

# Monte Carlo simulation of segregation in ceramic thin films

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A Monte Carlo exchange technique is used to study segregation in thin ceramic films with application to MgO/MnO. The approach is *not* restricted to the dilute limit. Surface concentrations as a function of temperature and film composition are determined directly from the simulations. For all compositions studied ( $\text{Mn}_\chi\text{Mg}_{1-\chi}\text{O}$ ,  $0 \leq \chi \leq 1$ ) the (001) surface is  $\text{Mn}^{2+}$  rich; the occupancy of sites by  $\text{Mn}^{2+}$  decreases rapidly with depth. The ratio of the number of  $\text{Mn}^{2+}$  to  $\text{Mg}^{2+}$  ions at the surface decreases as a function of temperature. The calculated enthalpies of segregation of  $\text{Mn}^{2+}$  for the thin film are strongly dependent on the total  $\text{Mn}^{2+}$  concentration at small  $\text{Mn}^{2+}$  concentrations, with the enthalpy of segregation varying by a factor of two with surface coverage.

## Introduction

The last decade has seen the emergence of tremendous interest in the properties of thin films, stimulated by their commercial potential in a wide range of products including catalysts, optoelectric devices and magnetic storage devices. Key to tailoring both the mechanical and the chemical behaviour of the films is doping with impurity cations or anions. Nevertheless relatively little effort has been devoted to the study of the thermodynamic properties of non-stoichiometric oxide thin films.<sup>1</sup> A particular motivation for their study is the experimental data now available. Substantial differences from bulk behaviour are expected due to different elastic properties and the influence of the substrate.

Somewhat surprisingly, atomistic simulations of oxide surfaces have largely concentrated on the growth of thin films<sup>2</sup> while recent simulations of thermodynamic properties of oxide mixtures and solid solutions have tended to be directed more towards disorder and phase equilibria in the bulk.<sup>3,4</sup> The primary aim of this paper is to extend these simulations to thin multilayered oxide films.

A number of atomistic simulation studies have examined the enthalpy of segregation of trace elements both in binary oxides<sup>5–8</sup> and in more complex oxides<sup>9</sup> such as  $\text{La}_2\text{CuO}_4/\text{Nd}_2\text{CuO}_4$ . These suggest coverage-independent enthalpies of segregation are a crude approximation, except at very low coverages. However these studies determined enthalpies of segregation *via* energy minimisation only in the *static limit* (*i.e.*, at 0 K and neglecting lattice vibrations) of small ordered surface supercells in which a periodic 'superlattice' of impurity ions was introduced at the surface plane. Enthalpies of segregation were calculated from the energies of these structures, together with the energy of the pure surface and *point* defect energies associated with isolated impurity ions in the bulk. These calculations thus apply only to crystals containing *low* levels of bulk impurity, *i.e.*, to the dilute limit in the bulk. A single surface-layer ordering for each coverage has generally been assumed. Another technique for calculating surface segregation in cubic oxides, presented in ref. 10, is based on an effective atom method (a variant of mean-field treatment), in

which interactions between neighbouring sites depend on the average concentration of both species in the system. Previously,<sup>11</sup> we have shown that the effective atom method can give enthalpies of mixing in bulk oxide mixtures far in excess of their experimental value because of poor treatment of local structural relaxation or clustering; we expect the same to be true for the surfaces.

The surface of a crystal always provides a different elastic and electrostatic environment to that of the bulk, and so there is a free energy difference between the energy associated with any defect, including an impurity, in the bulk and at the surface. Impurities are thus driven to or from the surface. A convenient description of this is given by a segregation isotherm. This is frequently assumed to be of the Langmuir (Langmuir–McLean) form<sup>5</sup> such that for a system containing two species, A and B, and the bulk concentration of species A,  $c$ , the surface concentration  $c_s$  of species A varies with temperature,  $T$ , according to

$$\frac{c_s}{1 - c_s} = \frac{c}{1 - c} \exp\left(-\frac{\Delta H^{\text{seg}}}{k_B T}\right) \quad (1)$$

$\Delta H^{\text{seg}}$  is a temperature and coverage independent enthalpy of segregation.<sup>12</sup> Surface and bulk atomic ratios (A : B),  $x_s$  and  $x$ , are given by  $c_s/(1 - c_s)$  and  $c/(1 - c)$ , respectively. Experimental enthalpies of segregation are conventionally extracted from plots of the logarithm of the surface atomic ratio *versus*  $1/T$ .

In this paper we report results of Monte Carlo simulations to determine the structure and thermodynamic properties of thin films comprised of a mixture of ionic materials, with initial application to a range of MgO(100)–MnO(100) thin films of varying MnO composition, all supported on an MgO(100) substrate. We have previously studied the thermodynamic behaviour of bulk MgO–MnO in detail using both Monte Carlo and direct free-energy minimization.<sup>13,14</sup> For our pilot study this is again an appropriate choice of prototype system due to the magnitude of the size difference between the larger  $\text{Mn}^{2+}$  and the smaller  $\text{Mg}^{2+}$  ion (Shannon and Prewitt ionic radii in six-fold coordination are 0.83 Å and 0.72 Å, respectively). This is neither so small that an essentially ideal solution is formed at all compositions and temperatures nor so large that there is always complete segregation by one cation under all conditions of interest. Our calculations explicitly include the

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effects of temperature, full surface relaxation and are not restricted to the dilute limit. Much larger surface supercells are used than in previous work,<sup>6–10</sup> which were typically either the primitive cell or a cell with a surface area two or four times that of the primitive, thus restricting these studies to a very few highly periodic surface arrangements. No assumptions are made as to the positions of the impurity/dopant atoms in the surface supercell corresponding to a particular coverage. Surface concentrations as a function of temperature are determined *directly* from the simulations without assuming any particular isotherm and we are able to examine straightforwardly order-disorder at the surface of the film both as a function of both film composition and of temperature. We discuss later the applicability of the Langmuir isotherm (eqn (1)) to the thin films studied in this paper.

## Methodology

The basis for all our calculations is the well-known Monte Carlo (MC) method modified for non-stoichiometric surfaces as described below. The surfaces are assumed to be planar, semi-infinite and periodic in two dimensions.<sup>15</sup> We have neglected segregation to kinks, steps or dislocations which real crystals undoubtedly possess. All thin film calculations were undertaken on 4MnO–MgO layers comprising 576 ions ( $12 \times 12 \times 4$ ), on a MgO substrate of 2880 ions ( $12 \times 12 \times 20$ ). The lattice parameters for the MgO substrate were held fixed at those obtained in a previous bulk MC simulation using the *NPT* ensemble at the appropriate temperature.

All calculations are based on an ionic model using two-body potentials to represent short-range forces.<sup>16</sup> The total long-range electrostatic energy is evaluated using the Parry summation.<sup>17</sup> The particular set of non-Coulombic interaction potentials employed is that of Lewis and Catlow first introduced in their study of the parent oxides,<sup>18</sup> and used here with a cut-off of 10 Å. No mean-field approximations are made. We have used this previously in studies of bulk MnO–MgO solid solutions and the resulting phase diagram, calculated<sup>14</sup> using exchange Monte Carlo and the semi-grand canonical ensemble is in good agreement with experiment with a calculated consolute temperature of  $\approx 1150$  K (experimental value  $\approx 1100$  K).<sup>19</sup>

In simulations of non-stoichiometric ionic materials and solid solutions using ‘standard’ MC, kinetic barriers prevent sampling the whole of the configurational space since almost always only one cation arrangement, the initial configuration, is sampled. We have described elsewhere<sup>3</sup> Monte Carlo exchange (MCX) simulations in which *both* the atomic configuration *and* the atomic coordinates of all the atoms are changed. Each calculation consisted of an initial equilibration of  $1.5 \times 10^4$  cycles followed by four simulations that combined both equilibration and production runs. The surface concentration presented is an average of these four production runs. The equilibration and production parts of the simulation involve  $5 \times 10^3$  and  $10^4$  cycles, respectively. A single cycle allows for both the displacement of all the ions and an exchange of ionic configuration. Allowing random moves of randomly selected atoms takes account of both surface relaxation and vibrational effects. To determine whether the change is accepted or rejected, the usual Metropolis algorithm is applied.<sup>20</sup> The maximum change in the atomic displacement for each ionic species has a variable  $r_{\max}$ , its magnitude is adjusted automatically during the simulation to maintain an acceptance/rejection ratio of approximately 0.5 ( $r_{\max}$  is approximately 0.1 at 1000 K). Changes in ionic configuration are attempted by exchanging the position of a  $\text{Mn}^{2+}$  ion and a  $\text{Mg}^{2+}$  ion, both chosen at random. Again, the Metropolis algorithm is used to accept or reject any attempted exchange. In order to represent the deposition of a film on an inert substrate, only the atoms within the four layers of the thin film were allowed to intermix. This allows us to discriminate

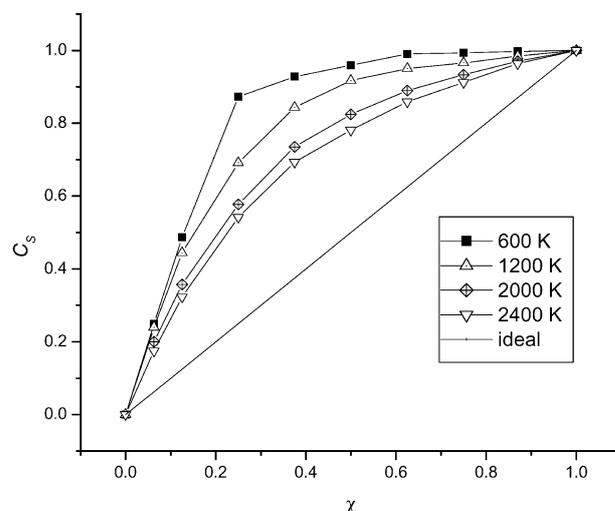
between the effects of the substrate on the overlying film and processes operating within the film. The number of atoms in each layer of the film is monitored as the simulation proceeds, and thus  $x_s$  is an average of values obtained during the simulation.

## Results and discussion

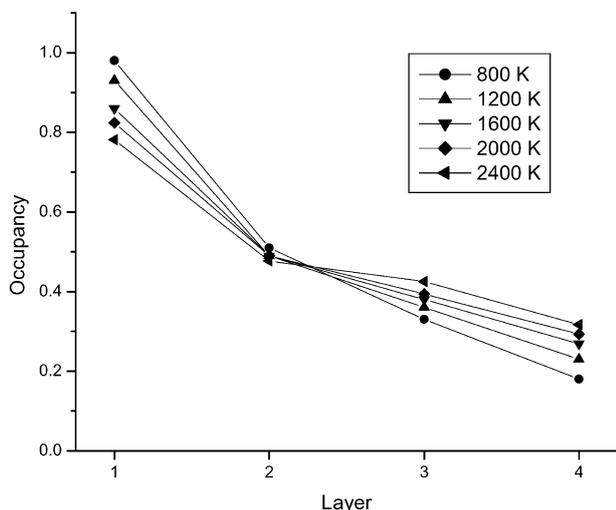
Fig. 1 displays the fractional surface coverage of  $\text{Mn}^{2+}$  ions at the 001 surface as a function of the overall mole fraction  $\chi$  of  $\text{Mn}^{2+}$  present in the film over a range of temperatures. Due to the small thickness of the films, it is not straightforward to define a so-called ‘bulk’ composition and so we have plotted quantities of interest as a function of the total mole fraction of  $\text{Mn}^{2+}$ . The straight line in Fig. 1 shows the behaviour expected if there were no segregation to or from the surface. The surface concentration of  $\text{Mn}^{2+}$  increases sharply as a function of overall concentration, with enrichment of the surface layer by the larger  $\text{Mn}^{2+}$  ion at all temperatures for *all* compositions. There are, in general, three main driving forces for surface segregation: (i) the difference in size between the two ions, leading to a difference in strain energy in the bulk or interior and at the surface, modified here by the presence of the substrate; (ii) the tendency to phase separate in the bulk and (iii) the difference in (relaxed) surface energies. The last of these, (iii), will always favour segregation by the *larger* ion to the surface, even for films rich in  $\text{Mn}^{2+}$  where the first term, (i), would favour segregation of the smaller  $\text{Mg}^{2+}$  to the surface. The literature on oxides has tended to emphasise (i) and often ignore (iii).

At other than the highest  $\text{Mn}^{2+}$  concentrations, the surface concentration varies strongly with temperature, as also clearly shown in Fig. 1. There is a marked decrease in the surface enrichment by  $\text{Mn}^{2+}$  with increasing temperature, as the entropic contribution drives the  $\text{Mn}^{2+}$  back into the interior of the film. For example, for an overall 20%  $\text{Mn}^{2+}$  composition ( $\chi = 0.2$ ), the fractional surface coverage decreases from  $\approx 0.7$  to  $\approx 0.4$  as the temperature increases from 600 K to 2400 K.

The ratio  $\text{Mn}^{2+} : \text{Mg}^{2+}$  decreases rapidly as a function of depth, as shown in Fig. 2 for an overall 50 : 50 composition. Only in the outermost two layers does the  $\text{Mn}^{2+}$  occupancy exceed 50%. As the temperature increases, consistent with Fig. 1, intermixing of all the layers increases with the occupancy of the lower two layers by  $\text{Mn}^{2+}$  increasing significantly. We do not see any oscillatory subsurface behaviour as noted by Battaile



**Fig. 1** The fractional surface coverage of  $\text{Mn}^{2+}$  ions plotted as a function of the overall  $\text{Mn}^{2+}$  mole fraction,  $\chi$ , in the thin film at different temperatures. Curves for 800 K and 1600 K have been omitted to aid clarity of the figure but follow the trends of the other temperatures.



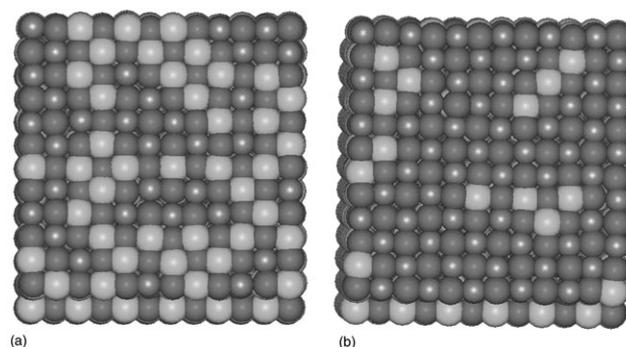
**Fig. 2** The fractional occupancy of  $\text{Mn}^{2+}$  ions in the four layers of the film as a function of depth and temperature. The example shown is for a 50 : 50 mixture. Layer 1 is at the surface and layer 4 directly above the substrate.

*et al.* (ref. 10, Fig. 2) in their mean-field simulation studies of similar systems such as  $\text{Ni}_{0.3}\text{Co}_{0.7}\text{O}$  and  $\text{Fe}_{0.1}\text{Mn}_{0.9}\text{O}$ .

In Fig. 3 we display representative snapshots of the surface structure at 800 K for total  $\text{Mn}^{2+}$  mole fractions  $\chi$  in the film of 0.125 (Fig. 3a) and 0.25 (Fig. 3b). The surface structure for  $\chi = 0.125$  is dominated by the formation of islands of  $\text{Mg}^{2+}$  ions. These islands are separated by lines of  $\text{Mn}^{2+}$  ions, which are aligned along the [110] direction (Fig. 3a). In contrast, when  $\chi = 0.25$  the surface occupancy by  $\text{Mn}^{2+}$  is 0.87 and the remaining  $\text{Mg}^{2+}$  ions tend to form chains along the [110] direction (Fig. 3b). For overall compositions with  $\chi$  greater than 0.375 the surface cations are almost all  $\text{Mn}^{2+}$ .

We now compare these results with those at a much higher temperature, 2400 K (Fig. 4). For  $\chi = 0.0625$  the  $\text{Mn}^{2+}$  ions are principally found as isolated ions at this elevated temperature (Fig. 4a). When the total Mn mole fraction is 0.25, the surface coverage of  $\text{Mn}^{2+}$  is now 0.54, and in contrast to the 800 K results, the  $\text{Mg}^{2+}$  ions at the surface form islands, with the  $\text{Mn}^{2+}$  forming chains along the [110] direction (Fig. 4b). When the overall mole fraction of  $\text{Mn}^{2+}$  is 0.5, the coverage at the surface is 0.78 and the situation is reversed with  $\text{Mn}^{2+}$  ions once more forming the background and  $\text{Mg}^{2+}$  ions in [110] chains (Fig. 4c).

We define the ‘interior’ of the film as comprising all the layers except the outermost. Fig. 5 plots for each film the logarithm of the ratio of the surface atomic ratio to the atomic ratio in the interior (*i.e.*  $\ln(x_s/x)$ ) against the reciprocal temperature. The linear plots for a given total film composition (fixed  $\chi$ ) suggests that, despite the somewhat non-uniform distribution of  $\text{Mn}^{2+}$  over the inner layers of the film shown

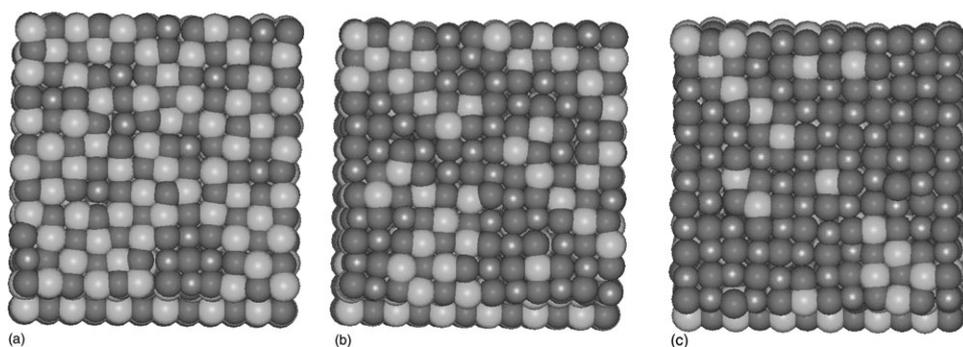


**Fig. 3** Snapshots of the surface structure at 800 K for total Mn mole fractions (a)  $\chi = 0.125$  and (b)  $\chi = 0.25$ . Red, green and purple in the colour version of the Figure available online represent oxygen, magnesium and manganese ions, respectively.

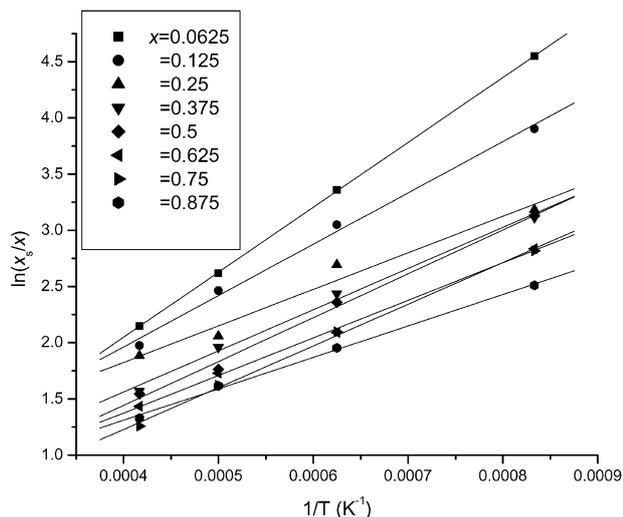
in Fig. 2, the overall segregation behaviour *in each film* is still given to a good approximation by an equation of Langmuir type (eqn (1)), where  $c$  on the right-hand side of this equation is no longer the bulk concentration but the mean concentration in the interior of the film.

Langmuir-like behaviour here is in contrast to experimental and theoretical results for Ca segregation at the (001) surface of  $\text{Ca}_x\text{Mg}_{1-x}\text{O}$ , where a ‘‘tailing-off’’ at low temperatures has been observed and attributed to non-equilibrium coverages<sup>21,22</sup> and the variation of the segregation enthalpy with coverage.<sup>5,6</sup> We have determined, for each composition, a value of the *effective* heat of segregation,  $\Delta H^{\text{seg}}$ , which we define as that obtained from the slope of a straight line fitted to the data points for a given composition in Fig. 5. The values of  $\Delta H^{\text{seg}}$  are displayed in Fig. 6 as a function of the total atomic  $\text{Mn}^{2+}$  ratio. This graph demonstrates that the value of  $\Delta H^{\text{seg}}$  varies strongly with the total composition for small  $\text{Mn}^{2+}$  concentrations.  $\Delta H^{\text{seg}}$  increases from  $-48$  to  $-27$   $\text{kJ mol}^{-1}$  (*i.e.* the driving force for segregation decreases) in the range  $\chi = 0.0625$  to 0.25. The variation at higher values of  $\chi$  is smaller and  $\Delta H^{\text{seg}} \approx 30$   $\text{kJ mol}^{-1}$  for  $\chi > \approx 0.2$ . There is some hint of a further decrease in the magnitude of  $\Delta H^{\text{seg}}$  at the highest Mn concentrations, where the surface coverage is close to a complete monolayer. Overall the enthalpy of segregation varies by a factor of approximately two with surface coverage.

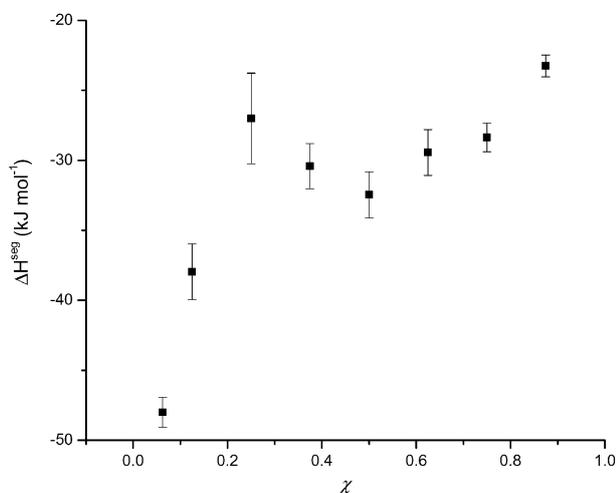
For comparison, values of  $\Delta H^{\text{seg}}$  of  $-44.4$  to  $-80$   $\text{kJ mol}^{-1}$  have been determined for  $\text{Ca}_x\text{Mg}_{1-x}\text{O}$  using a number of experimental methods<sup>21,22</sup> for bulk concentrations between 180 and 220 ppm. In addition, calculated values<sup>5</sup> for  $\text{Ca}_x\text{Mg}_{1-x}\text{O}$  lie between  $-105$   $\text{kJ mol}^{-1}$  for point defects (dilute limits in both the bulk and at the surface) and  $-40$   $\text{kJ mol}^{-1}$  for a fractional surface coverage of 1.0. These calculations were on dilute systems in contrast to our present calculations. Our results for  $\Delta H^{\text{seg}}$  of approximately  $-30$   $\text{kJ mol}^{-1}$  for a smaller impurity cation ( $\text{Mn}^{2+}$  as opposed to  $\text{Ca}^{2+}$ ) are thus not unreasonable.



**Fig. 4** Snapshots of the surface structure at 2400 K for total Mn mole fractions (a)  $\chi = 0.0625$ , (b)  $\chi = 0.25$ , and (c)  $\chi = 0.5$ . Red, green and purple in the colour version of the Figure available online represent oxygen, magnesium and manganese ions, respectively.



**Fig. 5** Logarithm of the ratio of the surface atomic ratio of  $\text{Mn}^{2+}$  to the atomic ratio in the interior of the film (i.e.  $\ln(x_s/x)$ ) as a function of reciprocal temperature.



**Fig. 6** Calculated values of  $\Delta H^{\text{seg}}$  ( $\text{kJ mol}^{-1}$ ) as a function of the total  $\text{Mn}^{2+}$  mole fraction  $\chi$ . The error bars are obtained from the linear fits to the data.

Thus at *all* compositions  $\text{Mn}^{2+}$  segregates to the surface, consistent with the smaller  $\{001\}$  surface energy of  $\text{MnO}$  relative to that of  $\text{MgO}$ . If the enthalpy of segregation of  $\text{Mn}^{2+}$  was both temperature and coverage independent, then all the points in Fig. 5 would lie on the same straight line; the form of the actual plot is consistent with a marked variation with coverage. The enthalpy of segregation for the lowest total concentrations of  $\text{Mn}^{2+}$  is larger than at higher concentrations, reflecting the larger release of strain accompanying the segregation at low  $\text{Mn}^{2+}$  concentrations which leaves the interior of the film largely  $\text{Mn}^{2+}$ -free. Close to complete surface coverages of  $\text{Mn}^{2+}$  the results suggest a further reduction in the magnitude of the enthalpy of segregation, possibly reflecting a larger strain term associated with very small concentrations of  $\text{Mg}^{2+}$  in the interior. Increasing the temperature leads to larger  $\text{Mn}^{2+}$  concentrations in the interior consistent with configurational entropy arguments.

## Conclusions

We have employed the Monte Carlo Exchange technique to calculate *directly* the surface concentration of  $\text{MnO}/\text{MgO}$  thin films on a  $\text{MgO}$  substrate as a function of temperature and bulk composition. At *all* concentrations the surface is  $\text{Mn}$ -rich; the lower surface energy of  $\text{MnO}$  dominates the energetics even

when the film is  $\text{Mn}$ -rich and segregation of  $\text{Mg}$  would reduce the strain energy in the interior of the film. The concentration of  $\text{Mn}^{2+}$  ions decreases rapidly with depth. At low temperatures and low concentrations  $\text{Mn}^{2+}$  ions form chains along the  $[110]$  direction in a  $\text{Mg}^{2+}$  matrix, whilst at higher concentrations the reverse is observed. At high temperatures the  $\text{Mn}^{2+}$  ions are more dispersed throughout the film. For a given film concentration, a Langmuir isotherm of the form of eqn (1) is a useful approximation, even though Langmuir-McLean theory is not valid (*cf.* section II in ref. 5). We stress the effective enthalpy of segregation is strongly dependent on the total  $\text{Mn}^{2+}$  mole fraction. An isotherm of the form of eqn (1) also neglects the less-marked segregation to layers other than the outermost (but which is evident from Fig. 2), and the non-ideality of the bulk solid solution. There thus remains considerable scope for deriving suitable non-Langmuir isotherms (*cf.* ref. 5) for segregation in solid solutions of oxides and including the segregation to the layers immediately under the surface layer. Our Monte Carlo method is general and we shall apply this in future work to more complex interfaces of technological importance.

## References

- 1 W. C. Mackrodt, C. Noguera and N. L. Allan, *Faraday Discuss.*, 1999, **114**, 105.
- 2 (a) D. C. Sayle and R. L. Johnston, *Curr. Opin. Solid State Mater. Sci.*, 2003, **216**, 3 and references therein; (b) See also, for example, D. J. Harris, J. H. Harding, M. Lavrentiev, N. L. Allan and J. A. Purton, *J. Phys.: Condens. Matter*, 2004, **16**, L187.
- 3 J. A. Purton, G. D. Barrera, M. B. Taylor, N. L. Allan and J. D. Blundy, *J. Phys. Chem. B*, 1998, **102**, 5202.
- 4 M. Y. Lavrentiev, N. L. Allan, G. D. Barrera and J. A. Purton, *J. Phys. Chem. B*, 2001, **105**, 3594.
- 5 W. C. Mackrodt and P. W. Tasker, *J. Am. Ceram. Soc.*, 1989, **72**, 1576.
- 6 P. W. Tasker, E. A. Colbourn and W. C. Mackrodt, *J. Am. Ceram. Soc.*, 1985, **68**, 74.
- 7 W. C. Mackrodt and P. W. Tasker, *Mater. Res. Soc. Symp. Proc.*, 1986, **60**, 291.
- 8 M. J. Davies, P. Kenway, P. J. Lawrence, S. C. Parker, W. C. Mackrodt and P. W. Tasker, *J. Chem. Soc., Faraday Trans 2*, 1989, **85**, 555.
- 9 P. R. Kenway, S. C. Parker and W. C. Mackrodt, *Surf. Sci.*, 1995, **326**, 301.
- 10 C. C. Battaile, R. Najafabadi and D. J. Srolovitz, *J. Am. Ceram. Soc.*, 1995, **78**, 3195. Unfortunately, there is a disagreement between the caption to their Fig. 1 and Fig. 1 itself in this reference, which makes further comparison and analysis with their results impractical.
- 11 J. A. Purton, G. Barrera, M. B. Taylor, N. L. Allan and J. D. Blundy, *Chem. Commun.*, 1998, 627.
- 12 G. Tréglia, B. Legrand, F. Ducastelle, A. Saúl, C. Gallis, I. Meunier, C. Mottet and A. Senhaji, *Comput. Mater. Sci.*, 1999, **15**, 196.
- 13 M. F. Wilkes, P. Hayden and A. K. Bhattacharya, *Appl. Surf. Sci.*, 2003, **206**, 12.
- 14 (a) N. L. Allan, G. D. Barrera, R. M. Fracchia, M. Yu. Lavrentiev, M. B. Taylor, I. T. Todorov and J. A. Purton, *Phys. Rev. B*, 2001, **63**, 094203; (b) I. T. Todorov, N. L. Allan, M. Yu. Lavrentiev, C. L. Freeman, C. E. Mohn and J. A. Purton, *J. Phys.: Condens. Matter*, 2004, **16**, S2751.
- 15 P. W. Tasker, *Harwell Lab. Rep.*, 1978, **R9130**.
- 16 *Computer Simulation of Solids*, ed. C. R. A. Catlow and W. C. Mackrodt, Springer-Verlag, Berlin, 1982, ch. 1, pp. 3–20.
- 17 (a) D. Parry, *Surf. Sci.*, 1975, **49**, 433; (b) D. Parry, *Surf. Sci.*, 1976, **54**, 195.
- 18 G. V. Lewis and C. R. A. Catlow, *J. Phys. C: Solid State Phys.*, 1985, **18**, 1149.
- 19 B. J. Wood, R. T. Hackler and D. P. Dobson, *Contrib. Mineral. Petrol.*, 1994, **115**, 438.
- 20 N. I. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller and E. Teller, *J. Chem. Phys.*, 1953, **21**, 1087.
- 21 R. C. McCune and P. Wynblatt, *J. Am. Ceram. Soc.*, 1983, **66**, 111.
- 22 R. C. McCune and R. C. Ku, in *Advances in Ceramics*, ed. W. D. Kingery, American Ceramic Society, Columbus, OH, 1984, **vol. 10**, pp. 217–237.