# Monte Carlo Simulations of Mg(Al)O Solid Solutions Based on Crystal Chemical Rules

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A new computational approach to modeling crystal structures based on the bond valence method is presented. The Monte Carlo technique is used to determine the atomic structure of perfect and defective crystals in accordance with crystal chemical valence sum and bond network rules. Using this method, the calculated MgO (001) surface relaxation was less than 1% of the interlayer spacing, a value that is consistent with experimental data and the results of other computational studies. The effects of Schottky defects and Al(III) impurities on the atomic relaxations at the MgO surface were determined in separate simulations. A Mg(Al)O solid solution with a Mg:Al ratio of 5:1, similar in composition to experimentally prepared calcined hydrotalcites, was also simulated, both in bulk form and with free surfaces. In agreement with experiment, simulation results indicated that Al(III) segregates to the surface. Further analyses of the simulation results are discussed with respect to surface reactivity, surface structure, and defect formation.

## Introduction

Crystal chemical rules established by Pauling[1] in 1929 allowed the structures of simple ionic compounds to be predicted in a qualitative but decidedly accurate way. More recently, Brown[2] and O'Keeffe[3] formulated a computational strategy for the systematic application of these rules that has come to be known as the bond valence method. Central to this method is a set of empirically derived parameters that relate a bond's valence, or strength, to its length.[4] The use of this quantitative relationship, together with two crystal chemical rules which we will refer to as the valence sum rule and the loop sum rule, allows the lengths of bonds in a preestablished network to be determined.[5,6] The valence sum rule states that the sum of the bond valences coordinating a given atom is equal to the formal valence of that atom. The loop sum rule states that the sum of bond valences taken with alternating sign around a closed loop is equal to zero. Two major limitations are associated with this method. The first is that the connectivity of the structure must be predefined. Although this task is straightforward for nondefective structures, ambiguities arise for more complex defective crystals. The second is that the connectivity must remain fixed, thus prohibiting bond reconstruction during relaxation.

The present paper describes a Monte Carlo (MC) simulation technique that relies on the same quantitative crystal chemical rules established by Brown[2] and O'Keeffe[3] but bypasses the need for predefining and fixing the crystal connectivity. Our approach is similar in spirit to the method of Pannetier et al.[7] who used an electrostatic interaction term in place of the loop sum rule. The method we describe here was suggested in ref 7 as an alternative but untested approach. This new method makes it possible to simulate large systems and allows the local structure near vacancies, substitutional impurities, defect clusters, dislocations, grain boundaries, or free surfaces to be simulated.

We have used this new MC bond valence method to simulate magnesia–alumina solid solutions. In equilibrium, MgO dissolves significant amounts of alumina only at temperatures above 1600 °C. The low solubility of alumina in magnesia below this temperature can be understood by considering the charge neutrality requirement that the dissolution of alumina be accompanied by the formation of charge-compensating defects. The stability of the divalent and trivalent oxidation states of Mg and Al, respectively, makes it unlikely that the charge of the aliovalent impurity would be compensated by electronic defects. Thus, the two possible point defect compensation reactions are, in Kröger–Vink notation

$$Al_2O_3 = 2Al^{\cdot}_{Mg} + V''_{Mg} + 3O^*_O \qquad (1)$$

$$Al_2O_3 = 2Al^{\cdot}_{Mg} + 2O^*_O + O''_i \qquad (2)$$
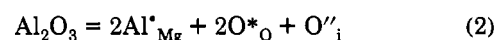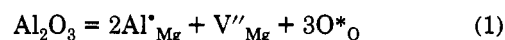
Considering the high packing fraction of the rock salt structure, it also seems unlikely that the Al impurities would be compensated by O interstitials, as indicated in reaction 2. Therefore, it is most likely that the substitutional Al(III) impurities are compensated by vacancies

(1) Pauling, L. *J. Am. Chem. Soc.* 1929, *51*, 1010.
(2) Brown, I. D. *Chem. Soc. Rev.* 1978, *7*, 359.
(3) O'Keeffe, M. *Acta Crystallogr.* 1990, *A46*, 138. O'Keeffe, M.; Brese, N. E. *J. Am. Chem. Soc.* 1991, *113*, 3226.
(4) Brown, I. D.; Altermatt, D. *Acta Crystallogr.* 1985, *B41*, 244.
(5) Brown, I. D. *J. Solid State Chem.* 1991, *90*, 155.
(6) O'Keeffe, M. *J. Mater. Res.* 1992, *6*, 2372.
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on the Mg sublattice, as indicated in reaction 1. Assuming this to be the case, the charge neutrality condition is

$$[Al^{\bullet}_{Mg}] = {}^1/_2[V''_{Mg}] \qquad (3)$$

The stoichiometries of our model systems were defined based on this compensation mechanism.

Despite the low equilibrium solubility of alumina in magnesia, kinetically stable solid solutions having the rock salt structure and containing up to 33 atom % Al(III) can be formed by calcining hydrotalcites at approximately 500 °C.[8-10] The spinel phase is not precipitated until approximately 925–1000 °C.[8,10] The so-called "calcined hydrotalcites" have come under recent experimental scrutiny because of their potential application as catalytic materials.[8-10]

One particularly interesting point concerning these materials is that existing experimental evidence is unable to specify the fate of the dissolved Al(III). Nuclear magnetic resonance (NMR) studies by Rey et al.[9] and McKenzie et al.[10] indicated that a significant portion of the Al(III) is found at tetrahedral sites. Conflicting NMR evidence reported by Kelkar et al.[11] indicated that Al(III) is primarily located at the normal octahedral sites in the rock salt structure. The differing results were attributed to different sample preparations.[10]

The extraordinary concentration of aliovalent impurities and cation vacancies present in these metastable Mg(Al)O solid solutions raises several interesting questions regarding the mixed oxide structure. For example, how are the Al cations distributed in the MgO framework? Are they spatially correlated with the charge compensating cation vacancies? Do the Al cations occupy tetrahedral or octahedral sites? Do they segregate to the surface? The simulations presented here were designed to explore the answers to these questions.

In the sections that follow, we will first describe our computational technique and then our results for the Al(III) doped magnesia system. Simulations of pure MgO, MgO with a Schottky defect, MgO with Al(III) as an impurity, and finally a Mg(Al)O solid solution containing 17% Al(III) will be described. Each simulation incorporates two free surfaces and allows for defect segregation and surface relaxation. In the final section, the simulation results will be compared to existing experimental data and other atomistic modeling results.

## Computational Method

The simulation technique uses the Monte Carlo method to determine atomic positions in defective ionic crystals. In contrast to conventional atomistic models, this new technique uses crystal chemical rules[3] instead of the crystal energy to determine the atomic structure. In a nondefective ionic crystal, these rules can be expressed as

$$cv_i = \sum_{j=1}^{Z} e^{(r^0_{ij} - d_{ij})/b} = fv_i \qquad (4)$$

$$loop = \sum_{k=1}^{2n(n \geq 2)} (-1)^k w_k e^{(r^0_{k,k+1} - d_{k,k+1})/b} = 0 \qquad (5)$$

where eq 4 is the valence sum rule and eq 5 is the loop sum rule. In these equations, $cv_i$ is the calculated atomic valence of atom $i$, $fv_i$ is the formal valence of atom $i$, $Z$ is the number of nearest neighbors of atom $i$, $r^0_{ij}$ is an empirically determined bond valence parameter for the specified atom pair, $b$ is an empirically determined constant for all bonds, $d_{ij}$ is the distance between atoms $i$ and $j$, loop is the sum of bond valences in a closed circuit of alternating cations and anions, $n$ is the number of cation–anion pairs in the loop, and $w_k$ is a weight factor for the bond between atoms $k$ and $k + 1$ given by the following expression:

$$w_k = 1/\left(\frac{fv_k}{Z_k} + \frac{fv_{k+1}}{Z_{k+1}}\right) \qquad (6)$$

To accommodate crystal structures with defects, we modified the weighting scheme originally proposed by O'Keeffe.[3] O'Keeffe weighted all bonds by the inverse of the Pauling bond strength (defined as the *cation* formal valence divided by its coordination number). In effect, this definition emphasizes the importance of the stronger, shorter bonds around high valence or low coordination number cations. Although this definition also places greater weight on bonds around undercoordinated cations neighboring anion vacancies, the definition does not include the anion coordination number. Therefore, bonds from anions neighboring a cation vacancy are not weighted differently from those around fully coordinated anions. In the spirit of O'Keeffe's work, the weighting factors defined in eq 6 simply combine the bond strengths of both end members of each bond, thus reflecting coordination changes of both cations and anions in defective structures.

The bond valence parameters, $r^0_{ij}$, for specific atom pairs were determined by Brown and Altermatt[4] from information in the crystallographic data base. Because the values are derived from many cation environments, they typically have standard deviations of less than 0.01 Å. This also makes them readily transferable from material to material, unlike the parameters in empirical potential energy models, such as Born–Mayer–Huggins, which must be fit to reproduce the properties (minimum energy lattice parameters, bulk modulus, etc.) of a specific crystal.

The underlying principle of our approach is that the atoms in a defective crystal should seek positions such that eqs 4 and 5 are satisfied as nearly as possible. Thus, whereas conventional atomistic MC codes accept or reject a new atomic configuration based on whether or not it has a lower energy than a previous configuration, our acceptance criterion is based on the degree to which the new configuration adheres to the crystal chemical rules as expressed in eqs 4 and 5. Specifically, the acceptance criterion is given by the following equation:

$$\exp[-s_1(\sum|cv_i - fv_i|_{new} - \sum|cv_i - fv_i|_{old}) - s_2(\sum|loop|_{new} - \sum|loop|_{old})] > 1 \qquad (7)$$

where $s_1$ and $s_2$ are scaling factors that weight the relative influences of the atomic valence criterion and the loop

(8) Sato, T.; Kato, K.; Endo, T.; Shimada, M. *React. Solids* **1968**, *2*, 253.

(9) Rey, F.; Fornés, V.; Rojo, J. M. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 2233.

(10) McKenzie, A. L.; Fishel, C. T.; Davis, R. J. *J. Catal.* **1992**, *138*, 547.

(11) Kelkar, C. P.; Schutz, A.; Marcelin, G. In *Perspectives in Molecular Sieve Science*; Flank, W. H.; Whyte, T. E., Eds.; American Chemical Society: Washington, 1988; p 324.

criterion. The scaling factors also enforce an effective "temperature" on the system. Lower values of the scaling factors increase the configuration acceptance rate, mimicking the effect of an increase in temperature.

For each new configuration, the valence sum is compared to the sum of the formal valences and the loop sum is compared to zero. If the differences decrease, the new configuration is accepted. If the differences increase, the exponential is compared to a random number generated between zero and one and the configuration is accepted only if the exponential is greater than the random number, consistent with Metropolis sampling.[12] This method allows for a certain number of "bad" configurations to be accepted, thus allowing for the possibility of "climbing over the energy hill" from a metastable configuration to a more stable one.

The detailed application of the code involves cycling through all of the atoms and changing their positions until the valence sum and the loop sum no longer change, at which point the crystal is considered to be in "equilibrium". Each atomic MC step either (a) randomly displaces an atom within a specified radius or (b) randomly chooses a second atom, displaces both, and then interchanges them. The latter type of step allows large-scale atomic segregation to happen within a reasonable time frame. Because it bypasses diffusional processes, it does not permit the actual path of an atom to be traced. Vacancies are specifically labeled such that a cation can swap places with a cation vacancy or an anion with an anion vacancy. However, vacancies are not considered to be members of loops, nor do they have associated valences. After each cycle through all of the atoms, the simulation "box" volume is given a random adjustment by independently changing the three box lengths. This feature allows tetragonal or orthorhombic distortions to occur, but not monoclinic or triclinic distortions.

To improve the efficiency of the code, first nearest-neighbor lists which include all atoms within a specified cutoff radius are tabulated at the beginning of a run and updated only when an atom moves a specified distance (0.25 Å was found to be sufficient) from its original location. Loop members are similarly tabulated and updated. At each atomic step, only the calculated valences of neighboring atoms and loops which include the specified atom are updated, since the others are unaffected. All valences and loops are recalculated each time the volume is changed. Writing the code in this way enabled systems containing on the order of $10^4$ atoms to be simulated on a workstation in a reasonable amount of time.

The same computational procedure was followed for each of the simulations described in the next section. Ions were initially placed at ideal rock salt atomic positions with defects (substitutional cations and vacancies) introduced randomly. An equilibration run of 10 000 cycles (where one cycle comprises a displacement of each atom in turn, as described above, followed by a change in volume) was carried out with scaling factors $s_1$ and $s_2$ equal to 20 and 10, respectively, and maximum atomic displacements of ±0.01 Å. The low scaling factors effectively created a high-temperature environment, allowing the structure to relax from ideal. The $s_1:s_2$ ratio of 2:1 was selected because in the rock salt structure, every bond is counted twice in the bond valence sum, but four times in the loop sum. Therefore, the 2:1 ratio balances the influences of the two
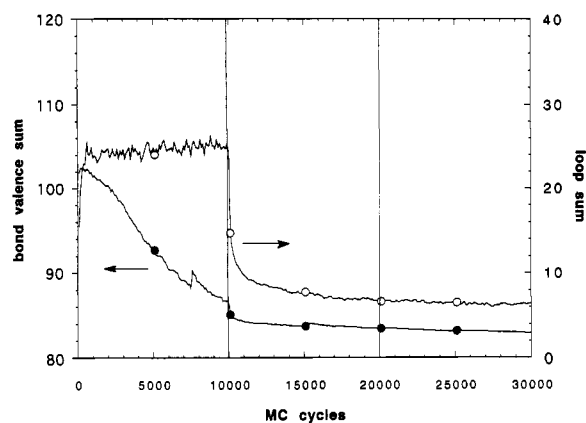
(12) Metropolis, N.; Rosenbluth, A. E.; Rosenbluth, M. N.; Teller, A. H.; Teller, E. *J. Chem. Phys.* **1953**, *21*, 1087.



**Figure 1.** Typical example of the MC bond valence equilibration procedure as described in the text.

acceptance criteria. Furthermore, the placement of atoms at ideal sites at the start of the simulation leads to a zero loop sum. Therefore, the heavier weight on the bond valence criterion allows new configurations which improve the valence sum to be occasionally accepted—based on the MC sampling procedure—even when they undermine the loop sum. A second equilibration run of 10 000 cycles was carried out at a lower effective temperature with scaling factors of 200 and 100, respectively, and maximum atomic displacements of ±0.0075 Å. Finally, a third 10 000 cycle run with the same scaling factors and displacements was used to calculate averages of the properties of interest, including the atomic positions, valences, and interlayer spacings. Figure 1 shows a typical example of the equilibration process for a crystal with two free surfaces. Vertical lines are drawn separating the three equilibration regions. As noted above, the imposed initial configuration of ideally occupied rock salt sites results in an initial loop sum equal to zero, but the bond valence sum is quite high. Improving the bond valence sum by atomic relaxation and segregation breaks the symmetry of the system, increasing the loop sum. Equilibration of the two factors results in a compromise between the two, as demonstrated by the simulation results.

## Simulation Results

**Ideal MgO with Two Free Surfaces.** A $6 \times 6 \times 6$ unit-cell cube with a total of 1728 atoms (for pure MgO) was used for all of the simulations. Periodic boundary conditions were enforced along the [100] and [010] directions, but the (001) surfaces were unconstrained. Average lattice parameters calculated after the equilibration period described above were 4.199, 4.199, and 4.199 Å for $a$, $b$, and $c$, respectively, indicating no bulk volume change or distortion. Very little surface relaxation was observed. The two outermost free surfaces contracted toward the bulk by 0.36% and 0.32%, respectively. (In all cases, we report the relaxation as a fraction of the calculated bulk layer spacing.) The layers immediately below the surfaces relaxed outward from the bulk by 0.05% and 0.03%. The remaining atoms occupied unrelaxed bulk positions, and the rumpling of the surface layer (the differential displacement of the anions and cations) was negligible.

Despite the small interlayer relaxation and negligible rumpling, atomic relaxation within the surface layer was observed. Had the surface been an ideal bulk termination layer, each surface ion would have had its coordination reduced symmetrically from 6 to 5, giving each ion a
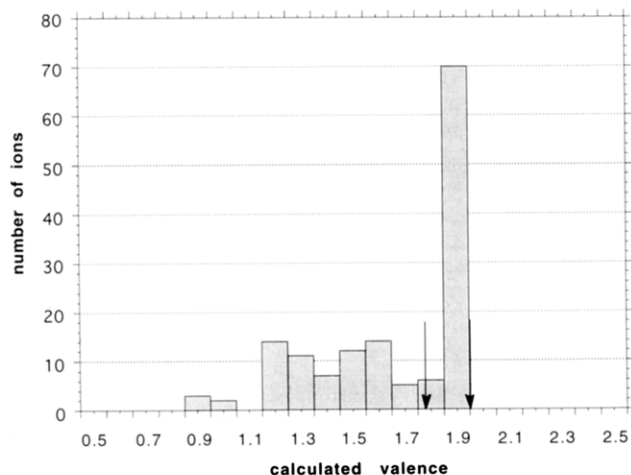
**Figure 2.** Calculated atomic valence distribution on the nondefective MgO (001) surfaces. The arrows indicate the locations of the bulk atomic valence for Mg cations and O anions (2.0) and of the expected atomic valence for Mg or O ions (1.83) on an unrelaxed bulk termination layer.

calculated valence of $(2 - 1/6) = 1.83$. Instead, a distribution of atom valences was observed, as demonstrated in Figure 2. From the figure it can be seen that half of the surface ions, 70 out of 144, attained close to their formal bulk valence of 2.0. To accommodate these "well-coordinated" ions, many of the remaining surface ions had to sacrifice their preferred coordination environment. Thus, one basic and possibly counterintuitive result of these calculations is that configurations which place the majority of the surface atoms at nearly ideal valence, at the expense of a few which exhibit larger deviations, globally adhere to the crystal chemical rules *better* than configurations that distribute smaller deviations equally among a greater number of atoms. The spatial distribution of the surface ion valences is shown in Figure 3. As a metric for quantifying the condition of the surface layer, we will report the fraction of surface ions having calculated valences different from their formal valences by more than 20%. Throughout the paper, such atoms will be called "unsatisfied". Although the 20% difference criterion is arbitrary, it was selected to exceed the valence deficit that would be caused by simply reducing the coordination number from 6 to 5. Using this metric, one third of the surface ions on the nondefective MgO (001) surfaces were unsatisfied.

**MgO with Two Free Surfaces and a Schottky Defect.** One Mg ion and one O ion were removed from randomly selected locations within the ideal 6 × 6 × 6 unit-cell MgO slab. Both the cation and anion vacancies segregated to one of the two free surfaces. No bulk volume change was observed, but the presence of the vacancies resulted in slightly more surface relaxation than in the ideal case. The outermost free surfaces contracted toward the bulk by 0.99% for the surface containing the two vacancies and 0.42% for the other free surface. Second layers relaxed outward by 0.11% and 0.08%, respectively. A very slight 0.01–0.02% relaxation away from the bulk was also observed for the third layers, but the remaining six bulk layers were unaffected. Rumpling of the surface layer was negligible. The presence of the vacancies in the one surface layer decreased the concentration of unsatisfied surface ions from one-third to one-fourth.

**MgO with Two Free Surfaces, Two Substitutional Al(III), and One Charge-Compensating Vacancy.** Two Al cations were substituted at randomly selected bulk Mg(II) sites and one Mg cation was removed to preserve
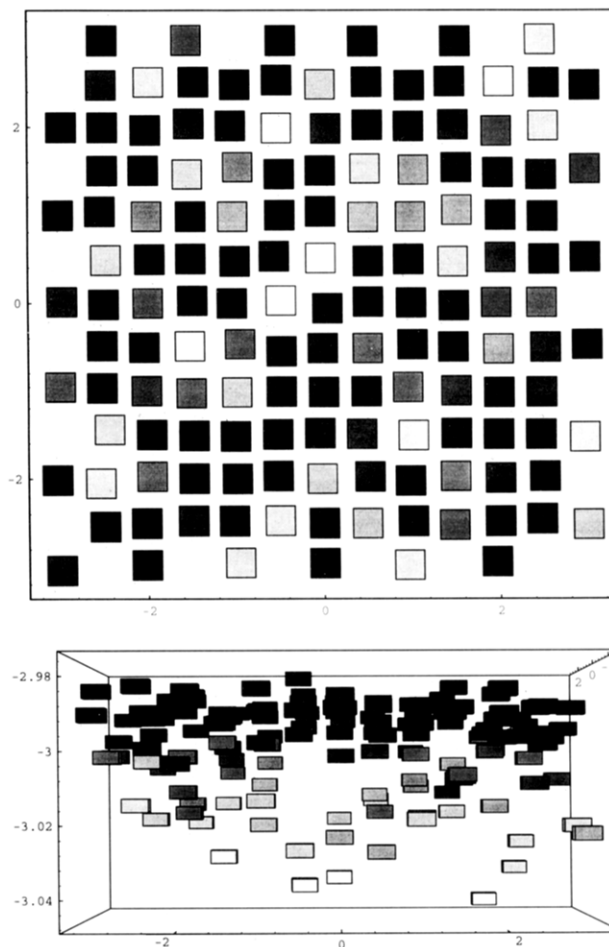


**Figure 3.** Spatial distribution of the calculated atomic valences on one of the nondefective MgO (001) surfaces. Shown is the bottom layer of the 6-unit-cell-thick slab at $z = -3$ lattice units. Spatial units are in lattice units of 4.199 Å. Mg and O ions are not distinguished, but they occupy alternating sites on the (001) surface. Black squares represent ions having an ideal atomic valence of 2.0 with decreasing atomic valence values represented by lighter shades of gray. (a, top) View looking down on the free surface. (b, bottom) View (a) rotated by 90° such that the view is parallel with the surface layer. Note that ions having closest to ideal valences (black) have relaxed further in toward the bulk crystal (positive vertical direction).

charge neutrality. Again, the defects were all observed to segregate to one of the free surfaces. The Al cations were unable to relax into positions such that their formal valence of 3.0 could be attained. Calculated valences for the two Al cations at the surface were 1.96 and 1.04, respectively. Surface relaxation was observed to be median between the ideal MgO surface and the MgO surface with the Schottky defect; the outermost layers contracted by 0.55% for the surface containing the three defects and 0.26% for the remaining surface. The second outermost layers relaxed outward from the bulk by 0.05% and 0.04%, respectively. Again, the remaining bulk layers were unaffected and rumpling was negligible. The concentration of unsatisfied surface ions was one-third on both surfaces.

**MgO with Mg:Al Ratio of 5:1.** Two simulations were carried out at this composition to study the influence of the free surfaces on the Al distribution. The first simulation enforced periodic boundary conditions in all three crystallographic directions, mimicking a bulk crystal, and the second incorporated two free surfaces as in the prior simulations. The 6 × 6 × 6 unit cell with a total of 864 cation sites contained 132 randomly distributed Al

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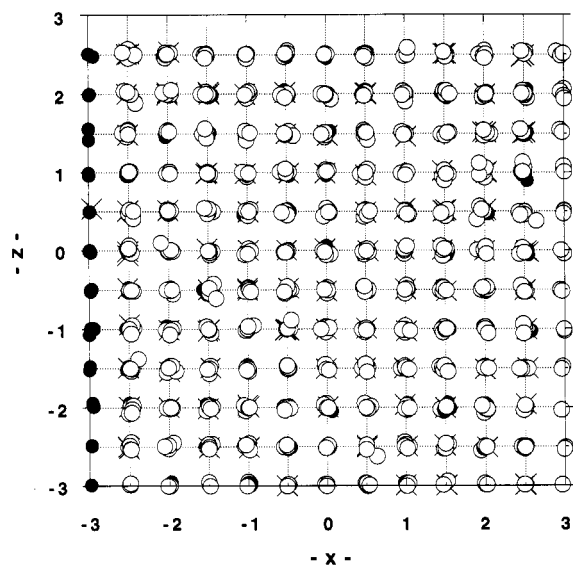
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**Figure 4.** Average ion positions in the bulk simulation of Mg-(Al)O with Mg:Al equal to 5:1. Coordinates are multiples of the cubic lattice parameter. View is parallel to the [010] direction. O anions are white circles, Mg cations are black circles, and Al cations are crosses.

cations charge compensated by 66 Mg vacancies.

The volume of the bulklike system with the periodic boundary conditions contracted significantly, a process that presumably was driven by the need for shorter Al–O bonds and by the presence of the large number of vacancies. The resulting cubic lattice parameter was 4.175 Å, a contraction of 0.57%. The fact that the crystal contracted is consistent with data reported by Sato et al.,[8] although the calculated magnitude of the contraction is approximately 3 times larger than that reported in ref 8. Despite the volume contraction, the average Mg–O bond length was 2.117 Å, 0.76% greater than the bond length in pure MgO. The average Al–O bond length was also compromised at 1.952 Å, 2.36% greater than ideal. The Al cations appeared to be randomly distributed throughout the bulk as shown in Figure 4. All Al cations appeared to be located at slightly distorted octahedral sites.

To probe the spatial distribution of the vacancies, partial radial distribution functions (prdf's) indicating the relative vacancy occupation of second, fourth, and sixth neighbor shells around Mg(II) and Al(III) were calculated. (Odd-numbered neighbor shells around cations are occupied by O anions.) Shown in Figure 5a, the calculated prdf's indicated that the positions of the vacancies were more highly correlated with the Al(III) positions than with the Mg(II) positions, particularly in the fourth-neighbor shell (distance of approximately 4.2 Å). This is reasonable in that O anions are expected to relax inward toward small Al cations but should relax outward from relatively negative Mg vacancies. As shown schematically in Figure 5b, fourth-neighbor Al(III)–vacancy pairs should best take advantage of this relaxation.

The Al(III) distribution in the simulated Mg(Al)O slab with two free surfaces was quite different from that in the bulklike simulation. Significant Al(III) and total vacancy segregation to the free surfaces were observed as depicted in Figures 6 and 7. The layer-by-layer compositional profile is shown in Figure 8. The outermost layers contained a Mg:Al ratio of 1:2, the second outermost layers increased in Mg content to a ratio of 2:1, and the bulk layers contained primarily Mg. An insignificant bulk volume change and distortion were observed, reflected in
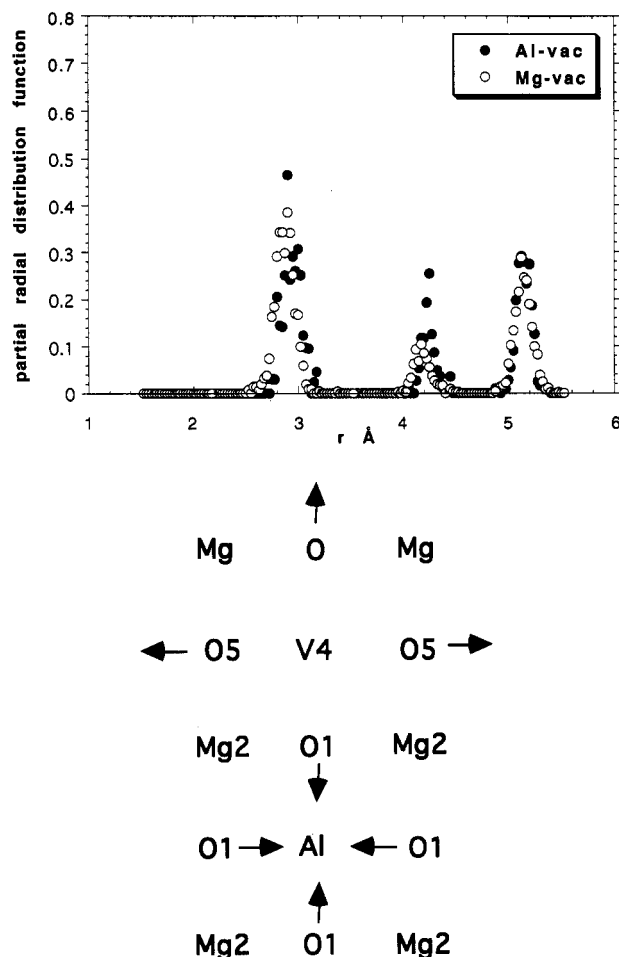


**Figure 5.** (a, top) Partial radial distribution functions (unitless) of vacancies around Mg(II) and Al(III). (b, bottom) Schematic diagram of the (001) surface showing O anion relaxation in the presence of a fourth-neighbor Al(III)–vacancy pair. Ion species are numbered according to the neighbor shell they occupy with respect to the Al(III). (For instance, O1 is an O anion in the first-neighbor shell of the Al(III).) The third-neighbor shell would be in the next layer.

the average lattice parameters of 4.195, 4.196, and 4.197 Å, for *a*, *b*, and *c*, respectively. However, the surface layer relaxations were significantly greater than those in the prior simulations. The outermost layers contracted by 9.86% and 10.20%, respectively. The second outermost layers also contracted toward the bulk, in contrast with the prior systems, by 0.11% and 0.40%, respectively. Much smaller contractions (the maximum of which was 0.06%) were observed for the third and fourth outermost layers. A small, but nonzero, rumpling occurred in the outermost surface layers. The difference between the average Mg-(II) and O anion locations was 0.3 Å and the difference between the average Al(III) and O anion locations was 0.15 Å. The average Mg–O bond length was 2.104 Å, very close to ideal, and the average Al–O bond length was 1.965 Å. Finally, the significant intralayer atomic relaxation within the surface layers, shown in Figure 7, resulted in all of the surface cations and 92% of the surface O anions attaining close to their formal valences.

## Discussion

Surface relaxations calculated by the MC bond valence method are summarized in Table 1 and compared with

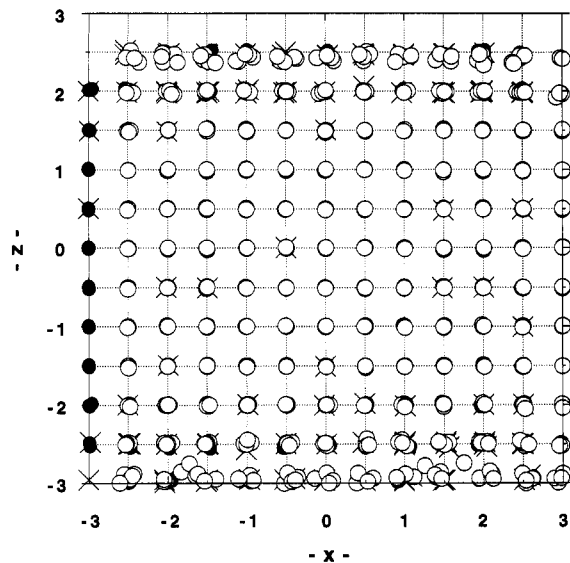(13) Kinniburgh, C. G. *J. Phys. C* 1976, *9*, 2695.

**Figure 6.** Average ion positions in the free surface simulation of Mg(Al)O with Mg:Al equal to 5:1. Coordinates are multiples of the cubic lattice parameter. View is parallel to the [010] direction. O anions are white circles, Mg cations are black circles, and Al cations are crosses.



**Figure 7.** Average ion positions in the free surface simulation of Mg(Al)O with Mg:Al equal to 5:1. View is parallel to the [001] direction. (a) Top layer in the 6-unit-cell-thick cell slab; $z = 2.5$ lattice units; (b) $z = 2.0$ lattice units; (c) $z = 1.5$ lattice units. O anions are white circles, Mg cations are black circles, and Al cations are crosses. Note the high concentration of Al(III) in the outer two surface layers and the more nearly ideal character of the third layer.

experimental and computational results from the literature. In general, all results agree that little surface relaxation occurs for pure MgO. The good agreement is perhaps fortuitous in that ambiguities exist with all of the techniques. The low-energy electron diffraction (LEED) analyses rely on careful comparison of experimental and calculated diffraction peak intensities. Calculations were carried out using first principles techniques, but the ionic positions, charges, and approximations for exchange correlation were assumed. Furthermore, the calculations assumed pure, nondefective MgO while the experimental results included the influence of small concentrations of defects. The shell model calculations involve interatomic potentials which were fit to reproduce bulk properties, making them less applicable for ions in nonequilibrium environments such as surfaces. MgO is, however, a good choice for such models because its properties do not change significantly from the bulk to the surface. In light of these remarks, the results of the MC bond valence method are no less uncertain than those from other techniques.

The results for the surface rumpling are more ambiguous. The experimental studies both claimed to be inconclusive. The MC bond valence results fell on the low end of the experimental results, indicating negligible rumpling. The shell model calculations, on the other hand, fell on the high end of the experimental results. Because electrostatic effects are not handled explicitly by the bond valence method, the ion polarization leading to rumpling is not captured by this method. However, the results are not inconsistent with experiment.

Point defect calculations in MgO have also been carried out by other methods. Mackrodt[16] calculated Mg and O vacancy formation energies both in the bulk and at the surface using the shell model. Assuming a flat surface, i.e., no rumpling, the vacancy formation energies at the surface were lower than those in the bulk, indicating that both cation and anion vacancies should tend to segregate to the surface. The MC bond valence results for the MgO
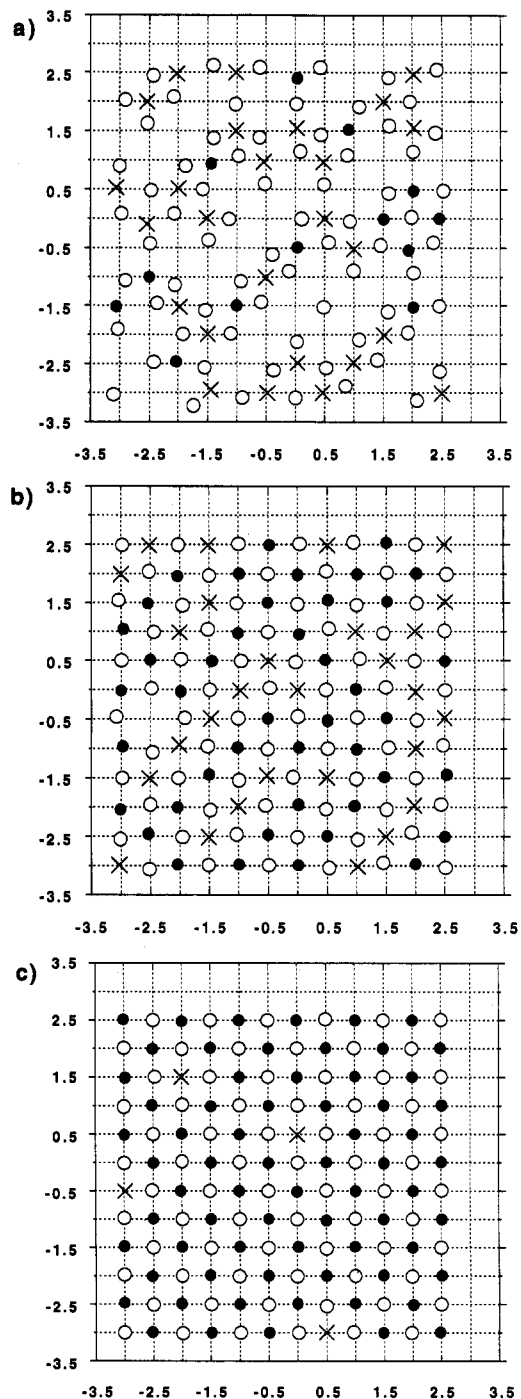
system with the Schottky defect are consistent with this result. However, Mackrodt carried out a second calculation of the vacancy formation energies assuming that the MgO surface is rumpled, as his results predicted it to be. Surface rumpling implies the existence of a charge dipole which creates a spatially extended potential throughout the entire crystal. This potential affects the defect formation energies. Mackrodt's results under the nonzero rumpling assumption show that while O vacancies should still segregate to the surface, Mg vacancies should be more

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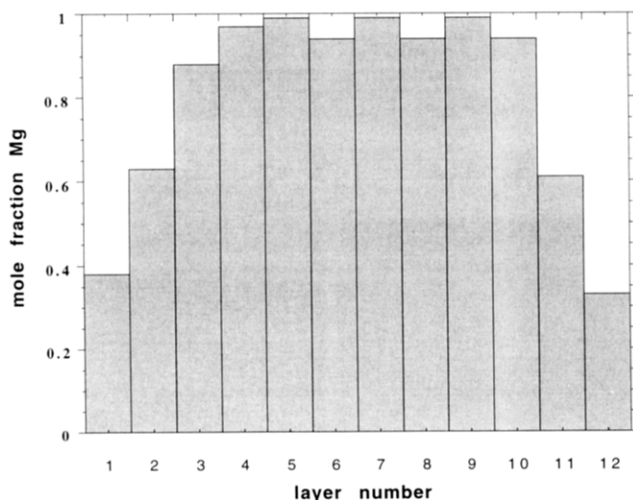*Chem. Mater., Vol. 6, No. 4, 1994* 507



**Figure 8.** Average layer-by-layer composition calculated for the free surface simulation of Mg(Al)O with Mg:Al equal to 5:1. Layers 1 and 12 are the free surfaces.

**Table 1. MgO Surface Relaxation and Rumpling. Values Reported as Percentages of the Calculated Bulk Layer Spacing**

|  | relaxation | rumpling |
|---|---|---|
| ideal MgO | −0.34 | ~0 |
| MgO with Schottky defect | −0.99 | ~0 |
| MgO with 2 Al, 1 Mg vacancy | −0.55 | ~0 |
| Mg(Al)O Mg:Al = 5:1 | −10.03 | 0.14 |
| MgO LEED[13] | 0 to −3 | 0 to +5 |
| MgO LEED[14] | 0 to +2.5 | ~0 |
| MgO shell model calculation[15] | 0 | ~7 |
| MgO shell model calculation[15] | 0 | 7 |
| MgO shell model calculation[15] | 0 to −2 | ~2.5 |
| MgO shell model calculation[16] | \|x\| < 3 | 3 |

stable in the bulk. Again, the limitations of the bond valence method do not allow us to probe this point.

Turning to the more complicated MgO solid solution with 17% Al(III), experimental information is available only for polycrystalline samples, and therefore detailed experimental data describing the surface relaxations are unavailable. However, X-ray photoelectron spectroscopy (XPS) results for samples with compositions similar to the one considered here indicated that the Al(III) segregates to the surfaces.[10] McKenzie et al. [10] reported a Mg:Al surface ratio of 2.4:1, compared to an elemental analysis derived bulk ratio of 4.57:1. The MC bond valence simulations resulted in a surface layer Mg:Al ratio of 1:2, a second outermost layer ratio of 2:1, and an approximately 19:1 ratio in the bulk. The extreme depletion of bulk Al(III) demonstrated by the bond valence calculations can be explained by the small total number of atoms and the resulting proportionately high (relative) surface area. Nonetheless, the simulated high Al(III) segregation to the surface is supported by the experimental results.

As discussed in the Introduction, one of our primary interests was to observe how the mixed oxide structure accommodates the Al cations. As mentioned earlier, NMR experiments have suggested both tetrahedral[9,10] and octahedral[11] coordination for Al(III). Normally, ions in the rock salt structure occupy only octahedral sites, but smaller tetrahedral sites do exist. (If all of the cations in

the rock salt structure are moved from the normal octahedral sites to tetrahedral sites, the sphalerite structure is formed.) None of the bulk Al cations in our simulations, neither in the bulklike simulation nor in the simulation of the slab, moved to the tetrahedral sites. Al ions at the surface in the slab simulation were certainly in distorted coordination environments, as demonstrated in Figure 7, but only two Al ions were found to have 4-fold coordination. McKenzie et al.[10] indicated that the relative number of tetrahedral to octahedral Al ions varied with sample preparation. It is possible that "annealing" schedules other than the one imposed during the MC bond valence simulations presented here could result in alternative local environments for the Al(III).

Finally, the MC bond valence method provides an intriguing means of explaining surface reactivities. McKenzie et al.[10] reported that the mixed Mg(Al)O materials have a lower concentration of surface base sites (10–15% of the surface sites) than pure MgO (25% of the surface sites) and a concentration of surface acid sites lower than pure $Al_2O_3$. In particular, they noted that even though the surface apparently possessed a high concentration of Al(III), the Al ions were not as reactive as those on pure alumina surfaces. If we make the assumption that surface ions possessing ideal formal valences are inert and that deviation from this ideal increases the reactivity of the ion, then we can correlate the concentration of the "unsatisfied" ions defined earlier to the surface reactivity. The simulation results indicate that, because of the amount of relaxation present on the Mg(Al)O (5:1) surface, none of the surface cations and only 8% of the surface oxygens are unsatisfied. On the other hand, the concentration of unsatisfied ions on the pure MgO surfaces and the MgO surfaces with small quantities of impurities was between 25% and 33%. Therefore, the experimental observation that the mixed oxide surfaces are less reactive than the pure oxide surfaces correlates with the more complete bonding on these surfaces predicted by the simulations.

## Conclusion

We have developed a new technique for simulating the atomic structure of ideal and defective crystals. A MC bond valence method was used to find an atomic arrangement that most nearly satisfies two empirical but quantitative crystal chemical rules. Simulations of the ideal MgO surface produced results consistent with experimental data. Simulations of Mg(Al)O solid solutions suggested that Al(III) substitutional impurities and cation vacancies segregate to the surface region, in accordance with experimental observations. Furthermore, the results indicated that ions on the surface of a concentrated solid solution (Mg:Al ratio equal to 5:1) have more nearly ideal bonding configurations than ions on the perfect MgO surface, suggesting an explanation for the reduced surface reactivity of the solid solution with respect to pure magnesia.