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LETTER TO THE EDITOR

***Ab initio* simulations of cation ordering in oxides: application to spinel**

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Abstract. At high temperature, MgAl_2O_4 spinel is stabilized by disorder of Mg and Al between octahedral and tetrahedral sites. Recent neutron experiments cover only a limited temperature range and are not sufficient to discriminate between analytic models. Electronic structure calculations have been used to parametrize on-site and short-ranged cluster potentials from a small number of disordered configurations. These potentials were then used in Monte Carlo simulations at finite temperatures to predict disordering thermodynamics beyond the range of experimental measurements. Within the temperature range of the experiment, good agreement is obtained for the degree of order.

Many oxides, including ceramics and minerals, have the potential for disorder of cations over different crystallographic sites. The entropy of such disorder can significantly stabilize these materials to an extent strongly dependent on temperature. The degree of order cannot always be easily measured experimentally, so we seek to develop first-principles models to both understand and predict such behaviour, which will have relevance to a wide range of oxides.

One example of such a material is the mineral spinel, MgAl_2O_4 . In the ordered structure Mg and Al ions occupy tetrahedral and octahedral interstices respectively, in a face-centred cubic lattice of oxygen ions (figure 1). However, on heating the structure becomes disordered by exchange of Mg and Al between sites. This in turn affects partitioning of Al between this and other mantle phases, and thus global geophysical and geochemical models. Accurate knowledge of the thermodynamics of this disorder is therefore required. Recent neutron diffraction measurements [1] obtained values for the order parameter and bondlengths up to approximately 1700 K. However, this range is insufficient to distinguish between different models of disorder and properly describe the degree of short-range order.

In this work we demonstrate a method of using *ab initio* electronic structure simulations to formulate a simple model for the effective interactions governing the disordering process, using one-, two- and three-body interactions between neighbouring sites. This model is then used in Monte Carlo simulations to predict the disordering thermodynamics over a wide range of temperatures without any input from experiment. We show that good agreement with experiment is obtained.

Cation disorder has previously been studied in several silicates using computer simulations, but in most cases disorder takes place between sites which are indistinguishable at high temperature, such as Al/Si disorder over equivalent tetrahedral sites. In such systems any transition will occur at a well-defined temperature T_c , since reversing the state of the system by replacing each cation with one of other species should have no effect on the energy. Such

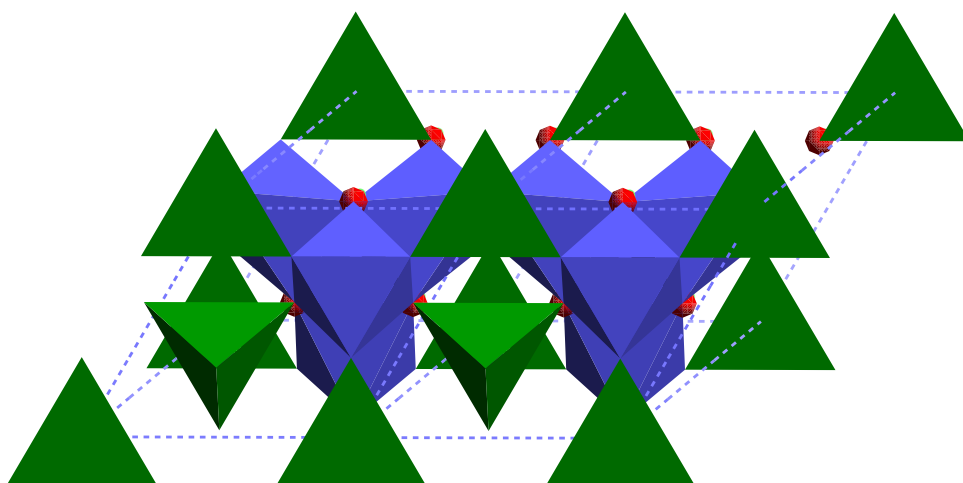


Figure 1. Two primitive unit cells of normal spinel. All tetrahedra contain Mg and all octahedra contain Al.

systems have been successfully modelled by a series of interactions between cations in different sites [2, 3]. In convergent ordering transitions the dominant mechanism for ordering is thus elastic interaction, so effective interactions may be fitted to the results of empirical models, which use interatomic potentials optimized for mineral systems.

In contrast, in spinel the two sites associated with Mg and Al at low temperatures are not equivalent, and even apart from the restrictions of stoichiometry the cation distribution could not be inverted without greatly changing the energy. An extra effect must therefore be included in any atomistic model. Here we refer to this as the ‘chemical potential’ μ in analogy to the effect of replacing a Mg by an Al ion. The existence of a chemical potential also affects the nature of the phase transition by removing the sharp transition point, rendering the transition non-convergent, with the order parameter never falling to zero. The chemical potential thus represents the energy difference between a Mg atom in a tetrahedron and in an octahedron, and must have its origins in complex electronic differences between these two environments.

In this work we use density functional theory (DFT) with pseudopotentials representing the atomic cores and a plane-wave basis set for the electron distribution [4], thus making no assumptions about the bonding. Empirical interatomic potentials are not usually optimized to give a reliable value for the change in energy when a cation changes its coordination. For this reason we need to use electronic structure calculations to give an accurate value for μ . In principle the empirical potentials could be modified to account for the changes in coordination of the Al and Mg cations, but this would require fitting to the DFT energies of different atomic configurations. In the present context this step was not considered to be worthwhile, but clearly in more complex cases there may be some value in this process, particularly if it could lead to a significant reduction in the number of DFT calculations required. Both the local density approximation (LDA) and the generalized gradients approximation (GGA) were used, giving two sets of results. Simulations were performed with the CETEP code [5] on a parallel supercomputer, using norm-conserving pseudopotentials, a supercell of 56 atoms, and a $2 \times 2 \times 2$ Monkhorst–Pack set of k -points.

For each cation configuration used, the cell vectors and atomic positions were relaxed to equilibrium, in recognition that each unit cell in a real crystal will not locally have precisely

equal and orthogonal lattice parameters. Because of high computational demands, the process was restricted to only ten configurations. These were chosen by first including the ground state and ordered (cubic) inverse configuration, and then selecting eight others with the number of Mg \leftrightarrow Al exchanges N ranging from one to eight. The positions of Mg and Al within this constraint were chosen randomly. The energies obtained with the LDA are shown in figure 2.

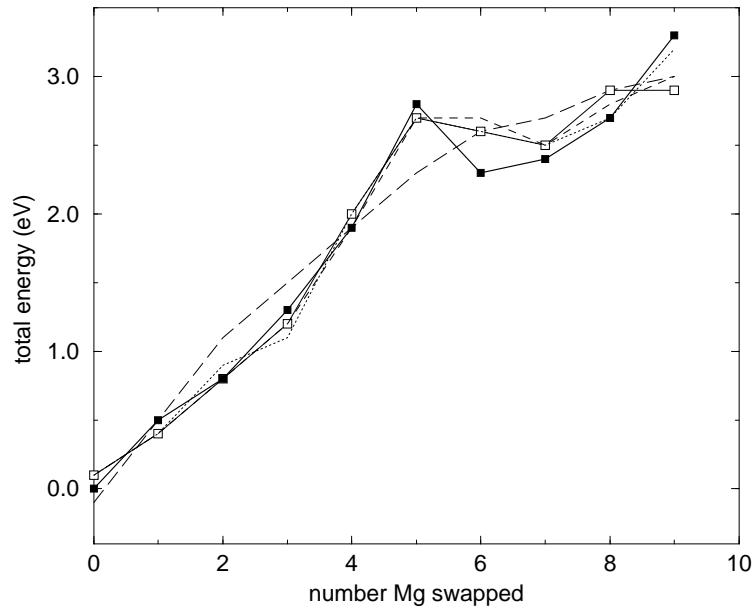


Figure 2. Total energy difference from DFT calculations of eight formula units with the LDA (■), against the number of Mg \leftrightarrow Al exchanges in a random set of configurations, with fits using varying numbers of terms. An ordered inverse configuration with $N = 8$ is shown at $N = 9$ for clarity. E_0 , μ and J_{46} are always fitted, plus others as follows: J_{66} , giving variance 0.77 (—□—); K_{466} , variance 0.35 (—□—); J_{66} and K_{466} , variance 0.31 (—·—); J_{66} , K_{466} and K_{566} , variance 0.23 (·····). Only fits including at least one three-body term reproduce the main deviation from linearity.

Traditional pair interaction terms of the form $J \sum \sigma_i \sigma_j$ were fitted for nearest-neighbour tetrahedron–octahedron (4–6) pairs and octahedron–octahedron (6–6) pairs, where $\sigma = 1$ represents Mg and $\sigma = -1$ for Al. Additionally, three-body terms were used with the form $K \sum \sigma_i \sigma_j \sigma_k$ for two different sets of clusters of a given geometry. Clusters in which all three polyhedra share a common oxygen were used (4–6–6 or 6–6–6).

A linear least-squares fit was used to find the parameters for fitting schemes with different combinations of terms. As shown in figure 2, at least one three-body term was found necessary for a good fit to the first-principles data. The scheme which was found to best fit the data with the smallest number of parameters, and thus to be the most robust, used only a single pair interaction term, between 4–6 pairs sharing oxygen atoms, and a 4–6–6 three-body term. Parameters are given in table 1 for the two sets of total energy data.

The parameters obtained by fitting to energies obtained using the LDA and the GGA appear to differ significantly (table 1). The total energies calculated with the GGA have a near-linear relationship to those with the LDA, so we believe the differences in fitted parameters are due to correlation between cluster populations rather than significant differences in the original calculations. Both sets of parameters were used for Monte Carlo calculations and gave very

Table 1. Values of model parameters obtained from DFT calculations with LDA and GGA.

(eV)	LDA	GGA
μ	0.4318	0.5568
J_{46}	0.0286	0.0707
K_{466}	-0.0153	-0.0284

similar behaviour at high temperatures. However, the GGA parameter set did not give the experimentally known ordered state at low temperatures, but instead a state with very slightly lower energy. We believe that this outcome from the GGA results is an artefact of the limited datasets and number of parameters, rather than a failure of the method as a whole.

The parameters described above define a very simple model which can then give the energy of any cation distribution to a good approximation. To take account of thermal fluctuations and obtain thermodynamic data over a range of temperatures, Monte Carlo simulations were used. Vibrational entropy is not included but is not expected to be the dominant effect [6]; this has not been proven but good results have been obtained in other systems with this assumption. Our Monte Carlo simulation cell contained $8 \times 8 \times 8$ unit cells, each of 24 cations as above. Simulations were performed with 10^7 attempted pair exchanges and separate runs started at different temperatures gave identical results within the level of noise.

Our model for disorder in spinel can be tested by comparing the average degree of

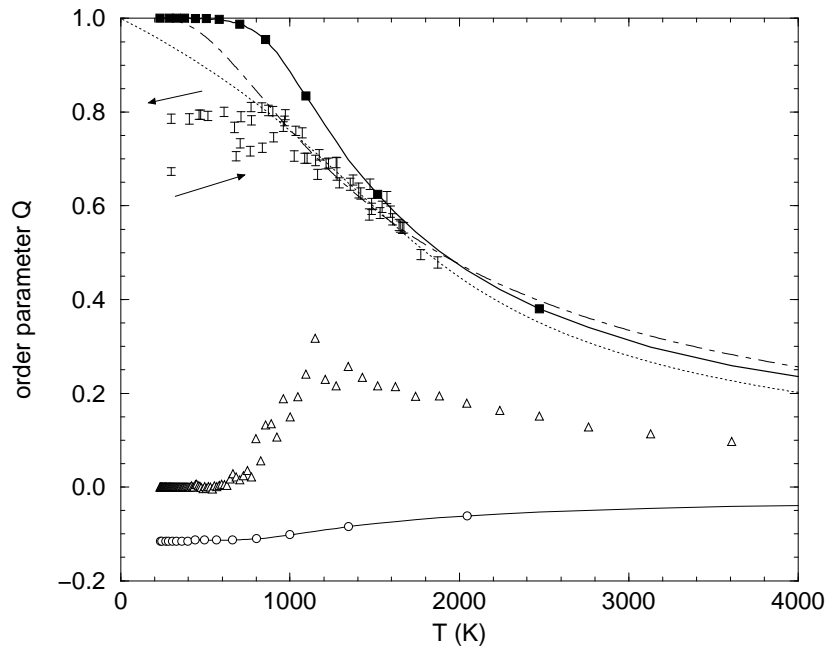


Figure 3. Results of Monte Carlo simulations, compared to results of three neutron scattering experiments and fits of analytic models to experimental data [1]. The order parameter Q is shown as \blacksquare , the energy of ordering as \circ , and the susceptibility $(\langle Q^2 \rangle - \langle Q \rangle^2)/T$ is amplified and shown as \triangle . The experimental values of Q were fitted by Redfern *et al* [1] to a Landau model (\cdots) and the model of O'Neill and Navrotsky ($-\cdot-$) [7]. The experimental data cover both heating and cooling, as indicated by arrows, and are kinetically limited below 1000 K.

order from the Monte Carlo calculations to the experimental measurements. As in all phase transitions, an order parameter Q may be formulated, defined as unity for perfect order and zero for the random state. The degree of exchange between tetrahedra and octahedra can also be quantified by the degree of inversion x , the fraction of Al in tetrahedral sites. Complete order thus has $x = 0$ and maximum exchange ($x = 1$) has octahedral sites half occupied with Mg, but may be ordered or random. These two indicators are related by $Q = 1 - 3x/2$.

The predicted order parameter (figure 3) is very close to that experimentally measured for almost all temperatures. Whilst not within experimental error bars, the agreement is striking for a model controlled only by three active parameters (since the reference energy E_0 will not affect the order parameter). This prediction is obtained only from first-principles data, without any input from experiment, and thereafter by introducing a large degree of simplification, so we regard this level of agreement with experiment as a successful demonstration of the method.

During the Monte Carlo calculations, a range of temperatures T is used, giving Boltzmann exponents of the form mJ/kT (for a representative interaction J and population m). This is analogous to using a variable interaction strength λJ where $\lambda = 1/T$. If λ falls to zero, a non-interacting system is obtained, in which only configurational entropy (S_{config}) contributes to the free energy. We thus have a natural link between a simple system for which the free energy is known and the full system for which we should like the free energy [8]. The method of thermodynamic integration can then be used, which yields the Helmholtz free energy $F(T)$ given the enthalpies of the intermediate systems.

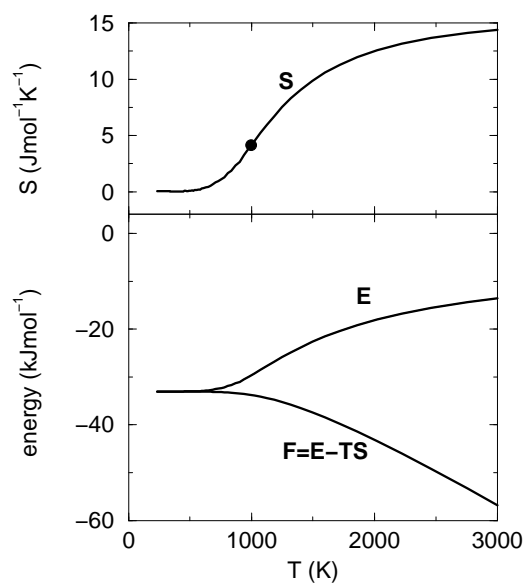


Figure 4. Enthalpy, entropy and free energy of disorder obtained from Monte Carlo simulations and thermodynamic integration, with a value deduced by Wood *et al* [9] in order to match known phase boundaries.

From values of $F(T)$ and $H(T)$ one can obtain $S(T)$. In the non-interacting system the entropy would be $k \ln W$ for the number of ways in which the cations could be distributed over available sites, but the fact that different configurations have different energies imposes at least short-range order, reducing the disorder and hence the entropy. At high temperatures, the system approaches complete cation disorder, and thus $S(T)$ approaches the maximum value

S_{config} ($15.88 \text{ J mol}^{-1} \text{ K}^{-1}$) asymptotically as Q approaches zero.

Figure 4 shows the calculated entropy and a value presented by Wood *et al* [9], who calculated the entropy needed to reproduce known phase boundaries at one temperature. At this temperature the theoretical predictions are in excellent agreement with the required value.

Without recourse to experimental data, we have thus obtained accurate predictions of the thermodynamics of the disordering process in spinels. From only a small number of first-principles calculations we have been able to successfully describe the behaviour of the order parameter in remarkably good agreement with experiment. This approach has powerful predictive capabilities and is applicable to a wide range of oxides.

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