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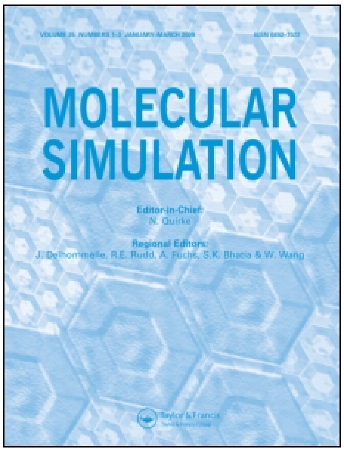

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Alkaline Earth Impurity Segregation at the Basal {0001} and Prism {1010} Surfaces of α-Al_2O_3

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ALKALINE EARTH IMPURITY SEGREGATION AT THE BASAL {0001} AND PRISM $\{10\bar{1}0\}$ SURFACES OF α-Al_2O_3

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Atomistic computer simulation methods have been used to model calcium and magnesium segregation at the basal {0001} and prism $\{10\bar{1}0\}$ surfaces of α-Al_2O_3 and their interaction with charge compensating defects. The results demonstrate that segregation is surface specific, varying with temperature, impurity ion size and concentration. The variation of defect energy as a function of distance from the basal surface is also given and the results are discussed in the light of the sintering behaviour of α-Al_2O_3 doped with calcium and magnesium.

KEY WORDS: Segregation, surfaces, alumina, alkaline earth impurities, atomistic simulation, sintering

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INTRODUCTION

Many properties of ceramic oxides are controlled by cation impurity segregation at their interfaces. However, experimental determination of the segregation processes at the atomic level is often difficult and therefore this is an area where atomistic simulation can play a useful role. An important example of segregation is the beneficial effect that magnesium, but not calcium, has on sintering α-Al_2O_3 to full density. This is thought to depend on the suppression of exaggerated grain growth which is observed for α-Al_2O_3 doped with MgO [1] but not CaO [2]. Exaggerated grain growth occurs when the grain-boundary mobility is much greater than the pore mobility. This may be altered by segregation of magnesium to the grain-boundary and its subsequent decrease in mobility by a solute-drag mechanism [3]. Alternatively magnesium may segregate to pore surfaces and influence surface diffusivity and pore mobility [1].

In an attempt to explain these phenomena more fully, recent experiments employing Auger Electron Spectroscopy and Low Energy Electron Diffraction have concentrated on calcium and magnesium segregation at low index surfaces of α-Al_2O_3. Baik *et al.* [4] have found that in a closed system magnesium segregates to the 0001 basal surface above 1573 K with an effective Langmuir heat of segregation of $-183\,kJmol^{-1}$ and have found evidence for the two dimensional surface reconstruction. This was further complicated by the presence of two other impurities, calcium and silicon which were also observed at the surface. Further work by Baik and White [5] on calcium doped sapphire showed that calcium will segregate to the $10\bar{1}0$ prism surface at temperatures greater than 1573 K but will not segregate to the basal surface by a measurable amount. More recently, Mukhopadhyay *et al.* [6] considered magnesium and calcium segregation at the $10\bar{1}0$ prism surface of magnesium doped sapphire. Magnesium was observed to segregate preferentially with an effective heat of segregation of $-135\,\mathrm{kJmol^{-1}}$ while calcium segregation did not exhibit Langmuir behaviour i.e. a plot of log (surface concentration) versus reciprocal temperature was not linear.

The aim of this paper is to demonstrate that atomistic simulation provides an alternative technique for resolving these questions of impurity segregation. Recent developments in this area have led to a number of theoretical studies on defect segregation in α-Al_2O_3 e.g. Mackrodt and Tasker [7], who predicted an enthalpy of $-158\,\mathrm{kJmol^{-1}}$ for the segregation of magnesium at the basal surface of α-Al_2O_3 and suggested that the observed two dimensional surface reconstruction was due to the formation of the spinel $MgAl_2O_4$. Further work by Mackrodt [8] on the segregation of Fe^{3+}, Y^{3+} and La^{3+} at the low index surfaces of α-Al_2O_3 ($0001, 10\bar{1}0, 10\bar{1}1, 10\bar{1}2, 11\bar{2}0$) showed that not all impurity cations segregate in contrast to the classical arguments based on elastic strain and ion size [9].

This paper is concerned with the technique of static lattice simulation and illustrates its advantages and limitations by considering the segregation of calcium and magnesium to the 0001 basal and $10\bar{1}0$ prism surfaces of α-Al_2O_3 and investigating the variation of calcium and magnesium segregation with temperature. In the next section the method of calculating segregation energies is outlined and the variation of surface defect coverage with temperature is discussed.

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THEORY

Atomistic lattice simulation based on the Born model [10] has been used successfully to calculate energies of bulk and surface point defects, and neutral surface defect clusters in inorganic crystals. The crystal is defined as a stack of planes perpendicular to the surface which are periodic in two dimensions and the ions are allowed to relax until they reach their mechanical equilibrium positions i.e. where no net forces act on them. Previous work on oxide surfaces (see for example Tasker [11]) has demonstrated that surface relaxation must be included to reliably model the surface and that a simple bulk termination model is inadequate.

The computer codes used in this work are: CASCADE [12] (available in the CCP5 program library), which gives bulk point defect energies: MIDAS [13], from which the surface energies can be calculated: and CHAOS [14], which is used to evaluate surface point defect energies.

The Potential Model used in these codes includes the electronic polarisability using the Shell Model [15] and the empirical Buckingham potentials of Lewis and Catlow [16] which were originally derived for short range interactions in the bulk of the crystal. Hence an important assumption of these calculations is that they are transferable to the surface. This assumption can be tested by comparing the results obtained using these potentials with those calculated using the non-empirical potentials of Mackrodt and Tasker [7]. Preliminary work on the comparison of these potentials shows good argeement. The segregation energy can be calculated from the energy difference in substituting an impurity for a host ion in the bulk and at the surface. This assumes that there are only two types of site in the crystal, one at the surface and one in the bulk. The ratio x_s is defined as $n_1^s/(n_1^s + n_2^s)$ where n_1^s is the number of ions of type 1 and n_2^s type 2 and x_b is defined in the same way but b represents bulk ions. Mackrodt and Tasker [7] have derived a coverage-dependent segregation isotherm, which using the above definition of surface coverage, corresponds to an isotherm of the form:-

$$x_s = \frac{1}{1 + (x_b A)^{-1} \exp\left[\left\{\Delta h + x_s \frac{d\Delta h}{dx_s}\right\} \Big/ k_b T\right\}} \qquad (1)$$

where A is a pre-exponential factor incorporating the entropy of segregation and Δh is a function of surface-coverage. Using this isotherm it is possible to compare experimental and theoretical segregation isotherms. However, a direct comparison of segregation energies is inappropriate as experimental values are often extracted from linear Arrhenius plots of log (surface concentration) versus reciprocal temperature using the equation:-

$$C_s \alpha\ C_b \exp(\Delta h/kT) \qquad (2)$$

where C_s and C_b are the surface and bulk concentrations respectively and Δh the heat of segregation. In equation 2, Δh is independent of coverage and is said to exhibit Langmuir behaviour. At low surface coverages this relationship is likely to hold, but as surface defect concentrations increase, defect-defect interactions will play a more important role in determining segregation enthalpies and thus non-Langmuir behaviour is expected.

Calculations of this type on idealised real systems invariably involve approximations. A potential source of error regarding the model is that impurity ions are assumed to segregate at planar, non-defective surfaces to form ordered structures. At low coverages in particular, step and kink sites may influence segregation behaviour although further calculations on Al_2O_3 are necessary to investigate this possibility. With regard to the calculations, the solutions energies are absolute energies. The reliability of such a calculation depends on the accuracy of the potential model (which was derived to reproduce observed bulk crystals properties e.g. dielectric constants) and on additional components of the energy such as ionisation potentials. However, segregation energies are relative and their reliability is demonstrated by comparison with experiment.

RESULTS

Defect Clusters

Any treatment of acceptor defects e.g. magnesium and calcium on the cation sublattice of Al_2O_3 to give M'_{Al} (using the Kroger-Vink notation) must take into account the formation of charge compensating defects e.g. $M_i^{\cdot\cdot}$ (M=Ca or Mg), O· and V_O^x possible interactions of charged defects with the surface space-charge (17). In the case of magnesium and calcium, the large binding energies, given in Table 1 suggest that these defects are strongly bound to oxygen vacancies in the bulk. Calculations given in Table 2 for surface binding energies, which include image charge effects also

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Table 1 Bulk Solution and Binding Energies (in kJmol^{-1} per M^{2+} ion) of Ca and Mg in α-Al_2O_3

M^{2+} ion	*Solution Energy*	*Binding Energy*
Mg	164	−116
Ca	309	−174

Table 2 Surface Binding Energies (in kJmol^{-1} per M^{2+} ion) of Ca and Mg at the basal and prism surfaces of α-Al_2O_3

M^{2+} ion	*Prism Surface*	*Basal Surface*
Mg	−183	−231
Ca	−125	−187

indicate that the majority of these impurities will exist in neutral clusters of the form $\{M'_{Al} - V^{x}_{O} - M'_{Al}\}$. The importance of this result is that space-charge effects, which represent the interaction of charged defects with the surface and are difficult to treat explicitly as they operate over hundreds of angstroms, can be neglected. Mackrodt and Tasker [7] adopted a similar approach using non-empirical potentials to model the short range interactions and found good agreement with experiment.

In the following sections the structure of the pure and defective surfaces are discussed and where possible the calculations are compared with experimental results.

The Pure 0001 and $10\bar{1}0$ Surfaces

α-Al_2O_3 has the corundum structure which consists of hexagonal close packed oxygen ions with aluminium cations in two-thirds of the octahedral sites, leading to six coordinate aluminium and four coordinate oxygen. Figure 1 shows the basal surface which terminates at a cation plane and has a repeat unit of Al–O–Al perpendicular

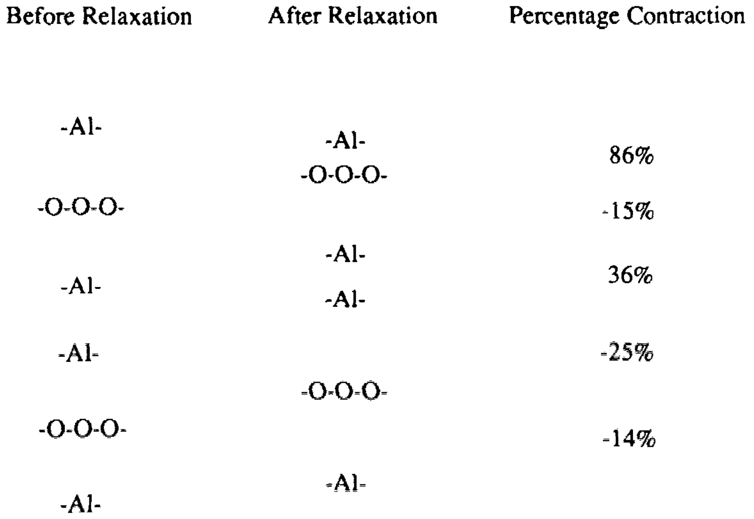

Figure 1 Pure basal surface of α-Al_2O_3 before and after relaxation

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to it. Only one-third of the available surface cation sites are filled and on relaxation this leads to the dramatic contraction of the basal surface. In contrast, the prism surface, which has a stoichiometric stacking sequence, (Figure 2) terminates at an oxygen plane. On relaxation the surface expands and the cation planes rumple as the repulsion between oxygen ions is relieved and the cation coordination changes. The corresponding calculated relaxed surface energies at the prism and basal surfaces are 2.7 and 2.3 Jm^{-2} respectively. In view of the different surface structures variation in defect behaviour might be expected.

DEFECTIVE SURFACES

1. The 10$\bar{1}$0 Prism Surface

Segregation energies as a function of magnesium defect cluster concentration are given in Figure 3 and compared with those of calcium. The segregation energy for the magnesium cluster becomes more exothermic by approximately 30 $kJmol^{-1}$ between zero and one quarter coverage and compares favourably with the effective experimental segregation enthalpy reported by Mukhopadhyay *et al.* [6] of 135 $kJmol^{-1}$. At

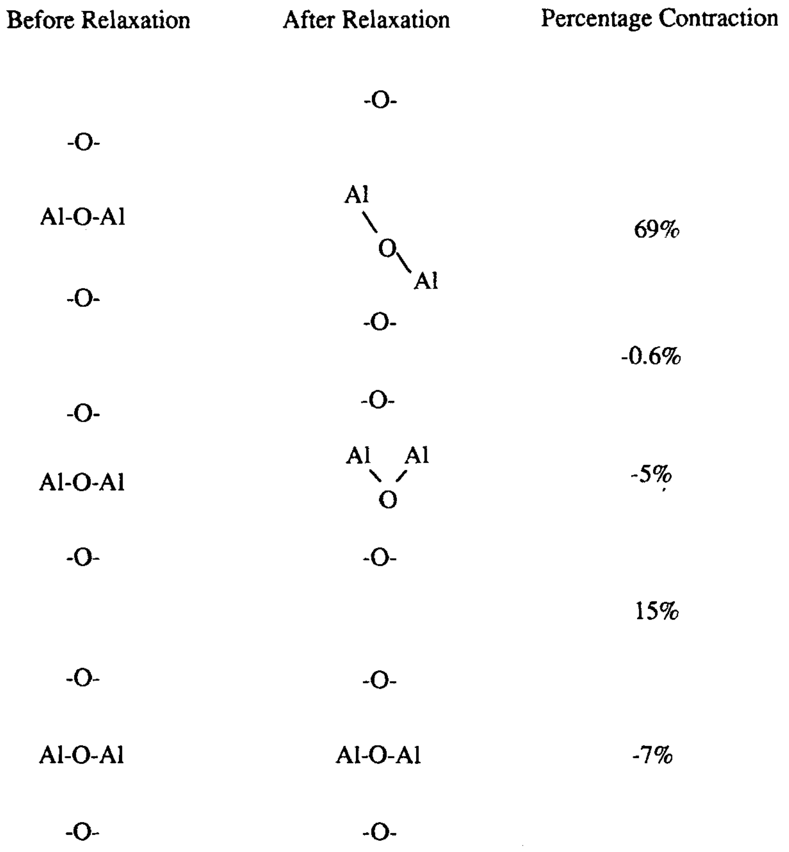

Figure 2 Pure prism surface of α-Al_2O_3 before and after relaxation

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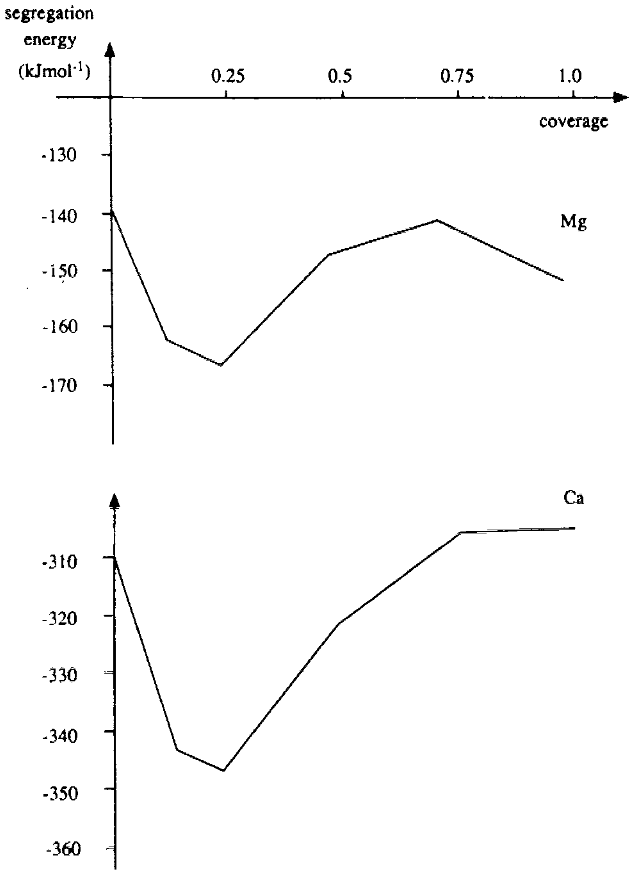

Figure 3 Plot of variation of segregation energy with coverage for $M'_{Al}-V_O^{x}-M'_{Al}$ (M=Mg, Ca) at the prism surface of α-Al_2O_3

coverages greater than 25% the segregation energy rises by 30 kJmol^{-1} but is still negative. Calcium segregation at this surface shows similar behaviour but is much more exothermic, as might be expected in view of the larger cation, and hence cluster size.

The variation of surface magnesium coverage with temperature using equation 1 is plotted in Figure 4. The results are compared with experiment by choosing a value for the pre-exponential factor that gives the experimental value at an observed coverage and then using this value of A over the given temperature range. This approach is necessary because the code required to calculate the surface entropy terms is still being developed. From Figure 4, the qualitative agreement between the experimental and calculated coverages is good. As the temperature increases from 1573 K to 1773 K the system does not exhibit Langmuir behaviour (as expected from Figure 3).

The equivalent plot using the results from equation 1 for calcium at the prism surface is given in Figure 5 and includes the experimental work of Baik and co-workers [5,6]. Again the qualitative agreement is good, the logarithm of surface coverage varies linearly with temperature (although from Figure 3 the segregation

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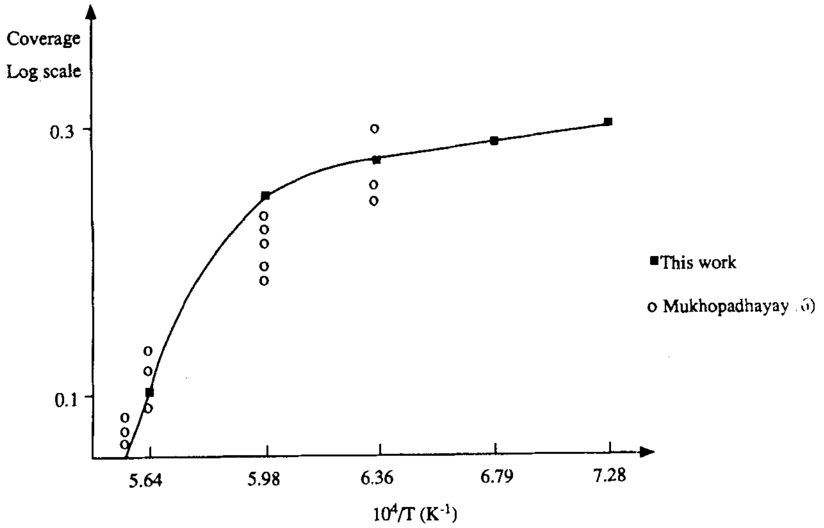

Figure 4 Calculated temperature dependence of the equilibrium Mg surface coverage at the prism surface of α-Al_2O_3

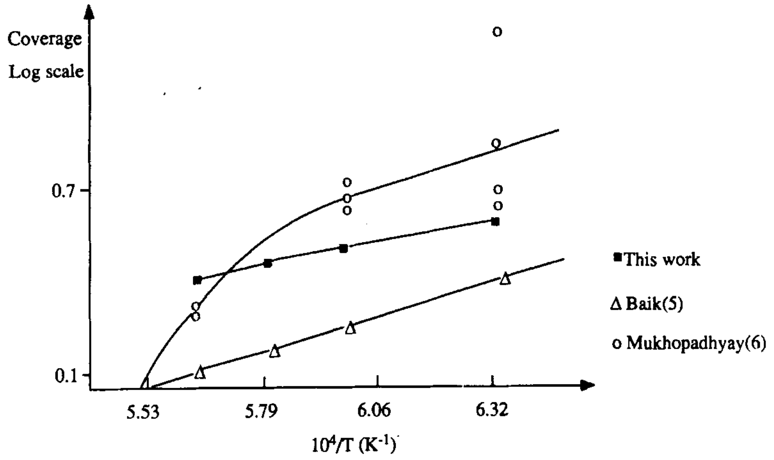

Figure 5 Calculated temperature dependence of the equilibrium Ca surface coverage at the prism surface of α-Al_2O_3

energy is not independent of surface coverage) and decreases as the temperature increases. The discrepancy between the two sets of experimental results demonstrates the need for the calculation of segregation free-energies so that direct comparison of theory and experiment is possible.

2. *The 0001 Basal Surface*

Magnesium segregation at the basal surface has previously been investigated both experimentally [4] and by lattice simulation using non-empirical potentials [7] (see

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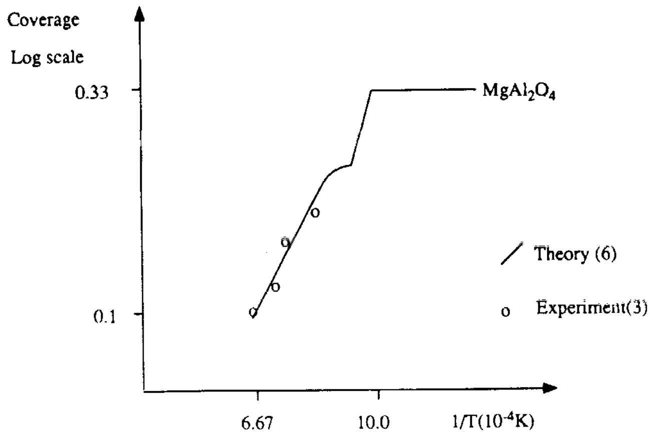

Figure 6 Calculated temperature dependence of the equilibrium Mg surface coverage at the basal surface of α-Al_2O_3

above) and the coverage versus temperature plot is given in Figure 6. In this instance, Langmuir behaviour is observed above a temperature of approximately 1350K. Below this temperature the observed two dimensional surface reconstruction has been interpreted as the formation of the spinel $MgAl_2O_4$.

The remainder of this paper deals with calcium segregation to the basal surface and highlights areas where the segregation model used thus far may be improved.

The segregation energy versus coverage isotherm for the calcium cluster at the basal surface is given in Figure 7. Between zero and one quarter coverage the segregation energy is more positive reaching a maximum at 25% surface coverage and then

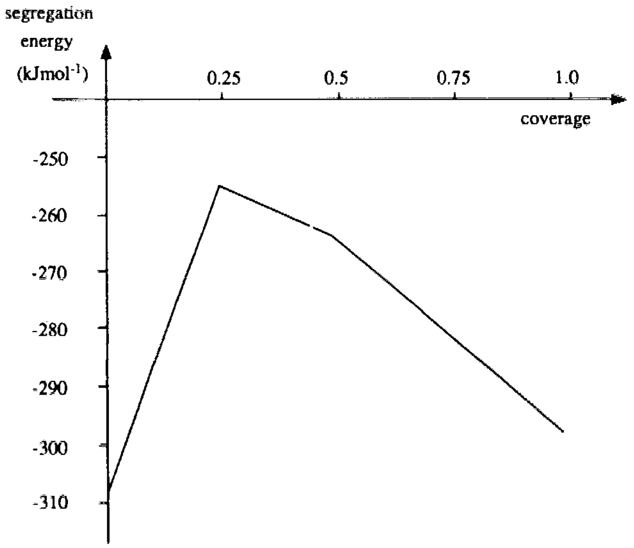

Figure 7 Plot of variation of segregation energy with coverage for Ca'_{Al}-V_O^x-Ca'_{Al} at the basal surface of α-Al_2O_3

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decreases until all surface sites are filled. Thus segregation is favourable over the whole coverage range and non-Langmuir behaviour is exhibited. This agrees with the experimental work [4] on magnesium segregation at the basal surface, where calcium was observed at sites unoccupied by magnesium but is contrary to the study [5] of calcium α-Al_2O_3 where calcium segregation was not detected. The mismatch between theory and experiment is perhaps surprising in the light of the agreement for magnesium and previously for isovalent segregation [7]. This disagreement may arise from deficiencies in either experiment or theory. Two possible limitations of the simulations are either the calculation of the pre-exponential term or that the model only identifies two sites (one surface and one bulk site). The calculation of free-energies is currently under investigation. The other possible limitation is that the two site model is inappropriate. Previous calculations on MgO [18] and Cr_2O_3 [19] show that defect stabilities vary dramatically over several sub-surface cation planes before reaching the bulk value (calculated from the CASCADE energy) even when little relaxation has been observed.

Point defect formation energies as a function of depth are presented in figures 8, 9 and 10 for aluminium vacancy, magnesium and calcium substitution energies in the sub-surface region of the basal plane. Figure 8 shows that the cation vacancy energy does vary with distance from the surface and approaches the bulk value around the 7th cation plane (approx. 6 Angstroms) below the surface. This is expected in view of the large relaxation seen in Figure 1 which leads to enhanced stability of vacancy sites on the 4th and 5th cation planes. The plots in Figures 9 and 10 for magnesium and calcium substitutions with depth both show a maximum around the 3rd and 4th cation planes, the differences in the energy between the 4th and 5th planes are 48 kJmol^{-1} for magnesium and 135 kJmol^{-1} for calcium. Substitution of calcium at the 2nd cation plane is unstable and the calcium ion migrates directly to the surface. Thus enrichment of the surface by magnesium and the sub-surface by calcium might be expected as the energy barriers to defect migration are markedly different. This would then explain why magnesium inhibits exaggerated grain growth by segregating to pore surfaces and subsequently controlling surface defect diffusion. In contrast, calcium may only segregate to the sub-surface layers and would be less effective as a sintering agent.

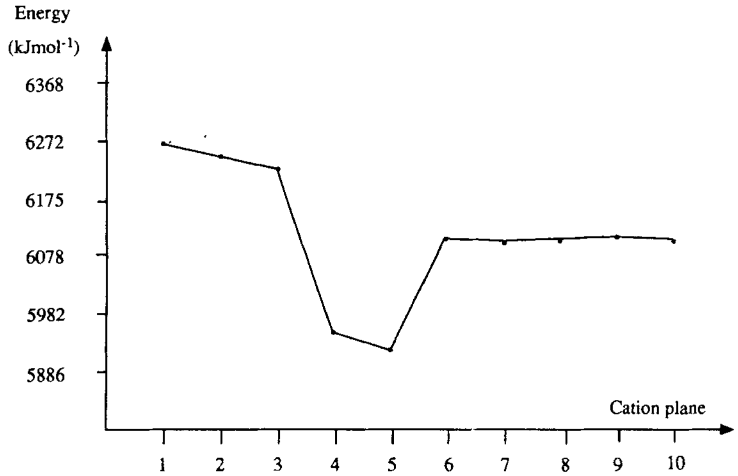

Figure 8 Variation of aluminium vacancy energies with distance from the basal surface

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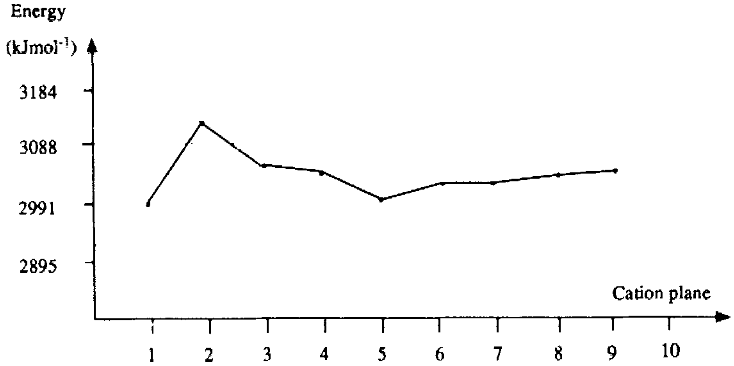

Figure 9 Variation of magnesium substitution energies with distance from the basal surface

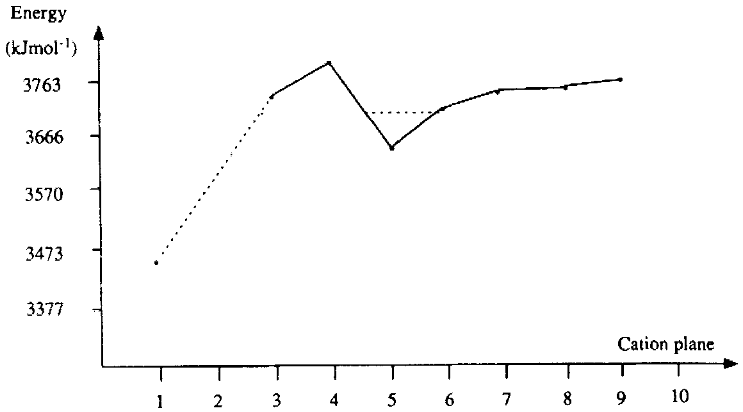

Figure 10 Variation of calcium substitution energies with distance from the basal surface

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CONCLUSION

Although the pre-exponential factor has only been estimated and assumed constant over the required temperature and coverage range, the agreement between experiment and theory is good. This is seen for magnesium at the prism and basal surface and for calcium at the prism surface. The apparent mismatch between theory and experiment for calcium at the basal plane, which is surprising in view of those discussed previously, prompted the investigation of defect energetics in the sub-surface region. This study highlights the effect that surface relaxation has on segregating defects and emphasises the importance of sub-surface defect segregation. This would also indicate that calcium does not control exaggerated grain growth as well as magnesium because it does not segregate to the surface cation layer and would thus have a smaller effect on surface diffusion in pores.

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