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Segregation Isotherms at the Surfaces of Oxides

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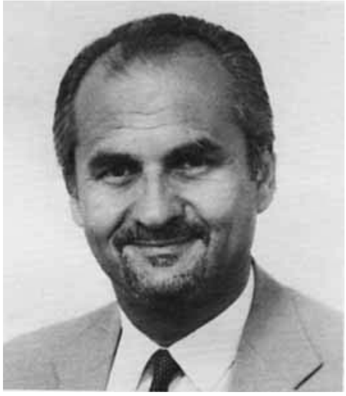

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A non-Arrhenius segregation isotherm is derived which includes the change in the heat of segregation with surface coverage due to impurity–impurity interactions. It is shown that a linear dependence of log (x_s) on the reciprocal temperature, where x_s is the surface atomic ratio, can derive either from a constant heat of segregation, i.e., Arrhenius behavior, or from a heat of segregation that varies as x_s^{-1}. This isotherm is then used to calculate the equilibrium surface coverages of Ca at the {001} surface of MgO, Mg at the {0001} surface of α-Al_2O_3, Y at the $\{10\bar{1}2\}$ and $\{1\bar{1}20\}$ surfaces of α-Al_2O_3, and Na at the {111} and {110} surfaces of Li_2O from the calculated heats of segregation. Where possible, comparisons are made with experiment. The more useful operational definition of the heat of segregation, namely, that derived from the measured coverage or that defined atomistically and obtained by calculation, is discussed. [Key words: oxides, isotherms, surface, magnesia, oxygen.]

I. Introduction

THE emergence of surface-sensitive analytic techniques such as Auger electron spectroscopy and low-energy ion scattering has led to renewed interest in the segregation of cation impurities at the surfaces of ceramic oxides.[1–4] The data that are obtained are surface concentrations of impurities, which are assumed to be equilibrated with the bulk, as a function of temperature. Heats or enthalpies of segregation are extracted from conventional plots of the logarithm of the surface concentration against the reciprocal temperature. These are often linear and it is commonly assumed that this is indicative of Arrhenius or Langmuir behavior, wherein the surface atomic ratio, x_s, is related to the bulk ratio, x_b, by an expression of the form

$$x_s \propto x_b \exp(-\Delta h/k_B T)$$

in which Δh is the *coverage-independent* heat of segregation and T the temperature.

On this basis, McCune and Ku[2] have obtained enthalpies between −44 and −80 kJ/mol for the segregation of calcium to the {001} surface of MgO in the temperature range ~1320 to 1720 K for bulk concentrations between 180 and 220 ppm and enthalpies between −156 and −189 kJ/mol for the segregation of calcium to the $\{10\bar{1}0\}$ surface of α-Al_2O_3 in the temperature range ~1650 to 1900 K for a bulk concentration of 40 ppm, while Mukhopadhyay *et al.*[5] observed magnesium segregation to the $\{10\bar{1}0\}$ surface of magnesium-implanted sapphire with an effective enthalpy of −135 kJ/mol. In the latter experiments non-Arrhenius segregation of calcium

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was also observed. Likewise, Baik *et al.*[3] derived an experimental enthalpy of −146 kJ/mol for the segregation of magnesium to the {0001} surface of α-Al_2O_3 in the temperature range ~1600 to 1800 K for bulk concentration of 40 ppm. McCune *et al.*[4] reported an enthalpy of −44 kJ/mol for the segregation of yttrium at the surface of polycrystalline α-Al_2O_3 in the temperature range ~2000 to 2200 K for samples containing 160 ppm of Y^{3+}; and most recently Baik and White[6] have confirmed the earlier observations by McCune and Ku[2] of the segregation of calcium to the $\{10\bar{1}0\}$ of α-Al_2O_3 with an enthalpy of −169 kJ/mol, but no enrichment of the {0001} basal plane up to 1500°C. This latter observation remains unexplained in view of the known segregation of magnesium to the basal surface and calcium to the prism surface and also recent calculations by Davies *et al.*[7] which suggest heats of segregation of 200 to 300 kJ/mol.

Even simple notions of steric hindrance, however, suggest that coverage-independent heats of segregation, i.e., constant Δh, are a crude approximation other than at very low coverages, while recent atomistic calculations[8–10] have confirmed that they are likely to be the exception rather than the general rule. Accordingly, this paper addresses the problem of impurity segregation at surfaces, with particular reference to cation impurities at the surfaces of MgO, α-Al_2O_3, and LiO. We begin by considering a simple statistical-mechanical model for equilibrium coverage and derive a segregation isotherm which allows for the variation of Δh with surface coverage. Assuming monolayer segregation, surface coverage can be equated to the surface atomic ratio, x_s. We show that a linear relationship between log (x_s) and reciprocal temperature is not satisfied solely by a constant heat of segregation. There is a general expression for $\Delta h(x_s)$ that satisfies a linear relationship between log (x_s) and $1/T$, with constant Δh as a special solution. An outcome of our analysis is that we raise the question as to what is the most useful *operational* definition of the heat of segregation. Next, we discuss four examples of calculated heats of segregation which exhibit non-Arrhenius behavior. Finally, we use these calculated heats to obtain equilibrium coverages. In three of the four cases we are able to compare our results with recent experimental measurements,[1,3,4] including one which exemplifies quite clearly that a strongly coverage-dependent Δh can give rise to a linear plot of log (x_s) against $1/T$ over a restricted experimental range of temperature.

II. Statistical-Mechanical Model for Equilibrium Coverage

Statistical-mechanical models of segregation have been derived by many authors, notably McLean[11] and Defay *et al.*[12] Previously, we have used a model, similar to that of Liu and Kung,[13] to derive an Arrhenius expression for the equilibrium surface concentration of segregated impurity, x_s, at a temperature T.[14] We start with derivation of this expression for a two-component system consisting of bulk and surface sites, each of one type only.

The total free energy, G, of a two-component system consisting of bulk and surface sites, each of one type only, is written as

$$G=n_1^b g_1^b+n_1^s g_1^s+n_2^b g_2^b+n_2^s g_2^s -k_b T \ln \Omega \tag{1}$$

in which n_i^b and n_i^s are the number of bulk and surface ion/atoms of type i with individual free energies g_i^b and g_i^s, respectively. Assuming a random distribution of ions, the configurational entropy, $k_B \ln \Omega$, is given by

$$k_B \ln \Omega=k_B \ln \frac{N^b!}{n_1^b!\,n_2^b!}\,\frac{N^s!}{n_1^s!\,n_2^s!} \tag{2}$$

where N^b and N^s are the total number of bulk and surface sites. When we write the total numbers of ions/atoms of each type as n_1 and n_2, the conservation equations are given by

$$n_1^b+n_1^s=n_1 \tag{3a}$$

$$n_2^b+n_2^s=n_2 \tag{3b}$$

$$n_1^b+n_2^b=N^b \tag{3c}$$

$$n_1^s+n_2^s=N^s \tag{3d}$$

The convention that we use is that ions/atoms of type 1 represent the impurity, so that in addition to the conservation equations (3*a*) to (3*d*) we have

$$n_1 \ll n_2$$

$$N^s \ll N^b$$

$$n_2^b \sim N^b$$

G can now be rewritten as

$$G=G_1+G_2 \tag{4a}$$

with

$$G_1=n_1^s(g_1^s-g_2^s-g_1^b+g_2^b)+n_1 g_1^b +N^s g_2^s+(n_2-N^s)g_2^b \tag{4b}$$

$$G_2=-k_B T \ln \Omega \tag{4c}$$

Differentiating with respect to n_1^s gives

$$dG_1/dn_1^s=g_1^s-g_2^s-g_1^b+g_2^b \tag{4d}$$

$$dG_2/dn_1^s=k_B T \ln [(n_1^s/n_2^s)/(n_1^b/n_2^b)] \tag{4e}$$

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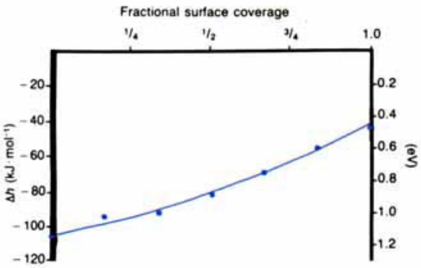

Fig. 1. Calculated heat of segregation, Δh, of Ca^{2+} at the {001} surface of MgO as a function of coverage.

From

$$dG/dn_1^s=0 \tag{4f}$$

we get

$$g_1^s-g_2^s-g_1^b+g_2^b+k_BT\ \ln\left[(n_1^s/n_2^s)/(n_1^b/n_2^b)\right]=0 \tag{4g}$$

Writing

$$n_1^s/n_2^s=x_s \tag{5a}$$

$$n_1^b/n_2^b=x_b \tag{5b}$$

$$g_1^s-g_2^s=\delta g^s \tag{5c}$$

$$g_1^b-g_2^b=\delta g^b \tag{5d}$$

$$\delta g^s-\delta g^b=\Delta g \tag{5e}$$

we get

$$x_s=x_b\ \exp(-\Delta g/k_BT) \tag{6}$$

which is the Arrhenius relationship. δg^b and δg^S are the bulk and surface substitution free energies, respectively.

To obtain a modified expression which includes solute interactions at the surface, G_1 of Eq. (4*b*) is written in the form

$$G_1=n_1^s\Delta g+n_1g_1^b+n_2g_2^b+N^s(g_2^s-g_2^b) \tag{7}$$

in which $N^s(g_2^s-g_2^b)$ can be identified as the surface free energy of the host lattice. Differentiating G_1 with respect to n_1^s, *allowing for a variation in* Δg *with surface concentration,* gives

$$dG_1/dn_1^s=\Delta g+n_1^s(d\Delta g/dn_1^s) \tag{8}$$

The modified expression for x_s, which allows for the variation of Δg as a function of coverage, is

$$x_s=x_b\ \exp\{-[\Delta g+x_s(x_s+1)\times(d\Delta g/dx_s)]/k_sT\} \tag{9}$$

If we write Δg in terms of Δh, the heat of segregation, and Δs, the vibrational entropy of segregation, the final form of the isotherm is

$$x_s=x_b\ \exp\{[\Delta s+x_s(x_s+1)\times(d\Delta s/dx_s)]/k_B\}\times\exp\{-[\Delta h+x_s(x_s+1)\times(d\Delta h/dx_s)]/k_BT\} \tag{10}$$

from which the slope of $\ln(x_s)$ against $1/T$ is not Δh as it is for an Arrehenius–Langmuir expression. It is important to note that in our notation x_s is the ratio of impurity/host ions at the surface and not a concentration. This is in line with the most common experimental measurements.

We now consider the interpretation of a linear relationship between $\ln(x_s)$ and $1/T$. Rewriting Eq. (10) in the form

$$\ln(x_s)=\ln(x_b)+[\Delta s+x_s(x_s+1)\times(d\Delta s/dx_s)]/k_B-[\Delta h+x_s(x_s+1)\times(d\Delta h/dx_s)]/k_BT=\Omega-H/k_BT \tag{11}$$

we seek solutions to the equation

$$\Delta h(x_s)+x_s(x_s+1)\times(d\Delta h(x_s)/dx_s)=H \tag{12}$$

where H is a constant.

$$\Delta h=H \tag{13}$$

is clearly the solution when $d\Delta h/dx_s=0$, so that one interpretation of a linear relationship between $\ln(x_s)$ and $1/T$ is that Δh is independent of x_s. The general solution, however, is

$$\Delta h(x_s)=H-\Lambda(1+1/x_s) \tag{14}$$

where Λ is an undetermined constant. Thus, systems for which $\Delta h\propto x_s^{-1}$ will exhibit Arrhenius behavior. Furthermore, in cases where $\Delta h\propto x_s^{-1}$ over a limited range of x_s, examples of which are given in the next section, a linear relationship between $\ln x_s$ and $1/T$ will follow only over a limited temperature regime.

Thus we have two possible definitions of the heat of segregation. The first is what might be described as an atomistic definition and embodied in Eq. (5). Physically it corresponds to the difference in the internal energy of an impurity between the bulk and a surface. Alternatively, the heat of segregation could be taken as H, the slope of $\ln(x_s)$ against $1/T$. Either would seem to be acceptable, provided the distinction between them is fully recognized.

Atomistic lattice simulations have been widely used for over a decade to study the bulk lattice and defect properties of ionic and semi-ionic materials, including oxides.[15] Essentially the same methods are used for surfaces, which, in most studies to date including the present one, are assumed to be planar, semi-infinite, and periodic in two dimensions. Most low-energy surfaces of ionic crystals have a structure which is close to, though not exactly, a simple termination of the bulk. Such systems are best described in terms of surface relaxations, which are distinguished from surface reconstructions where the surface structure differs substantially from that of the bulk. To obtain the surface structure the atomic positions and electronic polarization of ions in the immediate vicinity of the surface, typically within 5 to 10 lattice planes, are explicitly relaxed to the point at which there is zero force on these ions. For regions of the crystal further into the bulk, it is generally sufficient to regard the lattice as rigid and unpolarizable, which in any event can be confirmed by expanding the fully relaxed surface region. The relaxed positions give the surface structure and the difference in lattice energy per unit area at the surface compared with that in the bulk gives the (surface) energy of the nondefective surface. Defect energies, including those associated with impurity segregation, are calculated with respect to the fully relaxed surface. It has proved convenient to assume integral ionic charges associated with accepted chemical valence and electron counting, i.e., +2, +3, etc., for cations and −1, −2 for anions, for in addition to providing an accurate description of the principal lattice forces, a model of this type allows the useful concept of isovalent and aliovalent impurity substitution. A further assumption is not only that two-body potentials are adequate for a description of lattice defects in the bulk, but that they apply essentially unchanged to surfaces. The particular potentials that we have used here, as elsewhere,[8,9,16] are based on a modified electron-gas approximation discussed earlier.[17] An essential feature of these potentials is that they include the Dick–Overhauser shell model[18] for treating the electronic polarization of the lattice. This is particularly important when dealing with the surfaces of ionic materials, for substantial fractions of the relaxation energy and surface dipole derive from the polarization of the outermost ions.

The calculation of the energy and structure of an isolated impurity ion at the surface or in the bulk is carried out by a generalization of the Mott–Littleton method.[19] A finite region around the impurity is modeled explicitly with the ions relaxed to equilibrium. Outside this region, the crystal is treated as a dielectric continuum which is polarized by the net defect charge. The lattice sums must be formulated to divide correctly the terms between the two regions[20] and care must be taken in the surface case to calculate appropriately the polarization of a dielectric half-space.[21]

III. Heats of Segregation

The calculation of heats of segregation by atomistic simulation methods has been described previously in some detail.[8–10,14] In brief, our treatment assumes semi-infinite, planar surfaces to which impurity cations segregate from the bulk to form ordered, fully relaxed structures. It is from the energies of these structures, together with that of the pure surface and of isolated impurity ions in the bulk, that the heats of segregation are obtained. This is formally encapsulated in Eq. (5). Strictly speaking, therefore, our results apply to segregation from crystals containing low levels of bulk impurity. The heat of segregation, Δh, is not calculated as a continuous function of coverage, but only at specific coverages, e.g., ⅙, ¼, ⅓, etc., as indicated in Figs. 1 to 7. For convenience, smooth curves have been drawn through the calculated points. We recognize that at low coverages, in particular, the assumptions we make may be unrepresentative of real systems, because disordered segregation at steps, ledges, and other surface irregularities rather than at planar surfaces might well predominate. However, as shown in a later section, a comparison with experiment of the calculated isotherms based on these assumptions suggests that for the systems considered here they are not unreasonable.

Figures 1 to 4 show three examples of calculated heats of segregation of isovalent impurities at oxide surfaces: they are for Ca^{2+} at the {001} surface of MgO, for Na^+ at the {111} and {110} surfaces of Li_2O, for Y^{3+} at the $\{10\bar{1}2\}$ and $\{1\bar{1}20\}$ surfaces of α-Al_2O_3 and Y^{3+} at the surfaces of α-Cr_2O_3. It is evident that Δh varies with coverage in each case, most notably for Y^{3+} at the $\{1\bar{1}20\}$ surface of α-Al_2O_3, for which there is an approximate threefold decrease in Δh from zero to ½ coverage. Figure 3 also illustrates how radically different heats of segregation can be at different surfaces, even for isovalent impurities. As pointed out previously,[10,22] this is of particular significance in relation to the morphology of impure crystals. In the case of Ca^{2+} at the {001} surface of MgO, $-\Delta h$ is calculated to be in the range ~40 to 105 kJ/mol, which apparently is in good agreement with the reported range, ~44 to 80 kJ/mol.[2] For Y^{3+} at the $\{10\bar{1}2\}$ and $\{1\bar{1}20\}$ surfaces of α-Al_2O_3, on the other hand, the calculated heat, which varies from approximately −450 to −100 kJ/mol, is appreciably greater than the value of −44 kJ/mol reported by McCune *et al.*[4] for polycrystalline Al_2O_3. Our heats of segregation for Y:α-Al_2O_3 may be compared with similar calculations for Y:α-Cr_2O_3, based on empirical potentials reported recently by Davies *et al.*[7] and shown in Fig. 4. While the values of h are substantially smaller for the latter, partly because of the reduced difference in the ionic radii, 0.27 Å (0.027 nm), as opposed to 0.36 Å (0.036 nm) for Y^{3+} and Al^{3+} and possibly to differences in the interatomic potentials, there are two important similarities. The first is a minimum in Δh for segregation to the {1012} surface at approximately ¼ coverage; the second is the wide variation in the

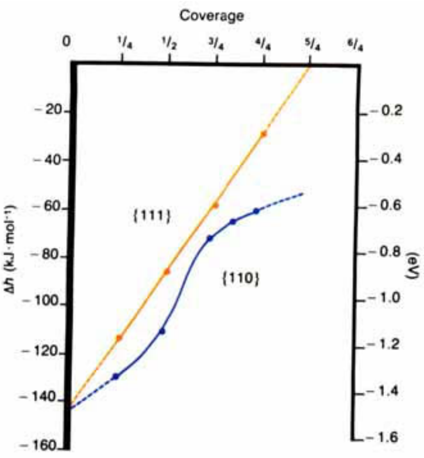

Fig. 2. Calculated heat of segregation, Δh, of Na^+ at the {111} and {110} surfaces of Li_2O.

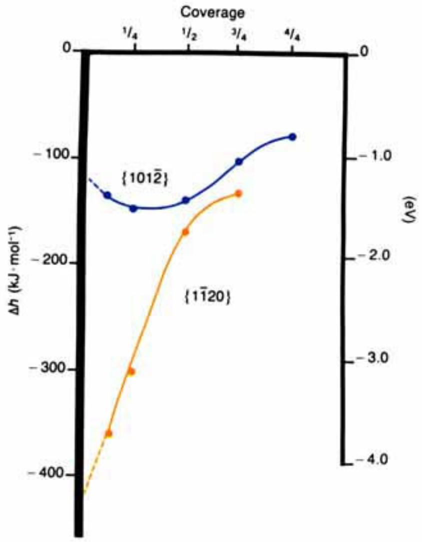

Fig. 3. Calculated heat of segregation, Δh, of Y^{3+} at the $\{10\bar{1}2\}$ and $\{1\bar{1}20\}$ surfaces of α-Al_2O_3.

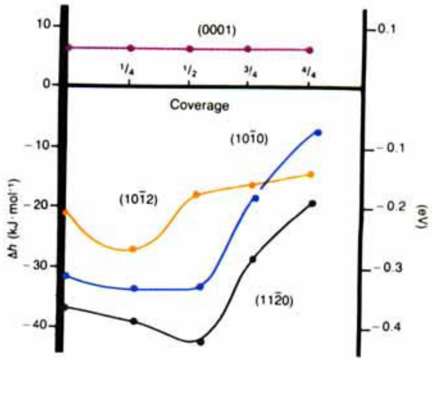

Fig. 4. Calculated heat of segregation, Δh, of Y^{3+} at the $\{10\bar{1}2\}$, {1010}, and $\{1\bar{1}20\}$ surfaces of α-Cr_2O_3.

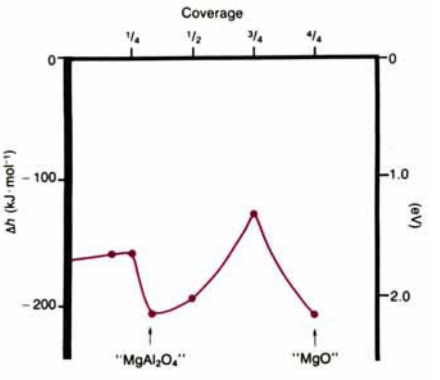

Fig. 5. Calculated heat of segregation, Δh, of magnesium at the {0001} surface of α-Al_2O_3.

segregation characteristics of different surfaces. We return to the comparison between the calculated and reported heats of segregation in a later section.

Turning now to an example of aliovalent impurity segregation, Fig. 5 shows the calculated heat as a function of coverage for magnesium at the {0001} surface of α-Al_2O_3. The model that we have used here, as elsewhere,[9] is based on the segregation of the neutral species, $\{Mg_{Al}–V_O–Mg_{Al}\}^x$. In so doing, we eliminate problems associated with the interaction of charged species such as Mg'_{Al} with the space-charge layer. Unlike the three previous examples, here we find Δh to be constant, or very nearly so, over a restricted range of coverage, namely, that between zero and approximately 1/4 coverage. Beyond this, Δh falls sharply to a minimum at approximately 1/3 coverage, after which it rises to a maximum at 3/4 coverage. The point at which Δh is a minimum we have designated at "$MgAl_2O_4$," since the ratio of Al^{3+} to Mg^{2+} ions is exactly that of spinel. In this case, and that of Y^{3+} at the {10$\bar{1}$2} surface of α-Al_2O_3, we have suggested[9,10] that the existence of a minimum in Δh is indicative of a coherent second phase, the composition of which corresponds to that of the coverage at the minimum. We consider the experimental evidence for this in a later section. Our value for constant Δh is approximately −158 kJ/mol, which seems to be in good agreement with the experimental value of −146 kJ/mol reported by Baik *et al.*[3] Our calculated heat of segregation of magnesium at the {0001} surface of Al_2O_3 may be compared with those of magnesium and calcium at the {111} surface of cubic ZrO_2, shown in Figs. 6(A) and (B). For both the latter coherent second phases at the surface are also predicted with compositions corresponding to $Mg_2Zr_5O_{12}$ and $CaZr_4O_9$ and heats of segregation in excess of 200 kJ/mol.[16] This is in contrast to the calculated heat of segregation of calcium at the basal of α-Al_2O_3 reported recently by Davies *et al.*[7] Figure 7 shows Δh for the lowest-energy configuration of $Ca_{Al}–V_O–Ca_{Al}$ at the surface taken from Ref. 7. Here we find no minimum, hence no second phase. However, the value of h, <250 kJ/mol, suggests that segregation should occur and it remains unclear why this has not been observed.

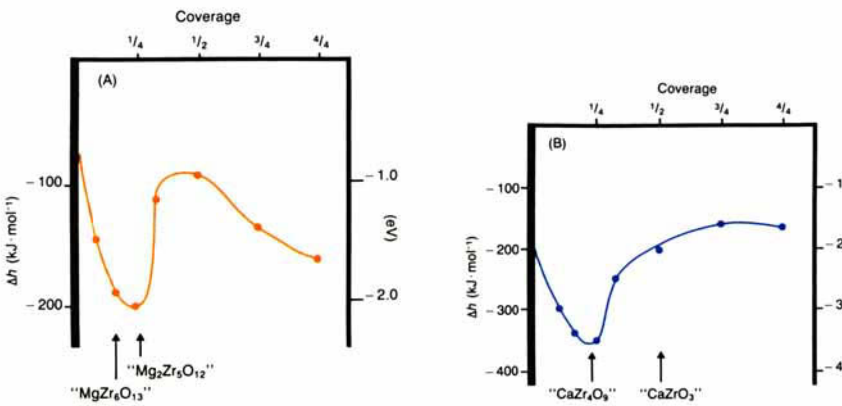

Fig. 6. (A) Calculated heat of segregation, Δh, of magnesium at the (111) surface of c-ZrO_2. B) Calculated heat of segregation, Δh, of calcium at the (111) surface of c-ZrO_2.

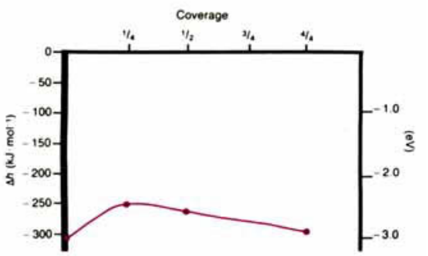

Fig. 7. Calculated heat of segregation, Δh, of calcium at the {0001} surface of α-Al_2O_3.

IV. Equilibrium Surface Coverage

To evaluate the surface atomic fraction of impurity, x_s, we need to know both $\Delta h(x_s)$ and $\Delta s(x_s)$. $\Delta h(x_s)$ has been evaluated for a number of systems, apart from those considered here, but not $\Delta s(x_s)$. In what appears to be the only reported calculation of the entropy of segregation, Masri *et al.*[23] obtained a value of $-0.24k_B$ for Ca^{2+} segregating to the {001} surface of MgO, at 50% coverage. At 1000 K the contribution to the free energy, Δg, is ~3 kJ/mol, compared with calculated and experimentally determined heats between −40 and −100 kJ/mol. In view of this relatively minor contribution, which admittedly is for a single system, as a first approximation we assume that Δs~0 and proceed to evaluate x_s from

$$x_s \approx x_b \exp\{-[\Delta h + x_s(x_s+1) \times (d\Delta h/dx_s)]/k_BT\} \qquad (15)$$

Figures 8 and 9 show the calculated equilibrium coverages or surface atomic fractions of Ca^{2+} at the {001} surface of MgO and Y^{3+} at the {10$\bar{1}$2} and {11$\bar{2}$0} surfaces of α-Al_2O_3 for bulk concentrations of 220 and 160 ppm, respectively, the values at which the observed data were obtained.[1,4] In the case of magnesium at the {0001} surface of α-Al_2O_3, impurity atomic fractions calculated from Eq. (15) are more than an order of

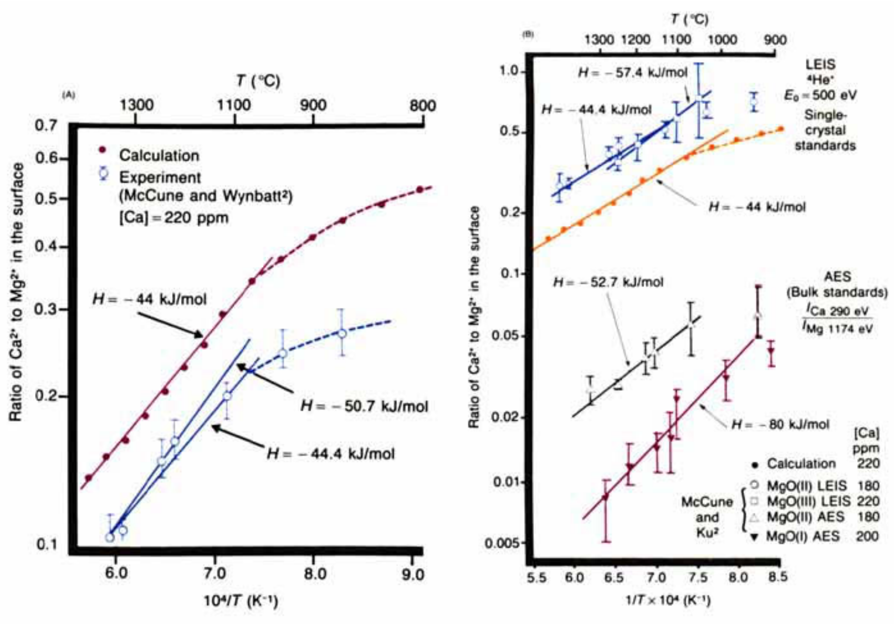

Fig. 8. Calculated and experimental equilibrium coverages of the {001} surfaces of MgO by Ca^{2+} as a function of temperature. (B) Calculated and experimental equilibrium coverages of the {001} surfaces of MgO by Ca^{2+} as a function of temperature.

magnitude greater than the reported values.[3] The reasons why this might be so are discussed later. However, since what is of primary concern is the *temperature dependence* of the coverage, for this relates directly to the heat of segregation, the calculated coverages can be scaled (down) uniformly for a comparison of the temperature dependence with experiment. The simplest way to do this is to write Eq. (10) in the form

$$x_s = x_b A \exp\{-[\Delta h + x_s(x_s+1) \times (d\Delta h/dx_s)]/k_B T\} \qquad (16)$$

and to fix A by equating the calculated and observed equilibrium coverages at a single temperature, in our case at 1500°C. The coverage at other temperatures can then be obtained from Eq. (16) using this fixed value of A. Figure 10 shows the scaled coverage as a function of temperature. Figure 11 shows the calculated equilibrium coverage of the {111} and {110} surfaces of Li_2O by Na^+, which, as far as we are aware, has not been determined experimentally.

V. Comparison with Experiment

In three of our four examples direct comparisons can be made with experiments; the fourth is a prediction. However, before we proceed with the details, it is important to note the approximations and assumptions that limit such comparisons. With regard to the physical model that we have used, we have assumed planar surfaces and ordered segregated structures: thus we neglect the presence and effects of irregularities such as kinks, ledges, etc., which real crystal surfaces undoubtedly possess. Next, our statistical mechanical model assumes that segregation can be described in terms of a single type of bulk and surface site, which further implies that all the segregated impurity is in the surface layer. Furthermore, the present calculations also neglect the vibrational entropy of segregation, which Masri *et al.*[23] have shown to be small in the case of Ca^{2+} at the {001} surface of MgO at 50% coverage. If we assume that their entropy of $-0.24k_B$ applies to all coverages, our calculated values are reduced by a factor of 0.89. Finally, measurements of surface impurity concentration inevitably sample a finite depth into the crystal beyond the surface plane. If all of the segregated impurity resides solely in the surface layer, the measured concentrations will inevitably be lower than the true values.

The most studied system to date is Ca^{2+} at the {001} surface of MgO.[1,2] Figure 8 shows the calculated coverage as a function of temperature compared with various sets of data reported by McCune and co-workers.[1,2] For clarity and convenience we have compared the calculated coverage separately with the individual reports, i.e., Ref. 1 in Fig. 8(A) and Ref. 2 in Fig. 8(B). Figure 8(A) shows that both experiment and calculation find a linear dependence of log ($[Ca^{2+}]/[Mg^{2+}]$) against $1/T$ down to ~1100°C with a "tailing-off" below this temperature. The calculated value of H ($k_B \times$ slope), −44 kJ/mol, is in good agreement with those of −44.4 and −50.8 kJ/mol that are obtained from the experimental data. The calculated coverage also lends support to the view[1] that at the lower temperatures the experimental coverage was unlikely to have reached equilibrium. Figure 8(B) shows a comparison with a wider range of data obtained using different analytic techniques. The calculated surface coverage lies conveniently between the AES and LEIS results with a slope that is tolerably close to three of the four sets of data, from which values of H ranging from −44.4 to −80 kJ/mol were obtained. The wide range in coverage and slope shown in Fig. 8(B) is indicative of the difficulty in obtaining consistent quantitative experimental data due to factors ranging from

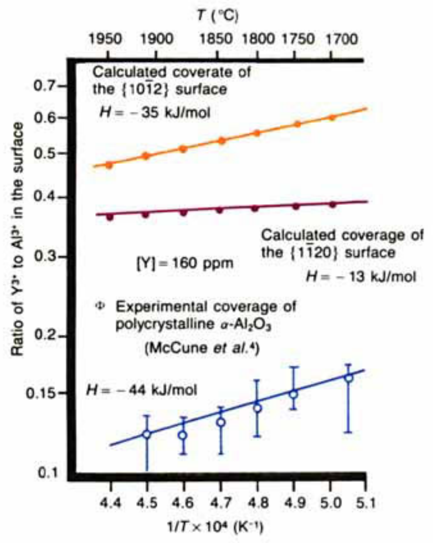

Fig. 9. Calculated and experimental equilibrium coverages of the surfaces of α-Al_2O_3 by Y^{3+} as a function of temperature.

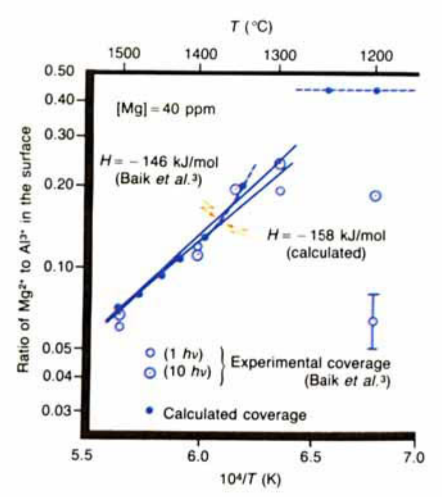

Fig. 10. Calculated and experimental equilibrium coverages of the {0001} surface α-Al_2O_3 by magnesium as a function of temperature.

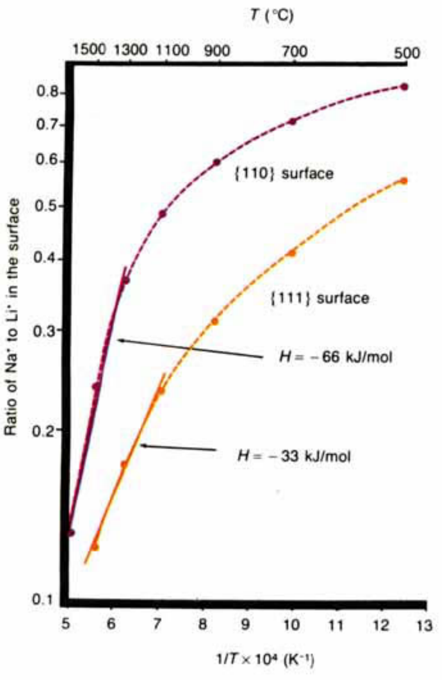

Fig. 11. Calculated equilibrium coverage of the {111} and {110} surfaces of Li_2O by Na^+.

sample control to the sensitivity of the analytic techniques for measuring surface enrichment and is perhaps a pointer to the utility of supplementary calculations of the type reported here for investigating impurity segregation. What emerges quite clearly from these results, however, is that the differences between calculated and experimental values of H are small compared with the differences between H, calculated or experimental, and the calculated value of Δh, which is in the region of −100 kJ/mol for impurity-to-host cation ratios in the surface of 0.15 to 0.3.

Figure 9 contains experimental data for and theoretical predictions of the segregation of Y^{3+} at the surfaces of α-Al_2O_3. This system can be viewed as a higher-valence analogue of Ca^{2+}:MgO. McCune *et al.*[4] have reported coverages of ≈12% to ≈16% at the surface of polycrystalline α-Al_2O_3 in the temperature range 1700° to 1900°C, from which a value of −44 kJ/mol has been obtained for H: for comparison we have calculated the coverages of the $\{1\bar{1}20\}$ and $\{10\bar{1}2\}$ surfaces. As shown in Fig. 9 the calculated coverages are found to be very close to linear in the temperature range 1700° to 1900°C, from which values of −13 and −35 kJ/mol for H can be extracted for the $\{1\bar{1}20\}$ and $\{10\bar{1}2\}$ surfaces, respectively. These compare with calculated values of Δh of approximately −300 kJ/mol for the $\{1\bar{1}20\}$ surface and of approximately −150 kJ/mol for the $\{10\bar{1}2\}$ surface at the same coverages, thereby confirming what was found for Ca^{2+}:MgO. However, unlike the latter, here we find appreciable differences between the calculated and observed coverages. The reason for this, apart from the question of depth sampling referred to earlier, can be readily understood. The reported data are for polycrystalline material, the surface of which is likely to comprise the lowest index planes. Of these, the {0001} basal surface is calculated to be lowest in energy, γ=2.03 J/m²,[10] and found by numerous workers, notably Chase,[24] to comprise at least 50% of the surface area in single crystals grown in a melt. It is not unreasonable to assume that the surface of polycrystalline material will also comprise a significant proportion, e.g., ~50%, of the basal surface. Now previous calculations[10] have predicted negligible segregation of Y^{3+} to the {0001} surface of α-Al_2O_3, which, if correct, implies at least *twice* the reported coverage of those surfaces of the polycrystalline material that are enriched. This does not lead to the calculated coverages, but when taken together with differences due to depth sampling, brings experiment and calculation about as close as it is for Ca^{2+}:MgO.

Our third comparison with experiment is that for the segregation of magnesium at the {0001} surface of α-Al_2O_3. We have noted already that for coverages of <25%, Δh is calculated to be constant at approximately −158 kJ/mol compared with the experimental value for H of −146 kJ/mol reported by Baik *et al.*[3] Figure 10 shows the calculated coverage, scaled to the experimental value at 1500°C,[3] compared with the remaining data. As shown, both theory and experiment find Arrhenius behavior up to ~1370°C. Below this temperature calculations predict a departure from Arrhenius behavior and between ~1350° and 1250°C a sharp increase in coverage, corresponding to a minimum in Δh at the cation composition of spinel, which is then predicted to remain constant at lower temperatures. While it seems unlikely that experiment will be able to verify (or refute) the predicted departure from Arrhenius behavior below 1350°C, since at these lower temperatures equilibrium surface concentrations appear to be difficult to attain, Baik *et al.*[3] observed LEED patterns which could be interpreted in terms of a cubic overlayer and this, we suggest, could correspond to the "spinel-like" coherent second phase that the calculated heat of segregation predicts at approximately ⅓ coverage. The reason why the departure from Arrhenius behavior cannot be located more precisely than the temperature range ~1350° to 1250°C, hence the break in the calculated (dashed) curve in Fig. 10, is simply that, as shown in Fig. 5, we find Δh to be more or less constant up to ¼ coverage, decreasing to a minimum at ⅓ coverage. However, we cannot locate the precise coverage between ¼ and ⅓ at which Δh decreases sharply and it is this uncertainty that limits the predicted temperature at which a departure from Arrhenius behavior occurs.

Finally, Fig. 11 shows the predicted equilibrium coverage of the {111} and {110} surfaces of Li_2O by Na^+. In the temperature range 900° to 1500°C these vary from ~60% of the {110} surface at 900°C to ~12% of the {111} surface at 1500°C. At present there would appear to be no experimental data available for comparison.

VI. Summary

In the preceding section we have shown that calculated coverages of oxide surfaces by cation impurities and, in particular, their temperature dependence are in good agreement with the available experimental data.[1–4] In some cases there is the possibility of confusion if calculated heats of segregation, Δh, are compared directly with "Arrhenius" enthalpies, H, which can be extracted from the gradient of the logarithm of the measured surface concentration (coverage) against reciprocal temperature. We have shown that a linear dependence of the logarithm of the surface concentration against reciprocal temperature does not necessarily imply Arrhenius behavior and that the numerical values of Δh and H can be quite different. However, since Δh cannot be measured directly and the logarithm of the surface concentration against reciprocal temperature is frequently linear, the gradient, H, might reasonably be taken as an operational definition of the heat of segregation, as distinct from an atomistic definition in terms of the difference in enthalpy between substituting an impurity for a host atom/ion in the bulk and at a surface. In this connection a use of the term "Arrhenius (or Langmuir) heat of segregation" for H, as distinct from the term "atomic heat of segregation" for Δh, might reduce any potential ambiguity that might arise when comparing calculations with experiment. Finally, we note that, as Blakely and Thapliyal[25] have pointed out, heats of segregation which are independent of the surface model can, in principle, be extracted from segregation isosteres rather than isotherms. While calculated isosteres present no more of a problem than isotherms, for the systems considered in this paper the necessary data to construct experimental isosteres for comparison appear not to exist.

References

[1] R. C. McCune and P. Wynblatt, "Calcium Segregation to a Magnesium Oxide (100) Surface," *J. Am. Ceram. Soc.*, **66** [2] 111–17 (1983).

[2] R. C. McCune and R. C. Ku, "Calcium Segregation to MgO and α-Al_2O_3 Surfaces"; pp. 217–37 in Advances in Ceramics, Vol. 10, Structure and Properties of MgO and Al_2O_3 Ceramics. Edited by W. D. Kingery. American Ceramic Society, Columbus, OH, 1984.

[3] S. Baik, D. E. Fowler, J. M. Blakely, and R. Raj, "Segregation of Mg to the (0001) Surface of Doped Sapphire," *J. Am. Ceram. Soc.*, **68** [5] 281–86 (1985).

[4] R. C. McCune, I. N. T. Donean, and R. C. Ku, "Yttrium Segregation and YAG Precipitation at Surfaces of Y-Doped α-Al_2O_3," *J. Am. Ceram. Soc.*, **69** [8] C-196–C-199 (1986).

[5] S. M. Mukhopadhyay, A. P. Jardine, J. M. Blakely, and S. Baik, "Segregation of Magnesium and Calcium to the {1010} Prismatic Surface of Magnesium-Implanted Sapphire," *J. Am. Ceram. Soc.*, **71** [5] 358–62 (1988).

[6] S. Baik and C. L. White, "Anisotoripic Calcium Segregation to the Surface of Al_2O_3," *J. Am. Ceram. Soc.*, **70** [9] 682–88 (1987).

[7] M. J. Davies, P. Kenway, P. J. Lawrence, S. C. Parker, W. C. Mackrodt, and P. W. Tasker, "Impurity Segregation to the Surfaces of Corundum-Structure Oxides," *J. Chem. Soc., Faraday Trans. 2*, **85**, 555–63 (1989).

[8] P. W. Tasker, E. A. Colbourn, and W. C. Mackrodt, "Segregation of Isovalent Impurity Cations at the Surfaces of MgO and CaO," *J. Am. Ceram. Soc.*, **68** [2] 74–80 (1985).

[9] W. C. Mackrodt and P. W. Tasker, "Calculated Impurity Segregation at the Surfaces of α-Al_2O_3," *Mater. Res. Soc. Symp. Proc.*, **60**, 291–98 (1986).

[10] W. C. Mackrodt, "The Calculated Equilibrium Segregation of Fe^{3+}, Y^{3+}, and La^{3+} at the Low-Index Surfaces of α-Al_2O_3"; pp. 293–306 in Advances in Ceramics, Vol. 23, Nonstoichiometric Compounds. Edited by C. R. A. Catlow and W. C. Mackrodt. American Ceramic Society, Westerville, OH, 1988.

[11] D. McLean, Grain Boundaries in Metals. Oxford University Press, London, 1957.

[12] R. Defay, I. Prigogine, A. Bellmans, and D. H. Everett, Surface Tension and Adsorption. Wiley, New York, 1966.

[13] S. Y. Liu and H. H. Kung, "Surface Cation Ratios of Binary Oxide Solid Solutions," *Surf. Sci.*, **110**, 504–22 (1981).

[14] E. A. Colbourn, W. C. Mackrodt, and P. W. Tasker, "The Segregation of Calcium Ions at the Surface of Magnesium Oxide: Theory and Calculation," *J. Mater. Sci.*, **18**, 1917–24 (1983).

[15] W. C. Mackrodt, "Calculated Point Defect Formation, Association, and Migration Energies in MgO and α-Al_2O_3"; pp. 62–78 in Advances in Ceramics, Vol. 10, Structure and Properties of MgO and Al_2O_3 Ceramics. Edited by W. D. Kingery. American Ceramic Society, Columbus, OH, 1984.

[16] W. C. Mackrodt, "Atomistic Lattice Simulations of the Structure, Energetics and Impurity Segregation Behaviour of Ceramic Boundaries"; pp. 271–80 in Materials Science Research, Vol. 21, Ceramic Microstructures '86—Role of Interfaces. Edited by J. A. Pask and A. G. Evans. Plenum Press, New York, 1987.

[17] W. C. Mackrodt and R. F. Stewart, "Defect Properties of Ionic Solids: II, Point Defect Energies Based on Modified Electron-Gas Potentials," *J. Phys. C*, **12**, 431–49 (1979).

[18] B. G. Dick and W. A. Overhauser, "Theory of Dielectric Constants of Alkali Halide Crystals," *Phys. Rev.*, **112**, 90 (1958).

[19] N. F. Mott and M. J. Littleton, "Conduction in Polar Crystals. I, Electrolytic Conduction in Solid Salts," *Trans. Faraday Soc.*, **34**, 485 (1938).

[20] A. B. Lidiard and M. J. Norgett, "Point Defects in Ionic Crystals"; p. 385 in Computational Solid State Physics. Edited by F. Herman, N. W. Dalton, and T. R. Koehler. Plenum Press, New York, 1972.

[21] D. M. Duffy, J. P. Hoare, and P. W. Tasker, "Vacancy Formation Energies Near the Surface of an Ionic Crystal," *J. Phys. C: Solid State Phys.*, **17**, L195 (1984).

[22] W. C. Mackrodt, R. J. Davey, S. N. Black, and R. Doherty, "The Morphology of α-Al_2O_3 and α-Fe_2O_3: The Importance of Surface Relaxation," *J. Cryst. Growth*, **80**, 441–46 (1987).

[23] P. Masri, P. W. Tasker, J. P. Hoare, and J. H. Harding, "Entropy and Segregation of Isovalent Impurity Cations at the Surfaces of an Ionic Crystal: MgO(100) Ca^{2+}," *Surf. Sci.*, **173**, 439–54 (1986).

[24] A. B. Chase, "Habit Modification of Corundum Crystals Grown from Molten PbF_2–Bi_2O_3," *J. Am. Ceram. Soc.*, **49** [5] 233–36 (1966).

[25] J. M. Blakely and H. V. Thapliyal, "Structure and Phase Transitions of Segregated Surface Layers"; pp. 137–74 in Interfacial Segregation. Edited by W. C. Johnson and J. M. Blakely. American Society for Metals, Metals Park, OH, 1979. □