and find convergence with supercells containing only 32 atoms; accordingly, we expect this cell to be sufficiently large to avoid artifacts due to cell size effects. In this cell we have 24 possible tetrahedral Al sites to be filled by 16 atoms. The total number of possible distinguishable structures is simply $2^4\text{C}_{16} = 735471$. Using an EV5 DEC alpha workstation a single lattice energy calculation for this supercell using GULP takes approximately 1.2 CPU seconds and so the complete set of structures can be assessed in a little over ten days. The amount of data generated would, however, require a considerable amount of computer storage and so to make these calculations feasible we have developed an automated driving program. All that is stored after each of the initial runs is the binary code and the lattice energy. The binary code is formulated so that each tetrahedral site in the structure is assigned a binary digit that is set to 1 for occupancy by Al and 0 for a vacant site. In the current study a 24-bit number uniquely identifies a configuration and is saved as an integer. The program generates all possible configurations simply by counting through all 24-bit integers and generating an input file for those which have 16 bits set to 1. As they are identified the lattice energy is calculated and both input and output files are replaced by the next configuration.

Our procedure gives an exhaustive list of tetrahedral Al occupancies and the corresponding lattice energies for the structure fixed at the standard spinel geometry. The resulting configurations were grouped according to calculated lattice energy and the number of configurations vs. lattice energy is shown in Fig. 1. Here we have calculated the lattice energy per mole of Al_2O_3 formula units: the lowest energy configuration was found to be unique together with the number of configuration peaks at around 200 kJ mol^{-1} higher energy where some 55 000 structures have similar energies. Since we store the code for each structure we can easily regenerate a configuration of interest. For example, we find that the lowest energy structures have a uniform distribution of tetrahedral Al atoms whereas the

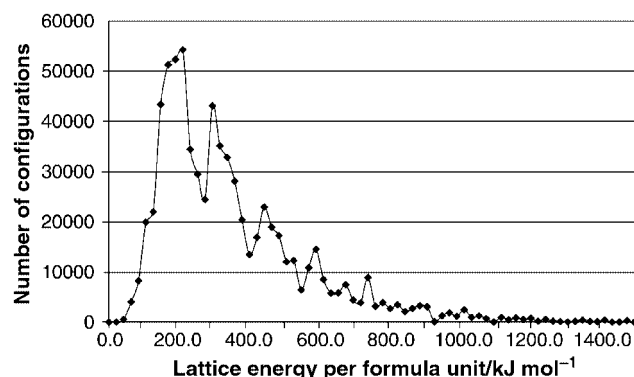


Fig. 1 The number of configurations as a function of calculated lattice energy. Structures are grouped in intervals of 21.1 kJ mol^{-1} .

highest energy structures have the occupied tetrahedral sites clustered together and one third of the unit cell contains no tetrahedral Al atoms. This calculation also gives us direct access to the partition function for the tetrahedral site distributions allowing the calculation of thermodynamic probabilities. For example, the probability, $P(\Delta E_i)$, of a given lattice energy is:

$$P(\Delta E_i) = \frac{n_i \exp\left(-\frac{\Delta E_i}{RT}\right)}{\sum_j n_j \exp\left(-\frac{\Delta E_j}{RT}\right)} \quad (1)$$

where n_i is the number of structures with energy ΔE_i greater than the lowest energy structure. Since γ -alumina is formed from boehmite at elevated temperatures we chose $T = 900$ K. Even at this high temperature the few low energy structures dominate despite the entropic factor in favour of higher energy states.

In these initial calculations no geometry optimisation was allowed so that all possible structures could be considered. It is well known that structural relaxation can be important in obtaining accurate relative energies using atomistic simulation. In this case the occupation of an Mg^{2+} tetrahedral site by a smaller Al^{3+} cation will cause lattice strain. Despite this we expect the ordering of the structural energies to be a good indication of which are the important structures to consider. Accordingly we carried out relaxations on the most probable of the lattices generated. The list of structures was ordered according to lattice energy and the program adapted to reconstruct them from the list and carry out lattice relaxations using GULP. To determine how far down the list to proceed the thermodynamic probability of each structure was calculated from eqn. (1) (with $n_i = 1$) using the recorded static lattice energy. Sub-sets of structures were generated by successively decreasing the acceptance probability limit. Geometry optimisations were performed using the same automated procedure as described previously but now the GULP input file was written to perform relaxations at constant pressure, *i.e.* a full relaxation of all atomic co-ordinates and lattice vectors.

Fig. 2 shows the probability distribution of lattice energies at 900 K after relaxations for three sub-sets containing increasing numbers of structures in roughly 50 000 steps. The distribution shows significant differences for the change from 78 137 to 129 205 structures but the addition of a further 50 000 structures results in only minor alterations suggesting that most of the additional structures do not optimise to thermodynamically accessible configurations. There are now two degenerate lowest energy structures. These are found in the smallest list and remain the minima for the longer lists indicating that the initial ordering by structural energy has allowed the minimum energy structure to be identified rapidly. After relaxation the number of

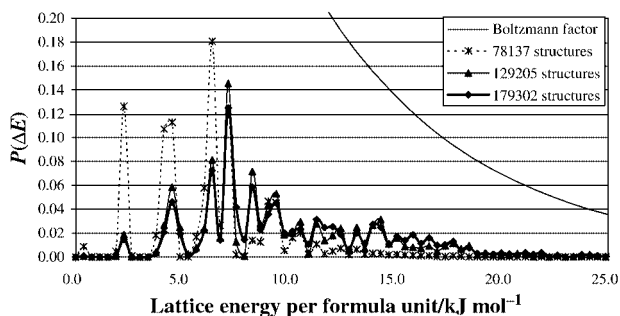


Fig. 2 Probability vs. lattice energy from eqn. (1) at 900 K with structural relaxation taken into account for three sub-sets containing 78 137 (crosses, dotted), 129 205 (triangles, thin solid) and 179 302 (diamonds, thick solid) structures. Boltzmann factor shown as a feint line. Structures grouped in 0.38 kJ mol^{-1} intervals.

Table 1 Comparison of calculated and experimental lattice vectors

	Number	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$
Expt. MgAl_2O_8		8.080	8.080	8.080
Expt. γ -alumina ²		7.911	7.911	7.911
Min. energy structure	1	8.277	8.245	8.203
Thermal average ^a	78 137	8.251	8.251	8.269
	129 205	8.254	8.254	8.271
	179 302	8.254	8.254	8.278

^a Thermal averages use eqn. (1) with $T = 900$ K.

structures within a few kJ mol^{-1} of the minimum is much greater than for the simple structural energy calculations and so the entropic effect of tetrahedral ion configurations is much greater. The probability of the lowest energy structures is extremely small and the probability distribution shows a great many structures with configurations up to 20 kJ mol^{-1} above the minimum being significant. The highest peak in $P(\Delta E_i)$ occurs at 7.2 kJ mol^{-1} and represents some 12 200 structural alternatives.

After relaxation the lattice parameters were also recorded for each configuration to allow the lattice vectors, a , b and c , to be calculated as thermodynamic averages of the relaxed structures. Based on the sub-sets of relaxed structures from Fig. 2 we find the lattice parameters given in Table 1 where we also compare the averaged data to experimental results and to one of the minimum energy structures. The other degenerate minimum energy form is identical to that in Table 1 with a and b interchanged. These minima structures show a distortion away from cubic symmetry. On averaging this is reduced to a small tetragonal distortion of the basic unit cell. The convergence of the cell dimensions with sub-set size is further confirmation that all thermodynamically significant configurations have been taken into account.

Early investigations of γ -alumina reported tetragonal distortions of the unit cell.⁹ It appears from these calculations that the observed symmetry comes about from the interplay of many possible configurations of cations. Closer inspection of the listed data shows that the individual microstates occur in pairs with equivalent distortions in the a and b directions, in the averaging process these are removed to give the experimentally observed cubic structure. In the real crystallites this tendency toward distortion will lead to lattice strain which may contribute to the longer scale defect structure of the material.

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