

Disordering of MgAl_2O_4 spinel from first principles

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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. This behaviour has been measured up to 1700 K in recent neutron experiments, but the extrapolation of subsequently fitted thermodynamic models is not reliable. First principles simulation of the electronic structure of such minerals can in principle accurately predict disorder, but would require unfeasibly large computing resources. We have instead parameterized on-site and short-ranged cluster potentials using a small number of electronic structure simulations at zero temperature. These potentials were then used in large-scale statistical 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. The entropy and free energy are calculated and compared to those from macroscopic models.

KEYWORDS: disorder, spinel, neutron experiment, electronic structure calculation, Monte Carlo.

Introduction

IN the ground state at zero temperature, MgAl_2O_4 spinel contains Mg in tetrahedra and Al in octahedra. At high temperatures, disorder from cation exchange between these sites increases the thermodynamic stability. 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 by Redfern *et al.* (1999) obtained values for the order parameter and bond lengths 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. Here we demonstrate a method of obtaining thermodynamic properties from first principles over a large range of temperatures, tested by reference to these experimental results.

Cation disorder has been studied in several mineral systems with computer simulations, but in most cases disorder takes place between sites which will be indistinguishable at high tempera-

ture, such as Al/Si disorder over equivalent tetrahedral sites. This has the consequence that the transition will occur at a well-defined temperature T_c , and that reversing the state of the system by replacing each cation with one of other species should have no effect on the energy. Such systems can be modelled by a series of interactions between cations in different sites and such models have been successfully demonstrated (Thayaparam *et al.*, 1996; Dove *et al.*, 1996).

However, 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' in analogy to the effect of replacing a Mg by an Al ion. The energy difference between a Mg atom in a tetrahedron and in an octahedron is therefore dependent on this chemical potential μ . This 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 degree of exchange between tetrahedra and octahedra can be quantified by the degree of

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inversion x giving the fraction of Al in tetrahedral sites. Complete order thus has $x = 0$ and complete anti-order at $x = 1$ gives maximum exchange with octahedral sites half occupied with Mg. A fully disordered structure has $x = 2/3$. Alternatively, the order parameter Q may be used, defined as unity for perfect order and zero for the random state. This generates the relation $Q = 1 - 3x/2$.

In this work we formulate a simple model for the disordering process in terms of one-, two- and three-body interactions between neighbouring sites. The strengths of these interactions are determined from very accurate electronic structure calculations. The simple model is then used in very large simulations to predict the disordering thermodynamics without any input from experiment, and we show that good agreement with experiment is obtained.

Determination of interaction parameters

We aim to represent the complex electronic effects involved in exchange of Mg and Al ions with a small number of effective interactions between sites. The exact choice of interactions is described below, but further details of the fitting process are described by Warren *et al.* (2000).

Interaction strengths can be determined from a more sophisticated model, by adjusting them to best reproduce the calculated energies of a set of cation configurations. The accuracy of the reference model will of course affect the reliability of the simple model generated, but as simulation methods increase in accuracy they also increase in the requirements for computational resources.

Several previous studies, referenced by Dove *et al.* (1996), applied this technique to results from an empirical code using interatomic potentials optimized for mineral systems, with successful results. However, all but one of these studies were applied to convergent ordering in systems with only one type of site, in which the dominant mechanism is elastic interaction via bond-bending and stretching. The one case in which sites were distinct concerned non-equivalent tetrahedral sites so is still rather different to the case discussed here.

However, in spinel there will be significant electronic effects as the number of coordinating oxygens changes around the cations, from [4] to [6]. A more sophisticated reference model is thus needed, which calculates the energy by finding the electron distribution, and so is capable of

accurately calculating the differences in bonding. In this work we use the density functional theory in the local density approximation, with pseudopotentials representing the atomic cores and a plane-wave basis set for the electron distribution (Payne *et al.*, 1992), thus making no assumptions about the bonding. Simulations were performed with the CETEP code (Clarke *et al.*, 1992) on a parallel super-computer.

For each cation configuration used, the cell vectors and atomic positions were relaxed to equilibrium, in recognition that the lattice vectors of individual unit cells in a real disordered crystal will vary between cells, and may not be orthogonal. These simulations required large amounts of computer time, and the process was restricted to only ten configurations. These were chosen by first including the ground state and an ordered (cubic) inverse configuration, and then selecting eight others with the number of Mg \leftrightarrow Al exchanges N_X ranging from one to eight. The positions of Mg and Al within this constraint were chosen randomly.

The energies obtained from this process showed a clear increase from $N_X = 0$ to both the random and ordered $N_X = 8$. In the absence of other interactions, the chemical potential would be obtained from linear fitting of these data; it was thus shown to be a significant effect which must be included for realistic modelling.

A variety of parameterization schemes were used, with between four and six terms: a reference energy, an on-site term, pair exchange energies and three-body terms. Three-body terms were found necessary for a good fit to the first-principles data, but good agreement with available experimental data was obtained with only one of each class of terms. A linear least-squares fit was used to find the parameters from each fitting scheme, discussed in detail by Warren *et al.* (2000).

The scheme which was found to best fit the first-principles data with the smallest number of parameters, and thus to be the most robust, used a single pair interaction term, between [4]-[6] pairs sharing oxygen atoms, and a [4]-[6]-[6] three-body cluster term for sites with a common oxygen atom. This choice of parameterization does not imply that these are the only active interactions in the system, but rather that it is empirically found to include the essential processes with simplicity at the cost of accepting that complicated interactions have been absorbed into representative terms.

The chemical potential was fitted using the number of $\text{Mg} \leftrightarrow \text{Al}$ exchanges which had been made in each structure. Pair interaction (J) terms were fitted by the number of unlike bonds (i.e. $\text{Mg}-\text{Al}$) in each structure for each set of interactions. The three-body terms were fit to the sums of the products of the three spins (where -1 represents Ca and $+1$ Mg). Values of $\mu = 0.4318$ eV, $J_1 = 0.0286$ eV and $K_{466} = -0.0153$ eV were obtained from this fit.

Monte Carlo simulations

The parameters described above define a very simple model which can then give the energy of any cation distribution to a good approximation. However, the average energy at a given temperature, taking into account thermal fluctuations, is required to describe the thermodynamics of disorder.

Monte Carlo simulations sample a large number of configurations and yield an average energy properly weighted with the Boltzmann factors of each contributing instantaneous configuration. The simplicity of the parameterized models allows a very large number of unit cells to be used to generate possible configurations, thus giving accurate equilibrium properties. The average order parameter can also be calculated, and in this work can then be compared directly to those from experimental measurements. The kinetics of the disordering process are not predicted by Monte Carlo simulations, since the diffusion paths and mechanisms for disorder are not considered.

The only structural information put into these simulations is the connectivity. Changes in the volume and bondlengths with different ionic configurations are included only via the parameterization of energies from full cell relaxation. Vibrational entropy is not included but is not expected to be the dominant effect (Dove, 1997); this has not been proved but good results have been obtained in other systems with this assumption. Furthermore, the fact that the results fit the experimental data, and that the experimental behaviour can be well fit with statistical disorder models (Redfern *et al.*, 1999) suggest that this assumption is valid.

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 exchanges and separate runs started at different temperatures gave identical results within the level of noise.

Order parameter

Figure 1 shows the order parameter as a function of temperature, over the range of the experimental data. Two fits by Redfern *et al.* (1999) to the experimental data, using both a Landau and the O'Neill and Navrotsky (O'Neill and Navrotsky, 1983) functions are shown, but the limited range of those measurements is not sufficient to distinguish between these models, or to distinguish clearly between different Landau formulations. The ordering process is kinetically limited below ~ 1000 K, so fitted functions are extrapolated below this point.

The order parameter predicted by the Monte Carlo simulations is higher than that measured experimentally for almost all temperatures, and does not lie within experimental error bars. However, it should be remembered that only four parameters were fitted to the first-principles data, and since the reference energy E_0 will not affect the order parameter, only three parameters are effectively controlling the disorder. This prediction is obtained without any input from experiment, and with a large degree of simplification, so we regard this level of agreement with experimental results as a successful demonstration of the method.

At higher temperatures than those shown in Fig. 1 the Monte Carlo results lie in between the two extrapolated fits, which differ in Q by less than 0.06. However, at high temperatures the energies of interaction are increasingly overcome by entropy of disorder, and so we would expect the model to perform well here.

The order parameter behaviour is discussed further below, in the context of the Landau model for phase transitions.

Thermodynamic properties

The Monte Carlo simulations give values for the enthalpy $H(T)$ over a range of temperatures, but we wish to extend this to give the entropy and free energy. The method of thermodynamic integration was used (Yeomans, 1992) in which the full system is compared to a simple system for which the free energy is known; the full free energy can then be calculated from the enthalpies of a set of intermediate systems. During the Monte Carlo calculations, a range of temperatures T are used, giving Boltzmann factors J/T (for a representative interaction J). This is analogous to using a variable interaction strength J/T at constant

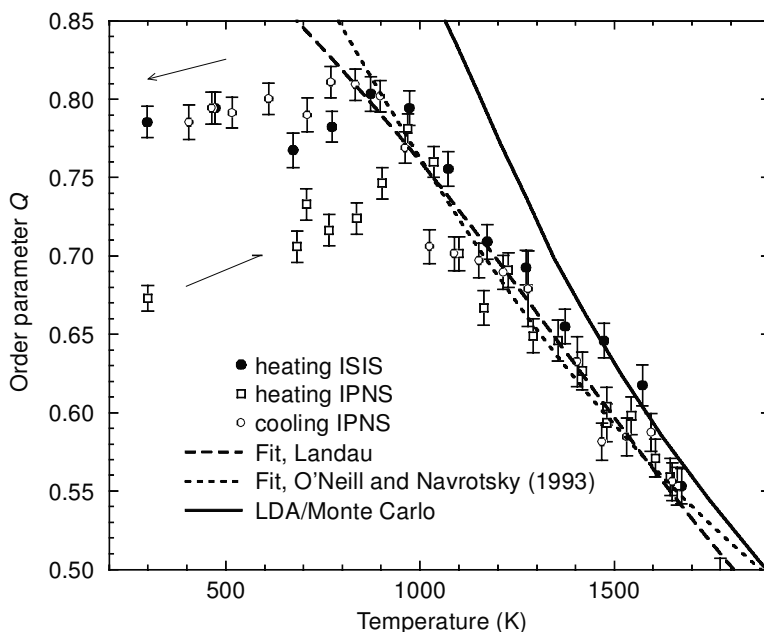


FIG. 1. Order parameter Q as a function of temperature over the temperature range of recent experimental measurements. Neutron diffraction measurements (Redfern *et al.*, 1999) were carried out at both the Rutherford Appleton Laboratory (ISIS) and the Argonne National Laboratory (IPNS) and at the latter measurements were made during cooling as well as heating. The experimental behaviour is affected by kinetics below 1000 K. The prediction from Monte Carlo calculations is shown (solid line) together with two fits of standard empirical models (dotted lines).

temperature. If J/T falls to zero, a non-interacting system is obtained, which will have complete disorder. In that extreme only a configurational entropy S_{config} contributes to the free energy. We thus have a natural link between a known simple system and the full system, and obtain the Helmholtz free energy $F(T)$ (Myers *et al.*, 1998).

From values of $F(T)$ and $H(T)$ one can deduce $S(T)$. In the non-interacting system the entropy would be $k \ln W$ for the number of ways W in which the cations could be redistributed, 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 its maximum value S_{config} asymptotically as Q approaches zero. S_{config} can be calculated analytically (O'Neill and Navrotsky, 1983) and is $15.88 \text{ J mol}^{-1} \text{ K}^{-1}$.

Figure 2 shows the calculated entropy and a value presented by Wood *et al.* (1986), who

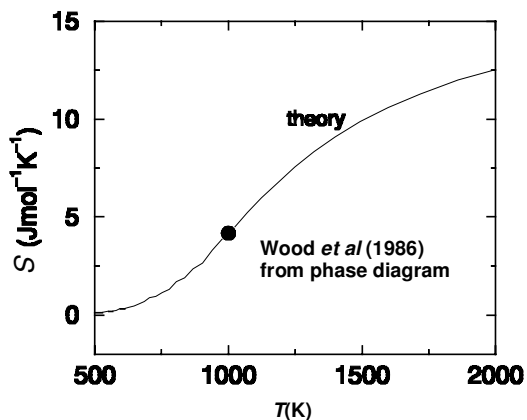


FIG. 2. Entropy as a function of temperature, calculated from thermodynamic integration of $H(T)$ obtained from Monte Carlo simulations. The entropy required to reproduce known phase diagrams (Wood *et al.*, 1986) at 1000 K is shown for comparison.

calculated the entropy needed to reproduce known phase boundaries at one temperature. The theoretical prediction presented here is in very good agreement with their value.

Fitting of Landau functions

Phase transitions in minerals are often described by the thermodynamics of a Landau function, which describes the free energy as a function of order parameter and temperature. It is usually written as:

$$F(Q; T) = F_0 + \frac{a}{2}(T - T_c)Q^2 + \frac{b}{4}Q^4 + \frac{c}{6}Q^6 + \dots$$

By requiring $\partial G/\partial Q = 0$ at any T , the equilibrium $Q(T)$ and $F(T)$ are obtained. The simulations in this work have produced values for both $F(T)$ and $Q(T)$, so if the Landau model is a good description of the system we should be able to fit both sets of data simultaneously with a single set of parameters.

However, for the case of spinel we include two further terms. Firstly the asymmetry between Q and $-Q$ expressed by the chemical potential removes the usual symmetry restriction to only even powers of Q , so a term hQ is included. Secondly, the free energy of the non-interacting reference system described above must be included. This is simply TS_{config} , representing the constant entropy of a fully disordered system. It is thus independent of Q and has no effect on the order parameter as function of T .

We thus expect a free energy of the form

$$F(Q; T) = F_0 + hQ + \frac{a}{2}(T - T_c)Q^2 + \frac{b}{n}Q^n - TS_{\text{config}} \quad (2)$$

where the highest power of Q has an exponent $n \geq 3$: here we try both $n = 4$ and $n = 6$. F_0 is independent of both Q and T ; temperature dependence of the reference free energy is represented by TS_{config} . At any given T , this predicts that the equilibrium order parameter is given by $\partial F/\partial Q$, so the T needed for some Q to be stable is

$$T = \frac{-h + aQT_c - bQ^{n-1}}{aQ} \quad (3)$$

and the free energy may thus be expressed as a function of T only. The value of T_c does not identify a sharp point where Q would fall to zero

TABLE 1. Values of parameters in the Landau free energy function, with either $n = 4$ or $n = 6$ and for different minimum temperatures. The known value of S_{config} was reproduced within 6% in a separate unconstrained fit. The function with an $n = 6$ term gave slightly better fitting for both T_{min} .

T_{min} n	700 K		1100 K	
	4	6	4	6
h (kJ mol ⁻¹)	-21.9	-25.0	-26.7	-27.4
T_c (K)	654	282	166	83
a (kJ mol ⁻¹ K ⁻¹)	0.030	0.030	0.030	0.030
b (kJ mol ⁻¹)	20.0		5.67	
c (kJ mol ⁻¹)		12.5		4.85

in a simple convergent phase transition, but is instead now a generalized reference temperature.

The Landau potential is well known to fail to describe behaviour at very low temperatures, since it cannot reproduce the plateau of $Q = 1$ in that region. We thus do not attempt to fit below some T_{min} : a high value of T_{min} gives a very good fit but a lower value does not perform so well and shows significant changes in the resulting parameters. Above this temperature, these adapted functions for $F(T)$ and $Q(T)$ were fitted simultaneously to the Monte Carlo data using a generalized least squares scheme for the parameters $\{F_0, h, a, b, T_c\}$, weighted between the two functions to best fit both of them. The results are shown in Fig. 3 and the parameters given in Table 1. The reference free energy F_0 is essentially arbitrary since it takes its reference point from the Monte Carlo parameterization, not the component oxides or other conventional energy.

Conclusions

We have demonstrated that even a limited number of accurate electronic structure calculations are sufficient to parameterize effective interactions and predict the thermodynamics of disorder in MgAl_2O_4 spinel. This work confirms that a chemical potential term is significant in this non-convergent system, and that its accurate determination requires first principles calculations. The success of this test against experimental results therefore provides confidence that the method may be applied to other systems.

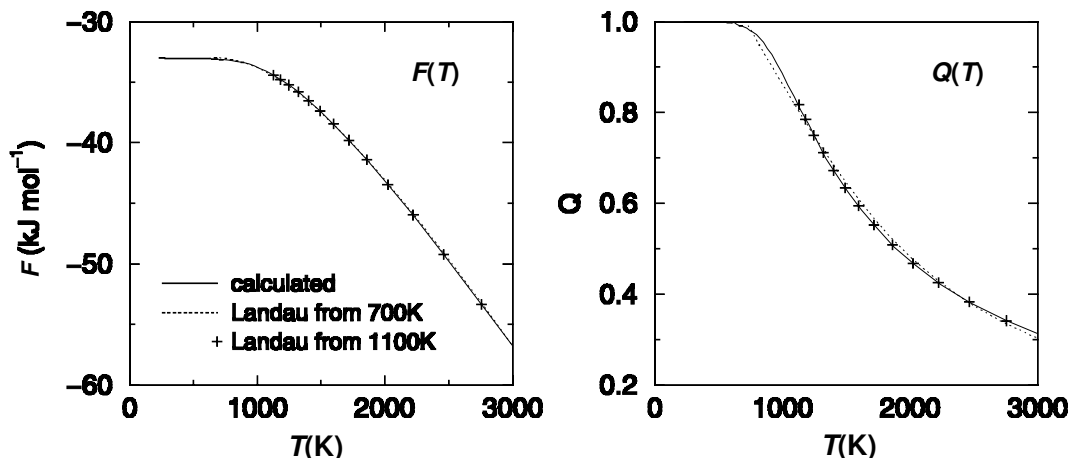


FIG. 3. Fits of the adapted Landau function with Q^4 to $F(T)$ and $Q(T)$ above 700 K and 1100 K. The fit with Q^6 cannot be distinguished on the scale of this graph.

A small number of reference calculations directly limits the number of terms which can be fitted reliably, and the small number of terms here will only be a generalized representation of the interactions rather than a comprehensive set of individual terms. Within this constraint three-body terms were found necessary to match reference energies well. However, the three active terms used in this work are thus not expected to be properly independent. As first principles methods become more efficient, and available computing power increases, larger number of configurations and thus more detailed fits will become practicable.

We have also shown that the Landau model for $F(Q,T)$ can be fitted consistently away from ordered state to obtain all parameters. However, the cleaner data provided by simulation serves to demonstrate that, as expected, at low temperatures the Landau description fails significantly and more sophisticated models would be needed to describe the whole temperature range. However, in the region of rapidly increasing disorder, a reasonable fit can be obtained.

The Monte Carlo method described here is presently being extended to systems with more than two cation species, in order to study systems with competing or cooperative disorder with more than one order parameter.

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