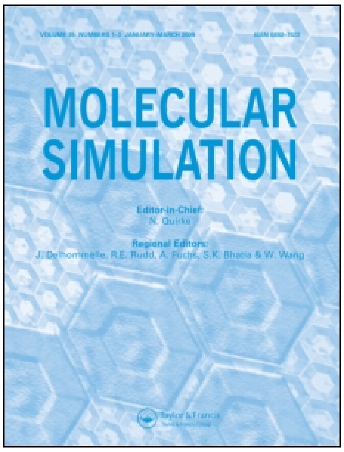

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Computer Simulation of Surface Segregation

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COMPUTER SIMULATION OF SURFACE SEGREGATION

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Computer simulation techniques can now reliably model the surface structure and energies of inorganic solids. We present recent work which has been directed at modelling the segregation of impurities. The techniques are based on energy minimisation where the forces between the atoms are described by the Born model of solids. We initially show that magnesium and calcium segregation to the prism surfaces of alumina reproduce the available experimental data within the uncertainties of the experimental technique. However, reliable experimental data is not always available, and hence we show using the examples of calcium segregation to zirconia surfaces can give insights to the surface structure and provide predictions for experiment to test. Secondly, the simulations can be verified by comparison with morphologies. This is illustrated by comparison of the experimentally determined morphology of calcite with magnesium and lithium impurities with those calculated. Next extensions to the energy minimisation methods are described using dynamical techniques based on lattice and molecular dynamics. Finally, we describe the situation where there is phase separation and the structure and stability of the interface is governed by the epitaxial relations between the underlying oxide and the impurity oxide.

KEY WORDS: surface segregation, impurities, energy minimization.

1 INTRODUCTION

The aim of this paper is to describe recent work at Bath on modelling the influence of impurities on the surface structure and energetics. Impurities at a surface are of fundamental importance in determining material properties. For example impurities will affect sintering, densification and the catalytic properties of the materials [1]. A comprehensive knowledge of the effects of impurity level concentrations on behaviour is therefore of critical importance in the design and implementation of technologically important materials and processes. The development of surface codes [2, 3] has given us access to a clearer understanding of the atomic processes that occur at surfaces and interfaces. These codes have been employed successfully to investigate tilt gain boundaries [4, 5] which have obvious implications for corrosion [6, 7] due to enhanced diffusion of cations along grain boundaries in the oxide layer.

One of the major problems in using these techniques to model the effect of impurities is the scarcity of experimental data to test and to verify the techniques. One approach is to compare with the simulated experimental segregation isotherms. The commonly used Langmuir/Arrhenius isotherm assumes the heat of segregation is independent of temperature. However, Mackrodt [8] has shown that this is merely a special solution of a non-Arrhenius isotherm which allows for the variation of the heat of segregation with surface coverage/concentration of the impurity ion. The problem is that the isotherms are often experimentally difficult to measure and there is reliable data only for segregation of impurities to alumina and magnesia surfaces [9, 10]. Hence we suggest an alternative strategy for low concentrations of impurities, namely comparison with the equilibrium morphologies of crystals. This is illustrated by the addition of Mg and Li impurities to calcite for which there are electron microscopy data which show a distinct change in the crystal habit on the addition of these impurities. For larger concentrations, where there is phase separation, there are even less data and the problem is centred on the lattice matching of the two phases. We show the example of epitaxial thin films of BaO on MgO.

The approach adopted for modelling surfaces is to use atomistic simulation where the interaction between each atom is described by parametrised potential functions based on the Born model of solids. Once the total interaction energy is obtained, energy minimisation is used to determine the most stable surfaces.

2 SURFACE METHODOLOGY

The most stable and hence the most common surfaces of a crystal are generally those of low Miller index. These planes are usually those which have the largest interplanar spacings. However in ionic crystals other constraints also apply. If the Madelung sums are not to diverge with increasing crystal size then the crystal must not only be electrically neutral but also have no net dipole moment perpendicular to the surface [11]. Bertaut [12] demonstrated that when there is a dipole moment perpendicular to the surface, the surface energy diverges and is infinite. Such surfaces are therefore unstable, and cannot occur naturally without the adsorption of foreign atoms or defect formation. This is best illustrated by considering the three types [11] of ionic surface, see Figure 1. Type 1 has equal number of anions and cations on each plane and common examples include the rocksalt (1 0 0) and (1 1 0) surfaces. Type 2 surfaces again have equal numbers of anions and cations such as corundum (0 0 0 1) surfaces [13, 14] but each plane has a finite thickness and is constructed of a symmetrical stacking sequence which removes the dipole moment perpendicular to the surface. Type 3 surfaces such as rocksalt (1 1 1), Figure 1(c) have a dipole moment perpendicular to the surface. It is these surfaces which can only be stabilised by substantial reconstruction.

The approach for calculating the change in structure and energy on introducing an impurity is to start with a pure surface structure in which the configuration has been relaxed until the lattice energy reaches a minimum. The impurity is then placed at a surface site. The crystal is divided into two regions; an inner region surrounding the defect which is relaxed explicitly, and an outer region which is treated as a dielectric continuum. The size of region 1 is chosen so that the defect energy has converged. This approach, developed at Harwell, is based on the code HADES3 [15–18] with modifications necessary to include the interface. The major limitation of these codes is that the thermal contributions from vibrational entropy and lattice expansion are neglected.

There are two methods for calculating the thermal contributions. The first is based on lattice dynamics. This is an approach for calculating vibrational frequencies in periodic structures by solving Newton's Laws of motion analytically [19]. This is achieved by using the harmonic approximation where the vibrational motions in the solid are assumed to be comprised of independent quantised harmonic oscillators. This can be extended to include the quasi-harmonic approximation where the frequencies vary with cell volume. This allows thermal expansion to be treated explicitly.

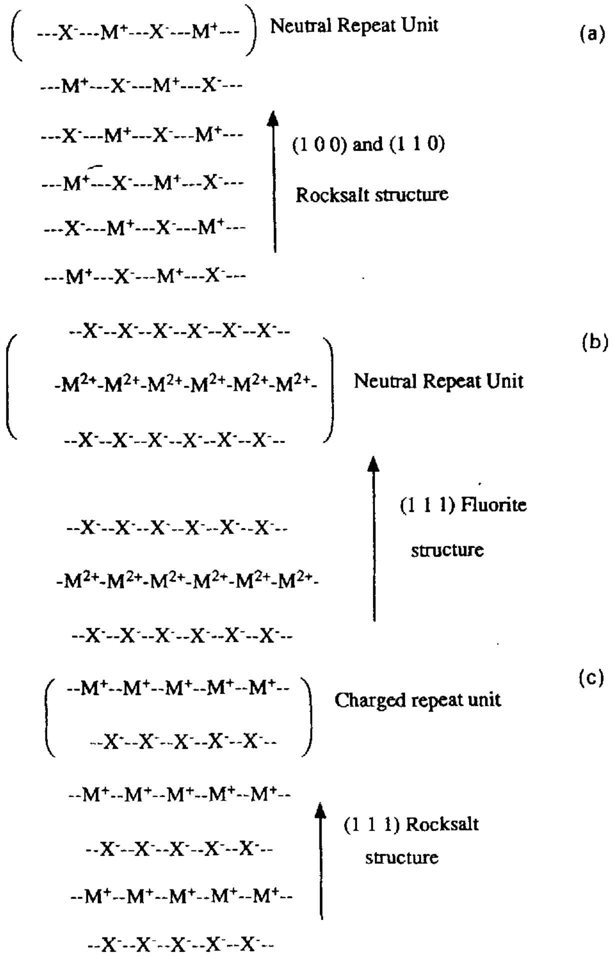


Figure 1 (a–c) Schematic representation of a type 1, type 2 and type 3 surface.

An alternative method for calculating the vibrational properties of solids is to use molecular dynamics where Newton's Laws of Motion are solved explicitly [20–22]. The major advantage of molecular dynamics is that the full anharmonicity of the potential energy surface can be calculated. This is possible because the atoms are in motion and hence after each time-step the atoms will sample a different part of the potential energy surface. In contrast, the atoms in lattice dynamics are held fixed when evaluating vibrational frequencies and thus only sample the energy at the specific lattice sites where the shape of the potential energy-well is assumed to be harmonic. The disadvantage of molecular dynamics is that the calculation of thermodynamic properties is intensive in computer cpu time, and hence certain terms in the potential model are usually neglected, particularly the electronic polarisability. Thus lattice dynamics currently provides the most efficient method for determining thermodynamic properties and phase stabilities, *provided* anharmonic effects are not significant as is the case when the temperature of the mineral approaches its melting point or if it undergoes a displacive or soft-mode phase transition. In contrast, molecular dynamics is best suited in cases where anharmonic effects are important or where there is diffusion.

3 IMPURITY SEGREGATION

3.1 Magnesia and Calcia Segregation to the Prism Surfaces of Alumina

Calcium and magnesium segregation is important in ceramic alumina (α-Al_2O_3) processing because small additions of magnesium oxide to alumina [23] prevent exaggerated grain growth during sintering and, therefore, promote densification. Exaggerated growth occurs when grain boundary mobility is much greater than pore mobility and this reduces the strength and toughness of the sintered ceramic. However, the role played by magnesium is still unclear: it may either segregate to grain boundaries and decrease mobility by a solute-drag mechanism [24] or, alternatively, segregate to pore surfaces and influence surface diffusivity and pore mobility [25]. These theories are further complicated by calcium, which has also been observed at grain boundaries [26] and free surfaces [27] but does not prevent exaggerated grain growth [28].

The experimental techniques used for surface analysis measure the surface impurity concentrations that are assumed to be equilibrated with the bulk as a function of temperature. Heats or enthalpies of segregation are then extracted from conventional plots of the log of the surface concentration against reciprocal temperature. These are often linear and it is commonly assumed that this is indicative of Arrhenius or Langmuir behaviour, wherein the surface atomic ratio of the impurity, x_s, is related to the bulk ratio, x_b, by an expression of the form:

$$x_s \propto x_b \exp(-H/kT).$$

H is a coverage independent heat of segregation, T is the temperature and k is Boltzmann's constant. This expression is likely to hold for low coverages, but as the surface defect concentrations increase, defect–defect interactions will play a more important role in determining the segregation energies and thus Langmuir behaviour will be the exception rather than the rule. This has been confirmed recently by atomistic simulations on iso- [29] and aliovalent [30] impurity segregation in α-Al_2O_3.

The plots of surface coverage against temperature for calcium and magnesium at the prism plane are given in Figures 2 and 3, assuming the heat of segregation is independent of temperature. The pre-exponential factor, A for magnesium segregation was taken from experiment [10] as 1.6×10^{-2}, which corresponds to a segregation vibrational entropy of 3.55×10^{-4} eV K^{-1}. The theoretical plot compares favourably with experiment [10]. For calcium segregation, the vibrational entropy was taken to be 1.24×10^{-3} eV K^{-1} and was extrapolated from the result of Mukhopadhyay *et al.* [10]. The results are compared with those of Mukhopadhyay *et al.* and Baik and White [9] in Figure 3. The qualitative agreement is again good and the variation of the logarithm of surface coverage with temperature is approximately linear. In this case the value of H is determined to be about -1.2 eV (per Ca).

3.2 Calcium Segregation to the Sufaces of Zirconia

The details of the variation of segregation with coverage also give valuable insights

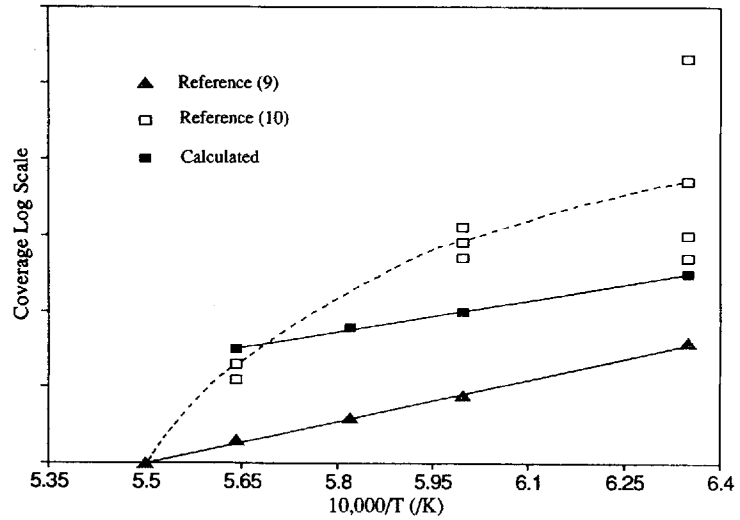


Figure 2 Comparison of the calculated and experimental [9, 10] coverages with temperature of calcium at the prism surface.

in to the surface structure and composition. This is particularly important for systems where there is little surface coverage data.

The segregation energies of calcium to the (1 1 0) and (1 1 1) surfaces of cubic zirconia were calculated for 0%, 25%, 50%, 75% and 100% coverage. As cubic zirconia adopts the fluorite structure [31], the (1 1 0) and (1 1 1) surfaces are the most

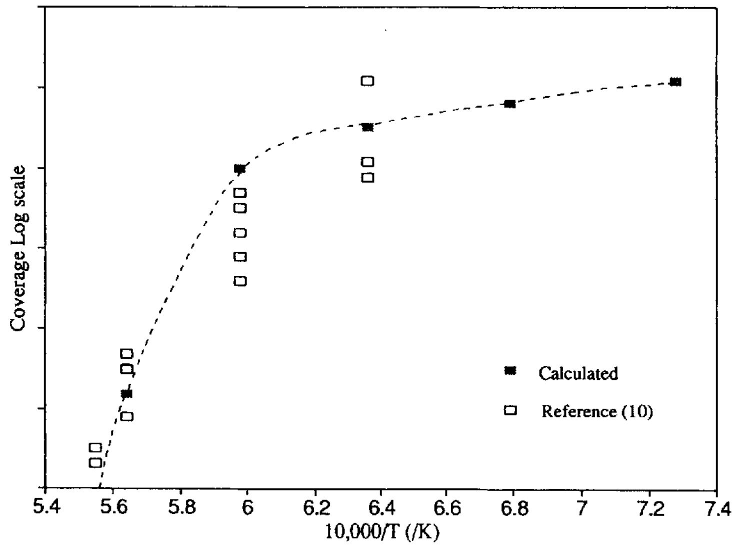


Figure 3 Comparison of the calculated and experimental [10] coverages with temperature of magnesium at the prism plane.

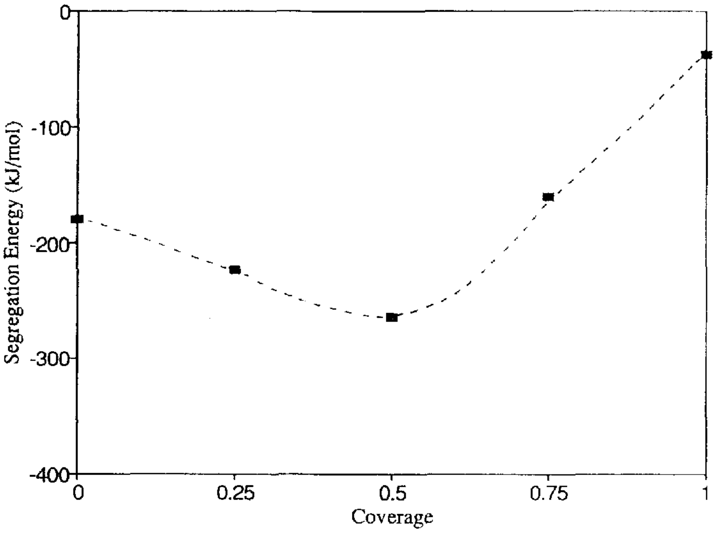


Figure 4 Variation of segregation energy of Calcium to the (1 1 1) surface of zirconia.

stable surfaces. The (1 0 0) surface is a type 3 surface and is far less stable. Figure 4 shows the segregation of calcium to the (1 1 1) surface. All the segregation enthalpies are exothermic with a minimum in the segregation energy occurring at 50% coverage. Simulating the surface coverage predicts the formation of a new phase of composition $CaZrO_3$ at the surface. However, segregation of calcium to the (1 1 0) surface of zirconia displays different behaviour, Figure 5. The segregation energy has a minimum at zero coverage and a linear decrease in segregation energy as a function of coverage. Both of these predictions could be tested by experiment.

3.3 The Influence of Impurities on Crystal Morphology

In general, when modelling segregation of impurities to oxide surfaces one of the few experimental observations which can be readily compared with simulation is the crystal habit. Calcite, $CaCO_3$, when grown in the presence of impurities Mg and Li is known to exhibit different morphologies. Therefore, on calculating the surface energies and the heats of segregation we can test the reliability of the simulation from the predicted morphologies.

The equilibrium crystal morphology can be determined by applying Wulff's Theorem [32], although it was Gibbs [33] who first proposed that the equilibrium form of a crystal should possess minimal total surface energy for a given volume, i.e.,

$$\delta_{\text{cryst}} = \Sigma_i \, \delta_i A_i = \text{minimum at constant volume.}$$

δ_i and A_i are the specific surface energy and specific area of the ith crystallographic face. Wulff proposed that the shape thus defined would be such that h_i the face normal vector from a point within the crystal would be proportional to δ_i or

$$h_i = \lambda \delta_i.$$

λ is a constant depending on the absolute size of the crystal. Strictly the theorem only

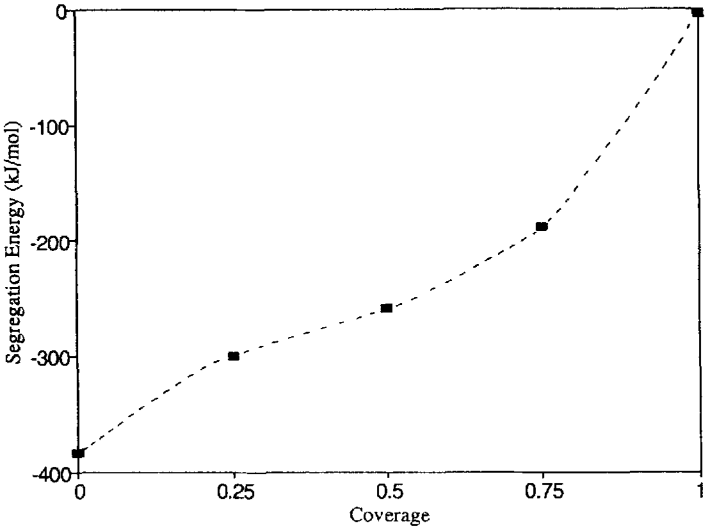


Figure 5 Variation of segregation energy of Calcium to the (1 1 0) surface of zirconia.

applies to small crystals as the theory assumes that the ions can diffuse readily from the face on which they adsorb initially.

In the presence of Mg^{2+} or Li^{+}, the defect surface energies were obtained by calculating and adding the heats of surface segregation per unit area to the corresponding energy of the free surface. The surface energies of calcite were calculated for both pure and defective surfaces at 0 K. After relaxation, energies for the pure surfaces were in the order of stability: {1 0 4} > {1 0 0} > {1 1 0} > (0 0 1), where the {1 0 4} face was the most stable and showed no surface reconstruction on relaxation. In the absence of additives, therefore, the {1 0 4} surface was predicted to dominate the calcite morphology (Figure 6a). The resulting rhombohedral habit is consistent with experimental observations of calcite crystallization.

On calculating the heat of segregation of Mg^{2+} to various calcite surfaces, magnesium clearly showed a marked energetic preference for the {1 0 0} face. The effect was such that the {1 0 0} faces became more stable than the {1 0 4} surfaces and the crystal morphology modified to a first-order prism capped with rhombohedral end faces (Figure 6b). This morphology is observed in experimental systems containing Mg^{2+}.

On substitution of Ca^{2+} ions with Li^{+}, the calculated defect surface energies showed that the polar (0 0 1) face became the most stable while all the other neutral faces were destabilised. The (0 0 1) face consists of alternating layers of calcium and carbonate, not unlike the rocksalt (1 1 1) surface discussed above. The surface is stabilised in pure calcite by terminating with the calcium surface in which only half the surface sites are occupied. On addition of lithium, the surface calcium is replaced and the surface is charge compensated by adding lithium to the unoccupied calcium sites. Thus the surface site density is restored. The predicted morphology was tabular comprising basal (0 0 1) and {1 0 4} side faces (Figure 6c). This is in complete agreement with recent experimental studies of calcite crystallization in the presence of Li^{+} ions [34].

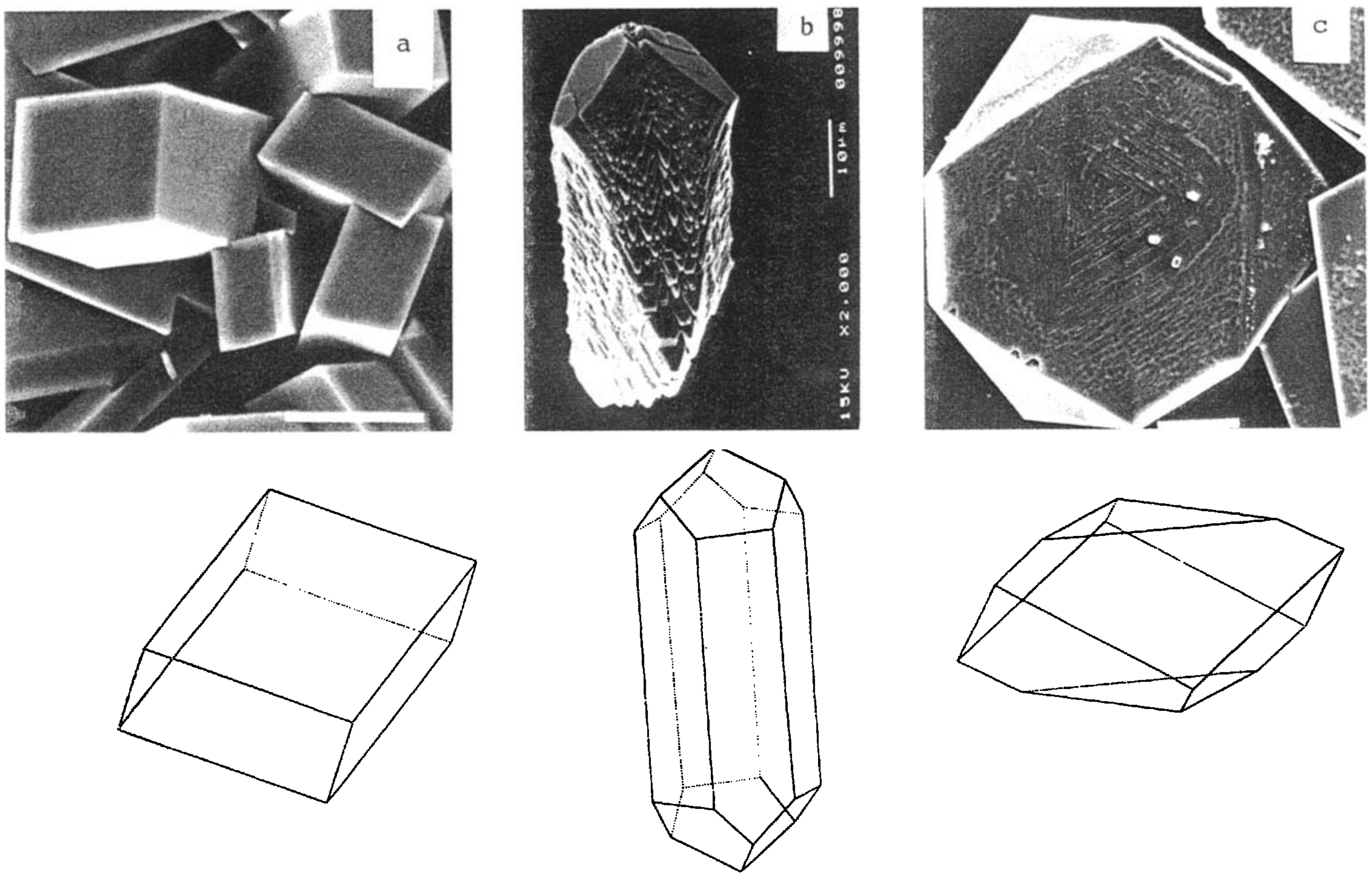


Figure 6 Observed (top) and predicted calcite crystal morphologies: (a) in the absence of additives; (b) in the presence of magnesium impurities; (c) in the presence of lithium impurities.

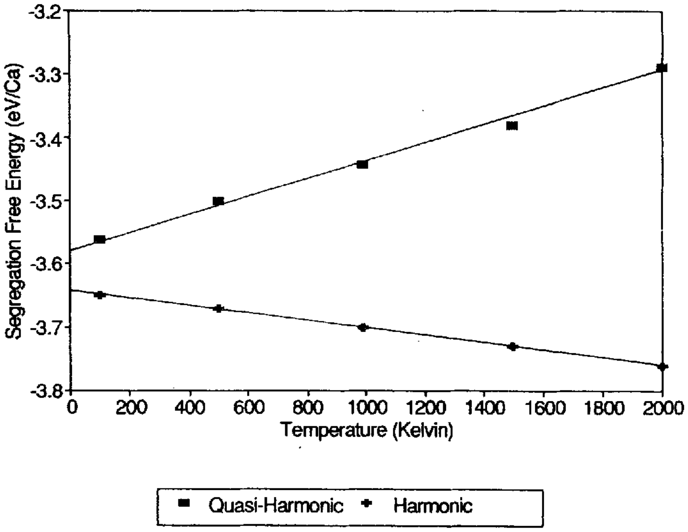


Figure 7 Calculated segregation free energy of (Ca'_{Al}–V_0–Ca'_{Al}) against temperature using a harmonic and quasi-harmonic approximation at 100% coverage.

4 SIMULATION OF THE THERMAL CONTRIBUTION TO SEGREGATION

4.1 Lattice Dynamics

We have used lattice dynamics to model calcium segregation to the basal plane of alumina. Static lattice simulations give a large segregation energy of calcium of about 2.6 eV. This strongly suggests that calcium should segregate. However, this is in contrast to experimental work by Baik and White [9] who found no evidence for calcium segregation to the basal plane of a single crystal doped with approximately 40 ppm of calcium. However, the absence of calcium may be attributed to kinetic factors [9, 35]. Another possible explanation is there is a large segregation entropy term which modifies the segregation free energy.

The change in the segregation free energy of calcium to the basal surface of α-Al_2O_3 with temperature, is given in Figure 7. The segregation free energy calculated by the harmonic approximation becomes more negative with increasing temperature. This corresponds to a positive entropy of segregation. Masri *et al.* [36] calculated a negative segregation entropy for Ca at the $\{001\}$ surface of MgO of -2.07×10^{-5} eV K^{-1} at 1000 K. The free energies of segregation, calculated using the quasi-harmonic approximation which includes lattice expansion, are also given in Figure 7. The free energy of segregation decreases with temperature. This is because as the lattice expands the potential energy component of the segregation free energy becomes less exothermic, hence the inclusion of thermal expansion results in a small but negative entropy term of -2.6×10^{-6} eV K^{-1}. However, the inclusion of the segregation entropy does not greatly modify the segregation free energy, and therefore we have to consider other possible reasons for the apparent lack of calcium at the basal plane.

The migration behaviour of ions in the sub-surface region will not necessarily be the same as in the bulk. In Figure 8 the defect Mg'_{Al} and Ca'_{Al} energies with depth are

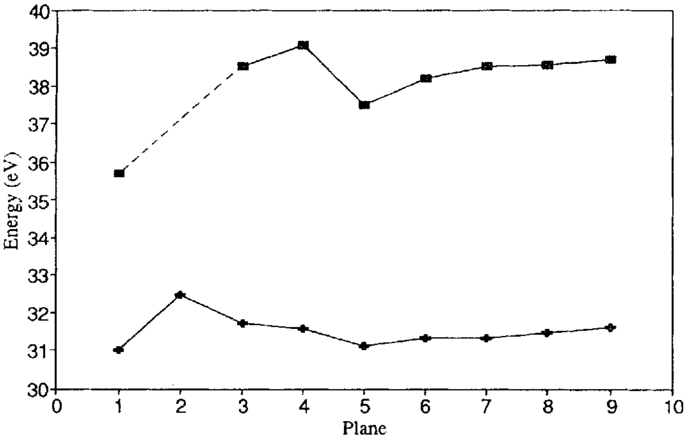


Figure 8 Variation of calcium and magnesium substitution energy from the basal surface of α-Al2O3.

given and show a maximum around the 3rd and 4th cation planes. The difference in the energy between the 4th and 5th planes are 0.50 eV for Mg'_{Al} and 1.40 eV for Ca'_{Al}. 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 are markedly different. It remains to be seen, however, whether such a subtle difference can be detected by experiment.

4.2 Molecular Dynamics

Molecular dynamics (MD) is a well-established technique for modelling the properties of solids. Our aim was to investigate the possibility of using this technique for simulating segregation. One of the major advantages over lattice dynamics is that the anharmonic contributions can be treated explicitly. We present preliminary work on the segregation of calcium and barium to the (1 0 0) surface of MgO.

The MD calculations performed in this work are at constant pressure [37], constant temperature [38] and include quantum corrections [39]. The surface was generated using a slab of 720 ions with a thickness of 10 layers and the surface comprising 6 × 6 unit cells. Initially all of the ions in the MD box were given a random velocity. Therefore, scaling of these velocities to the temperature of the simulation was required. The amount of scaling performed was dependent on the temperature fluctuation. We found that surfaces needed more scaling than bulk calculations probably due to the surface having greater freedom of movement causing a greater fluctuation of the temperature. Generally scaling of not less than 6×10^{-12} s (6000 time steps) was used.

Figures 9(a, b) show the trajectories of the barium and calcium ions for 6000 time steps at a simulation temperature of 600 K. The underlying MgO lattice was also in motion but for clarity we show only the time evolution of the impurity ions. The

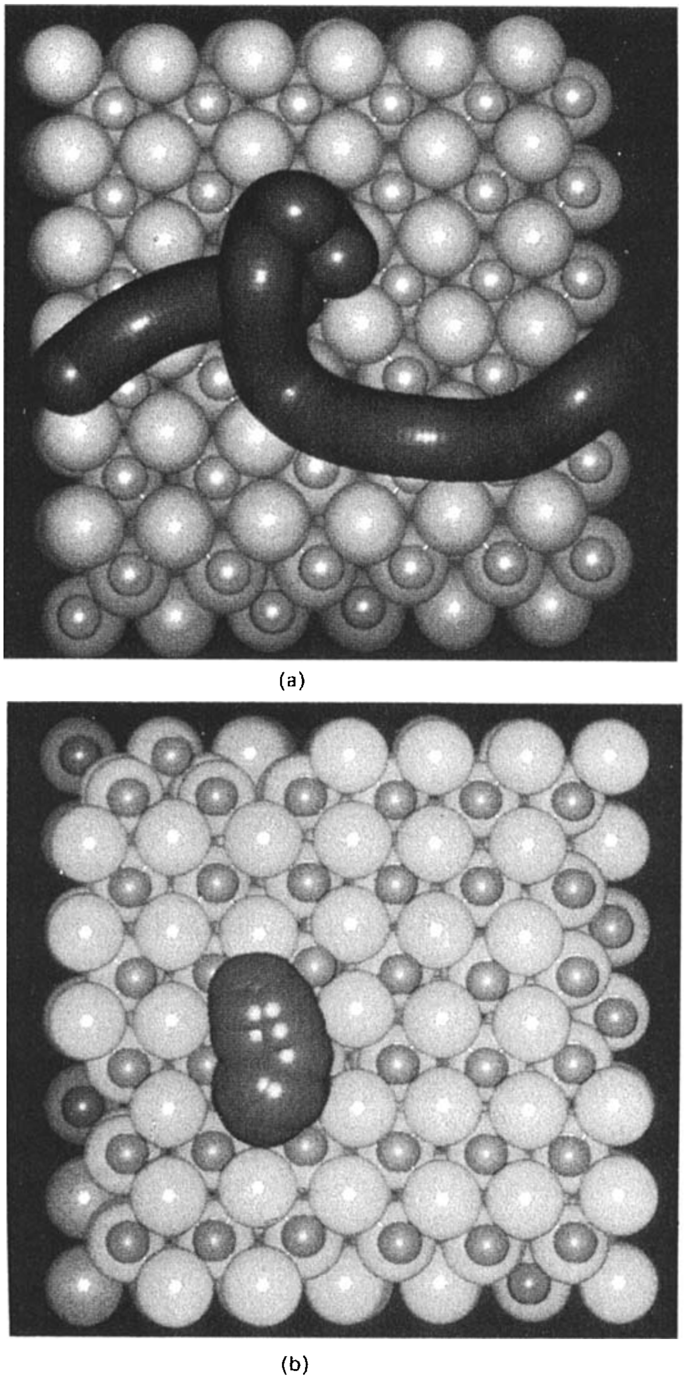


Figure 9 Trajectories of (a) barium and (b) calcium ions on the (1 0 0) surface of MgO. (see colour plates)

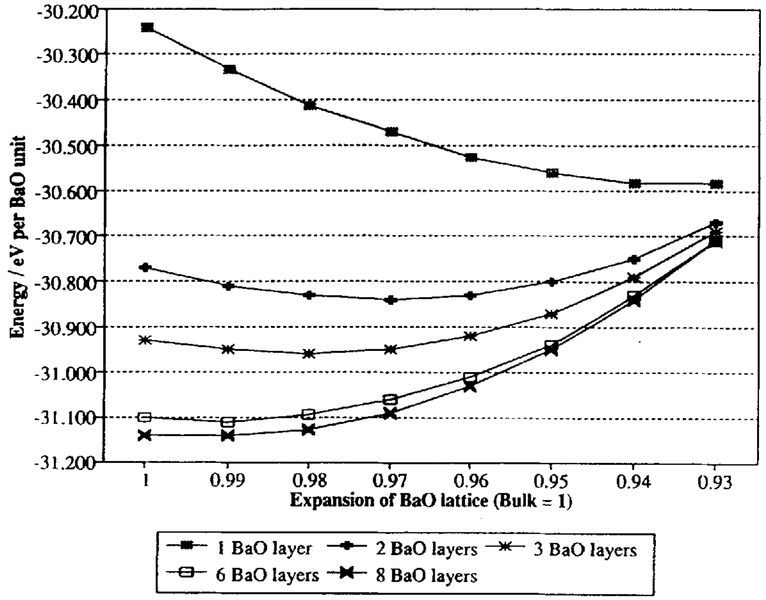
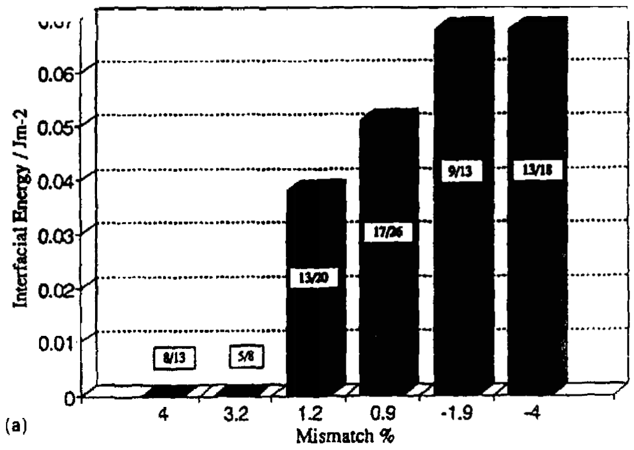


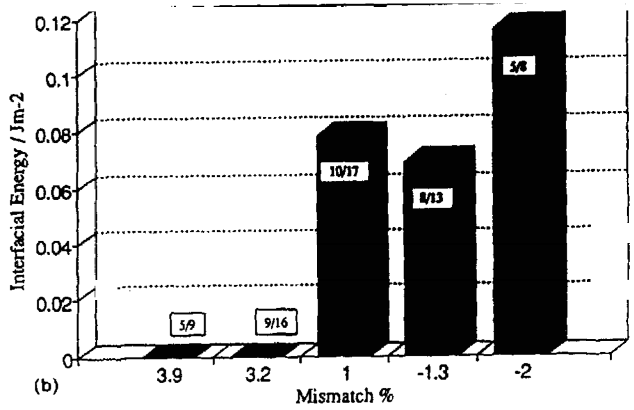
Figure 10 Variation of BaO energy against lattice parameter for 1, 2, 3, 6 and 8 hypothetical BaO layers in vacuum.

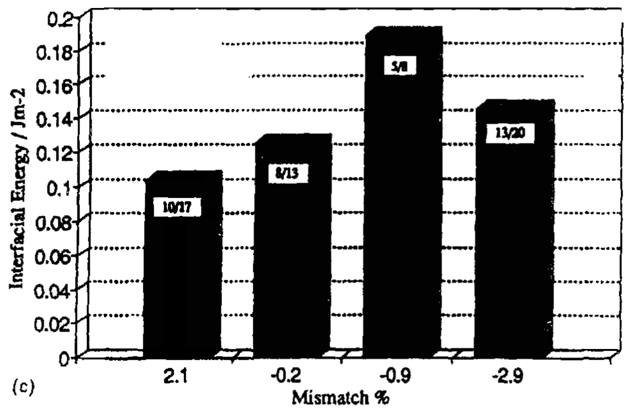
calcium ion shown in Figure 9(b) did not move appreciably from its starting position, and simply vibrated about the magnesium vacancy as expected. In contrast the barium ion unexpectedly moved a considerable distance across the surface. Static simulations showed an unusually large relaxation away from the surface but clearly could not show barium's comparatively high mobility about the magnesium vacancy. Thus from these results we may infer that molecular dynamics may prove a valuable technique for modelling segregation when considering segregation of individual ions where the mismatch between the size of the host and impurity ions is great and hence the impurity may not be tightly bound to the surface.

5 SIMULATION OF HETEROEPITAXIAL INTERFACES

Once the surface has at least one monolayer of impurity then the surface structure starts to reflect the impurity oxide and hence we must consider the epitaxial relationships between the two oxides. Most of the work on interfaces has been concerned with grain boundaries [40]. However the simulation techniques can be equally applied to include interfaces between dissimilar materials. The BaO/MgO interface has been investigated by Cotter, Campbell, CaO, Egdell and Mackrodt [41, 42] who consider idealised BaO layers whose 2D lattice parameters conform to the relationship $a_0(\text{BaO}) = \sqrt{2}a_0(\text{MgO})$. This however constrains the BaO overlayers to accommodate a 7% expansion ($a_0(\text{BaO}) = 5.53$ Å, $a_0(\text{MgO}) = 4.20$ Å) of the BaO lattice. The strain energy on forming such as mismatch starts to become prohibitive. Thus we sought BaO overlayers with a lower mismatch using a near coincident site lattice (NCSL) approach [43, 44] for BaO layers on an MgO (1 0 0) substrate.







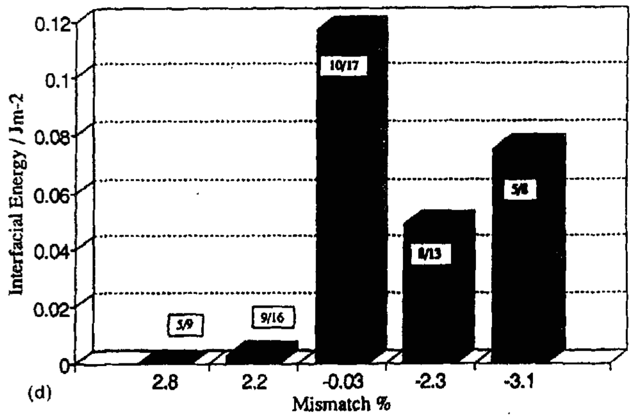


Figure 11a Stabilities of various NCSL's for BaO monolayer coverage on an MgO (1 0 0) substrate. The annotations on the graphs indicate the near coincident site lattice following the notation of reference [43].

Figure 11b Stabilities of various NCSL's for 2 BaO layers on an MgO(1 0 0) substrate.

Figure 11c Stabilities of various NCSL's for 3 BaO layers on an MgO(1 0 0) substrate.

Figure 11d Stabilities of various NCSL's for 6 BaO layers on an MgO(1 0 0) substrate.

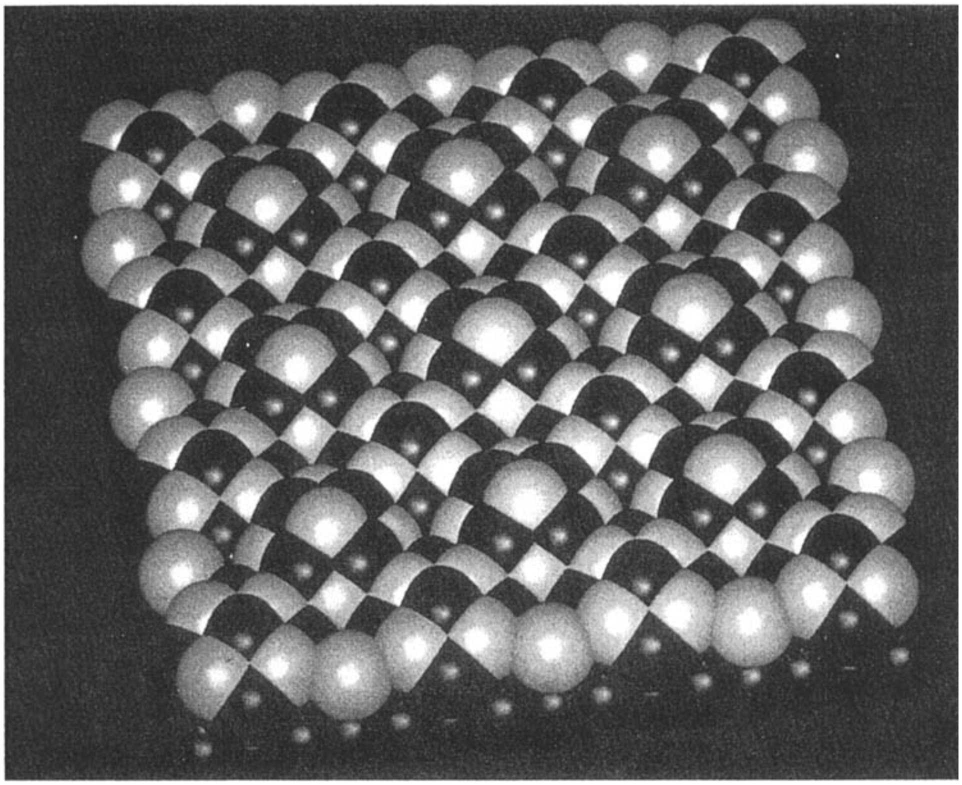


Figure 12 σ 9/13 interface (BaO monolayer) after relaxation. (see colour plates)

On simulating a hypothetical BaO monolayer in a vacuum, the 2D lattice parameter was found to be lower than bulk BaO. Figure 10 shows the calculated energies of 1, 2, 3, 6 and 8 BaO layers against lattice parameter. From Figure 10 one can see the optimum lattice parameter for a BaO monolayer is 3.91 Å or a 7% contraction compared to the bulk value. Figures 11(a–d) show the relative stabilities of 1, 2, 3 and 6 BaO layers respectively on an MgO substrate as a function of mismatch for the various near coincident site lattices. The stabilities of the near coincident site lattices with mismatch of up to ± 4% were calculated. The stabilities of the various NCSL's are given in J m^{-2} where the energy required to remove the BaO layers from the MgO surface:

$$\Delta E = [E_{\text{interface}} - (E_{\text{BaO}} + E_{\text{MgO}})]/(2 \times \text{area}).$$

The figure shows that the stabilities of the various interfaces can be predicted on a purely geometrical basis as considered by earlier workers [45–47] in comparison to experiment. Figure 12 shows the σ 9/13 BaO//MgO interface with a BaO monolayer on the MgO substrate. The figure illustrates the extent of relaxation of the interface required to reduce the mismatch and resulting strain in the system.

6 CONCLUSIONS

This paper has highlighted the application of computer simulation methods to the study of impurity segregation to oxide surfaces. The development of efficient computer simulation codes over the last twenty years has provided, and will continue to provide a notable complement to experiment in determining the properties and characteristics of a wide range of materials. An important recent development has been the explicit inclusion of temperature using lattice and molecular dynamics. We envisage that in the near future all simulation studies will include these techniques, particularly as the availability of computer resources increases. Another important area will be the study of the oxide-metal interface which will allow these methods to be applied more widely to important areas of corrosion, catalysis and even composites.

Acknowledgements

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