

Ordering in spinels—A Monte Carlo study

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ABSTRACT

We have extended a recently developed Monte Carlo technique which includes explicit exchange as well as movement of ions to systems involving heterovalent exchange. These Monte Carlo computer simulations, based on analytical inter-atomic potentials, are capable of providing detailed quantitative information concerning the thermodynamics of ordering of spinel (MgAl_2O_4), gahnite (ZnAl_2O_4), hercynite (FeAl_2O_4), NiAl_2O_4 , and magnesioferrite (MgFe_2O_4) over a range of pressures and temperatures. At all temperatures and pressures ionic relaxation, lattice vibrations, and pressure are *explicitly* taken into account. Each compound has a larger expansion coefficient and smaller bulk modulus in the normal than in the inverse spinel structure. We predict only a small variation of order parameter with pressure, and that this will be more pronounced for inverse than normal spinels. We examine, briefly, the consequences of our results for the kinetics of cation ordering in these solids.

INTRODUCTION

The continuing growth in computer power has led to a tremendous increase in the contribution of computer simulation to the understanding of the physical and chemical properties of minerals. Atomistic simulation techniques and ab initio methods have proved extremely useful in providing detailed and accurate predictions of the structures and properties of silicate minerals. The principal objectives of these computations are to obtain insight into atomistic or microscopic processes that underlie macroscopic phenomena and to carry out simulations at pressures and temperatures beyond the accessible range of experimental techniques (e.g., Hazen and Downs 2000; Allan et al. 2001). For example, calculated seismic velocity profiles can be used to supplement models of density contrasts derived from seismic tomography and test proposed compositional models for the mantle.

Geological materials are often poorly characterized since many minerals occur deep within the Earth's mantle and there are limitations in experimental techniques. This problem is acute since naturally occurring minerals contain a large number of elements, including minor and trace element impurities, which may be disordered over several crystallographic sites. Unfortunately, the present computational techniques available are largely restricted to *idealized* end-member systems (e.g., pure MgSiO_3 perovskite) since kinetic barriers prevent classical Monte Carlo and molecular dynamics simulations being undertaken within a realistic timescale. Contact between experiment and theory is thus considerably restricted which is unfortunate considering the importance of solid solutions in mineral physics.

This paper seeks to address some of these problems and to describe and apply a Monte Carlo technique that can be readily employed to study the ordering mechanisms of solid (or liquid) mechanisms of solid (or liquid mixtures). As an example, we calculate the degree of ordering of the spinels AB_2O_4 (e.g.,

MgAl_2O_4 , ZnAl_2O_4 , FeAl_2O_4 , NiAl_2O_4 , and MgFe_2O_4) over a range of temperatures and pressures. We compare our results with experimental data (where available) and calculations in the static limit using a parameterized Hamiltonian (Warren et al. 2000).

The structure of spinel is shown in Figure 1 (e.g., Sickafus et al. 1999). The O ions form a cubic-close packed array and in each unit cell there are 32 octahedral and 64 tetrahedral holes available for occupation by cations. Of these, 16 octahedral and eight tetrahedral sites are occupied by cations in a regular manner so that octahedra share edges with one another and the tetrahedra share corners with the octahedra. In "normal" spinels all the A-cations are at the tetrahedral sites and the B-atoms are entirely at the octahedral sites. In the "inverse" structure half the B-cations occupy the tetrahedral sites while the remainder and all the A-cations occupy the octahedral sites. Thus, the normal structure is completely ordered, while in the inverse structure, configurational disorder remains between A- and B-cations at the octahedral sites. However, this is an idealized picture. Spinel usually demonstrate some degree of disorder and in real systems the distribution of cations lies between the extremes represented by "normal" and "inverse" and is a function of temperature and pressure. Usually, the distribution of cations between tetrahedral and octahedral sites is described by the so-called inversion parameter, x : $(\text{A}_{1-x}\text{B}_x)_\text{T}(\text{B}_{2-x}\text{A}_x)_\text{O}_4$, where subscripts T and O refer to the cations at tetrahedral and octahedral sites, respectively (Navrotsky and Kleppa 1967; Navrotsky 1994). In this paper, we prefer to use an alternative description of spinels in terms of the order parameter, Q (Carpenter and Salje 1994; Harrison and Putnis 1999), which is defined as $Q = 1 - 3x/2$. Q varies from a value of one for completely normal spinels to -0.5 for completely inverse spinels. Q equals zero for a random arrangement of cations. Positive values of Q indicate thus a degree of normal ordering in spinels, while the negative values indicate some inverse ordering. Of the systems studied in this paper, MgAl_2O_4 , ZnAl_2O_4 , and FeAl_2O_4 are classified as normal spinels and NiAl_2O_4 and MgFe_2O_4 as inverse.

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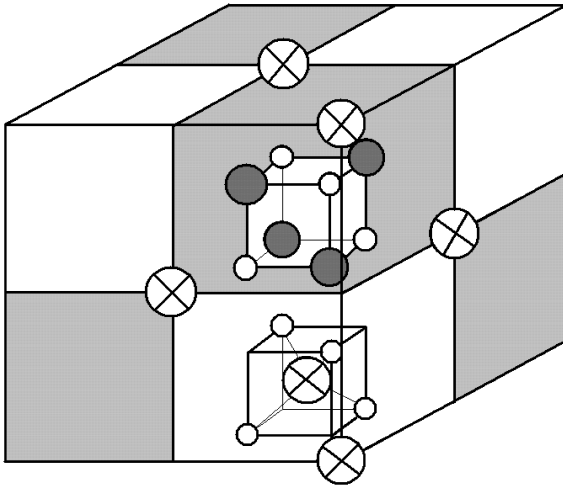


FIGURE 1. Cubic unit cell of AB_2O_4 spinel. A-cations = crossed circles, B-cations = grey circles, O atoms = small empty circles. The structure of normal spinel is shown, with A-cations occupying tetrahedral, and B-cations occupying octahedral positions.

Spinel, and especially $MgAl_2O_4$, are a geologically important group of minerals. For example, $MgAl_2O_4$ may exist up to 50–80 km within the upper mantle and reacts with pyroxene to form olivine and garnet. An understanding of the thermodynamics of ordering of $MgAl_2O_4$ and thus its stability has implications for trace element partitioning of transition metals and Al with other mantle phases. This paper is primarily concerned with the simulation of the disorder of spinels over a range of pressure and temperature.

METHOD

A key objective of our recent work (see for example Purton et al. 1998, 1999; Allan et al. 2001) is to study the phase equilibria of complex systems such as oxides, silicate melts, and minerals at any given temperature and pressure. Any technique that can be applied to systems of geological interest must meet the following criteria: (1) The kinetic barriers that prevent diffusion on the time scale of atomistic simulations must be overcome by generating the large number of configurations possible within a disordered phase. This can be achieved by making random changes to the identity of the ion(s) occupying a crystallographic site and sampling a range of low energy states. (2) Ions must be allowed to “relax” fully around the impurity ion. The importance of local relaxation around defects in polar solids is much greater in oxides than in metals and has been discussed extensively in the literature (Catlow and Mackrodt 1982). (3) Lattice vibrations must be included in the calculation. The role of lattice vibrations on the stability of materials is ambiguous. For example, in Ni_2Al the experimental difference in vibrational entropy between the ordered and disordered phases is approximately $0.2k_B$ (Fultz et al. 1995). The origin of this difference is controversial and may be due to a nearly uniform softening of modes caused by the increased volume of the disordered phase (Ravelo et al. 1998) or a significant decrease in the number of high frequency vibrational modes during the disordering process (Anthony et al. 1993). In addition, Purton et al. (1998) have demonstrated that removing the atomic vibrations from the simulation can influence the degree of ordering in $MgMnSiO_4$. (4) Methods must be extendable to different ensembles (i.e., the effects of pressure can be easily included in the simulation).

One approach, which has been used extensively to study metal alloys (for a review see de Fontaine 1996), binary oxide mixtures (Tepesch et al. 1995; Kohan and Ceder 1996), and more recently minerals (e.g., Bosenick et al. 2001), is to construct an effective lattice Hamiltonian by expanding the pseudobinary system in an orthogonal basis set of cluster functions. The expansion coefficients are derived from a least squares fit to energies obtained from either atomistic

simulations or ab initio electronic structure calculations. Once the Hamiltonian is constructed the cluster variation method (CVM) or Monte Carlo techniques can be used to examine the ordering behavior and thus to construct the phase diagram of the material. Although this approach has provided important insights into the phase behavior of metals, there are a number of problems with this method when applied to systems of geological interest. In particular vibrational and pressure effects cannot be included easily during the parameterization of the Hamiltonian (however, see van de Walle et al. 1998 and Sluiter et al. 1996). For this reason we have decided to build on atomistic simulation techniques (i.e., we have included ionic interactions explicitly) and omit the parameterization step, even though these simulations are computationally more expensive.

Monte Carlo simulations

As a starting point we describe the classical Monte Carlo technique for atomistic simulations and then discuss how this has been extended. During one step of the Monte Carlo simulation a random decision is made to alter one of the variables of the calculation, which may either be an atomic position or the cell dimensions, i.e., all simulations are carried out within the NPT ensemble and lattice vibrations are automatically included (Frenkel and Smit 2002). The magnitude of the change is also chosen at random, but within a specified amount and governed by the variables r_{max} and v_{max} respectively. The magnitude of these variables is adjusted automatically so that the magnitude of the acceptance/rejection ratio is 0.3. After each move/volume alteration the change in energy is calculated and a decision whether to accept or reject this is made according to the standard Metropolis scheme (Metropolis et al. 1953). We have extended this approach to allow the atomic configuration to evolve during the simulation (Purton et al. 1998). In addition to random movements of atoms or cell volume we also make an exchange of two cations (for example, Mg^{2+}/Al^{3+}) chosen at random with the acceptance/rejection decision made using the Metropolis scheme. In the minerals in this paper, the efficiency of this exchange is very low due to the difference in charge of the divalent and trivalent cations. For example, in $MgAl_2O_4$ at 1000 K the rate of successful exchanges of Mg^{2+} and Al^{3+} is only 1.6%, rising to 18% at 2500 K. Low exchange rate slows the equilibration, so that special methods are necessary to increase the rate of successful exchanges. To speed up the speed of sampling configurations we have applied the biased sampling technique, widely used in the simulation of molecules and polymers (e.g., Frenkel and Smit 2002). In our exchange-biased Monte Carlo (Lavrentiev et al. 2001), instead of considering a single trial exchange, a set of trial exchanges is picked at random. Suppose an exchange take place between atoms A and B. First, k pairs $\{A^i, B^i, i = 1, \dots, k\}$ are randomly chosen. We denote the system energy in the initial configuration as U_{old} and the energy of the system after exchange of atoms in the i th pair as U_{new}^i . One of the new configurations is then chosen with probability

$$p_i = \frac{\exp(-\beta(U_{new}^i - U_{old}))}{W_{new}}, \quad \beta = (kT)^{-1} \quad (1)$$

where

$$W_{new} = \sum_{i=1}^k \exp(-\beta(U_{new}^i - U_{old})) \quad (2)$$

The chosen configuration i (that after the exchange of the i th pair) with energy $U_{new}^i \dots U_{new}$ is then the trial configuration. However, the usual acceptance rule cannot be directly applied. Instead, starting from the new configuration, a further $k-1$ pairs $A^j, B^j, j = 1, \dots, k-1$ are chosen. Denoting the energy of the system after exchange of atoms in the j th pair U_{old}^j , we evaluate the expression

$$W_{old} = \exp(-\beta(U_{old} - U_{new})) + \sum_{j=1}^{k-1} \exp(-\beta(U_{old}^j - U_{new})) \quad (3)$$

Fulfilling detailed balance, the criterion for the acceptance of the new configuration is

$$\text{acc}(\text{old} \rightarrow \text{new}) = \min \left[1, \exp(-\beta(U_{old} - U_{new})) \frac{W_{new}}{W_{old}} \right] \quad (4)$$

Use of the exchange-bias technique with $k = 10$ makes possible Monte Carlo simulations with a successful exchange rate of Mg^{2+} and Al^{3+} in $MgAl_2O_4$ of 15%

at 1000 K and as high as 59% at 2500 K. This rate of exchange is sufficient for convergence for the systems of interest in this paper at the temperatures studied. All calculations were performed using a periodic cubic simulation cell containing eight unit cells (448 ions), and 5×10^6 steps in the accumulation stage following an initial equilibration of 2×10^6 steps. The resulting errors (standard deviations) were typically as follows: for the volume $\sim 0.02\%$; for the enthalpy $\sim 0.004\%$; for the the bulk modulus $\sim 4\%$; for the expansion coefficient $\sim 14\%$.

Potentials

All calculations are based on the ionic model using two-body potentials to represent the short-range forces [for a full discussion of this well-known model see, for example, Catlow and Mackrodt (1982) and Catlow (1997)]. We adopted the common Born-Mayer form for the potentials, with the O-O interaction supplemented by an r^{-6} attractive term: $V(r) = A \exp(-r/\rho) - C/r^6$, where A and ρ are constants. As a starting point, we chose the set of cation-O atom potentials derived for binary oxides by Lewis and Catlow (1985) and subsequently corrected and tabulated by Cormack et al. (1988), and the O-O potential derived by Catlow (1977). An important feature of this set of potentials is their dependence on the coordination number of the cation. Lewis and Catlow (1985) alter the preexponential factor when an atom changes coordination from octahedral to tetrahedral according to $A_{\text{tet}} = A_{\text{oct}} \exp(-\Delta r/\rho)$, where Δr is the difference in ionic radii between the two environments ($\Delta r = r_{\text{oct}} - r_{\text{tet}}$). Lewis and Catlow (1985) set Δr equal to $0.06r_{\text{oct}}$ and take r_{oct} from Goldschmidt (1948).

We have adjusted these potentials in several ways in the present study. The original set of potentials were obtained by fitting so that the experimental lattice parameters of the binary oxides at room temperature were reproduced by energy minimizations in the static limit, which neglect vibrational terms, and thus thermal expansion. To remove this inconsistency, the parameters ρ for the cation-O atom potentials and the charge of the Al ion were fitted using the Monte Carlo simulations described above to reproduce as closely as possible both the lattice parameter of MgAl_2O_4 at 973 K (Wood et al. 1986) and the observed order parameter of MgAl_2O_4 at 1500 K (Redfern et al. 1999). The resulting value of the parameter ρ for the cation-O atom potentials was 6% smaller than that of Lewis and Catlow (1985) and the ionic charges of Al and O were +2.3 and -1.65 respectively. This scaling of ρ was performed for all the cations and these values of charges were used for all the trivalent cations and O atoms in this study.

Potentials obtained in this way were used for MgAl_2O_4 and ZnAl_2O_4 . These potentials were also sufficient to give, for FeAl_2O_4 , NiAl_2O_4 , and MgFe_2O_4 , qualitative agreement with the observed order parameter (i.e., normal or inverse behavior at low temperatures) and good agreement with the experimental lattice parameters. We then made a few changes to the Fe-O and Ni-O potentials. In simulations of NiAl_2O_4 we chose also to alter A_{tet} for the Ni-O potential so as to reproduce the experimental order parameter at 1500 K (O'Neill et al. 1991). Similarly, for the Fe-O potentials in FeAl_2O_4 (divalent Fe) and MgFe_2O_4 (trivalent Fe), both A_{tet} and A_{oct} were altered so as to reproduce the experimental order parameters at 1000 K (Harrison et al. 1998; O'Neill et al. 1992). The data used in the fitting and the final fitted values are listed in Table 1a. The final set of potentials is collected together in Table 1b.

RESULTS AND DISCUSSION

An important test of the new potentials is their ability to describe structural parameters of the systems studied not used in the fitting procedure, and their variation with temperature. For example, we calculated cation-O atom bond distances for MgAl_2O_4 at 1000 K. The average cation-O atom distance was 1.889 \AA for the tetrahedral sites; for the octahedral sites it was 1.938 \AA . In Table 2 we compare our results with two sets of experimental data as well as with results from the periodic Hartree-Fock ab initio calculations of Catti et al. (1994). Experimental results indicate the average cation-O atom distances in MgAl_2O_4 at 1000 K are in the region of $1.91\text{--}1.92 \text{ \AA}$ at tetrahedral and $1.93\text{--}1.94 \text{ \AA}$ at octahedral sites, respectively. Our simulation results are very close to experimental values for octahedral cation-O atom distances and differ by not more than 1–2% for tetrahedral cation-O atom distances. In contrast, Catti et al. (1994) obtain a cation-O atom distance for the tetrahedral

TABLE 1A. Experimental data used in the potentials fitting together with the final fitted values

System	Experimental data		Fitted value
	Lattice parameter	Order parameter	
Spinel (MgAl_2O_4)	8.0834 Å (973 K, Wood et al. 1986)		8.050 Å (1000 K)
Spinel (MgAl_2O_4)		0.61 (1480 K, Redfern et al. 1999)	0.624 (1500 K)
NiAl_2O_4		–0.1835 (1523 K, O'Neill et al. 1991)	–0.17 (1500 K)
Hercynite (FeAl_2O_4)		0.802 (973 K, Harrison et al. 1998)	0.81 (1000 K)
Magnesianoferrite (MgFe_2O_4)		–0.2165 (973 K, O'Neill et al. 1992)	–0.214 (1000 K)

TABLE 1B. Potential parameters used in this study

Ion pair	A (eV)	ρ (Å)	C (eV Å ⁶)
O-O	22764.0	0.149	20.37
Zn-O (tetrahedral)	488.1	0.3421	0.0
Zn-O (octahedral)	561.1	0.3421	0.0
Mg-O (tetrahedral)	710.5	0.3047	0.0
Mg-O (octahedral)	821.6	0.3047	0.0
Divalent Fe-O (tetrahedral)	510.0	0.3195	0.0
Divalent Fe-O (octahedral)	590.6	0.3195	0.0
Trivalent Fe-O (tetrahedral)	903.3	0.3101	0.0
Trivalent Fe-O (octahedral)	992.2	0.3101	0.0
Ni-O (tetrahedral)	635.6	0.3132	0.0
Ni-O (octahedral)	683.5	0.3132	0.0
Al-O (tetrahedral)	1012.6	0.2931	0.0
Al-O (octahedral)	1114.9	0.2931	0.0
Ion	Ionic charge ($ e $)		
O	–1.65		
Mg	+2		
Zn	+2		
Fe (divalent)	+2		
Ni	+2		
Al	+2.3		
Fe (trivalent)	+2.3		

Notes: The form of the potential function is $V(r) = A \exp(-r/\rho) - C/r^6$. Note different Fe-O potentials are used for divalent (FeAl_2O_4) and trivalent iron (MgFe_2O_4).

TABLE 2. Comparison of calculated and experimental data for cation-O atom distances in MgAl_2O_4

	Cation-O atom distance (Å)	
	Tetrahedral sites	Octahedral sites
Our results, $T = 1000 \text{ K}$	1.889	1.938
Redfern et al. (1999), $T = 1000 \text{ K}$	1.925	1.94
Andreozzi et al. (2000), $T = 1000 \text{ K}$	1.9141	1.9309
Catti et al. (1994), calculated (periodic Hartree-Fock theory, $T = 0$)	1.939	1.908

sites that was larger than that obtained for the octahedral sites, in marked disagreement with experimental results.

Thermal expansion

Figure 2 shows the temperature variation of the lattice parameters for the five spinels, and compares these with experimental data, where available. We also compare our calculated results for the lattice parameters with experimental data in Table 3. For all of the systems studied, our results are within 1–2% of the experimental data. A contentious issue is the thermal expansion of spinels. For example, for MgAl_2O_4 Andreozzi et al. (2000) reported that the lattice parameter actually decreases between 600 and 1100 °C, in contradiction, as shown in Figure

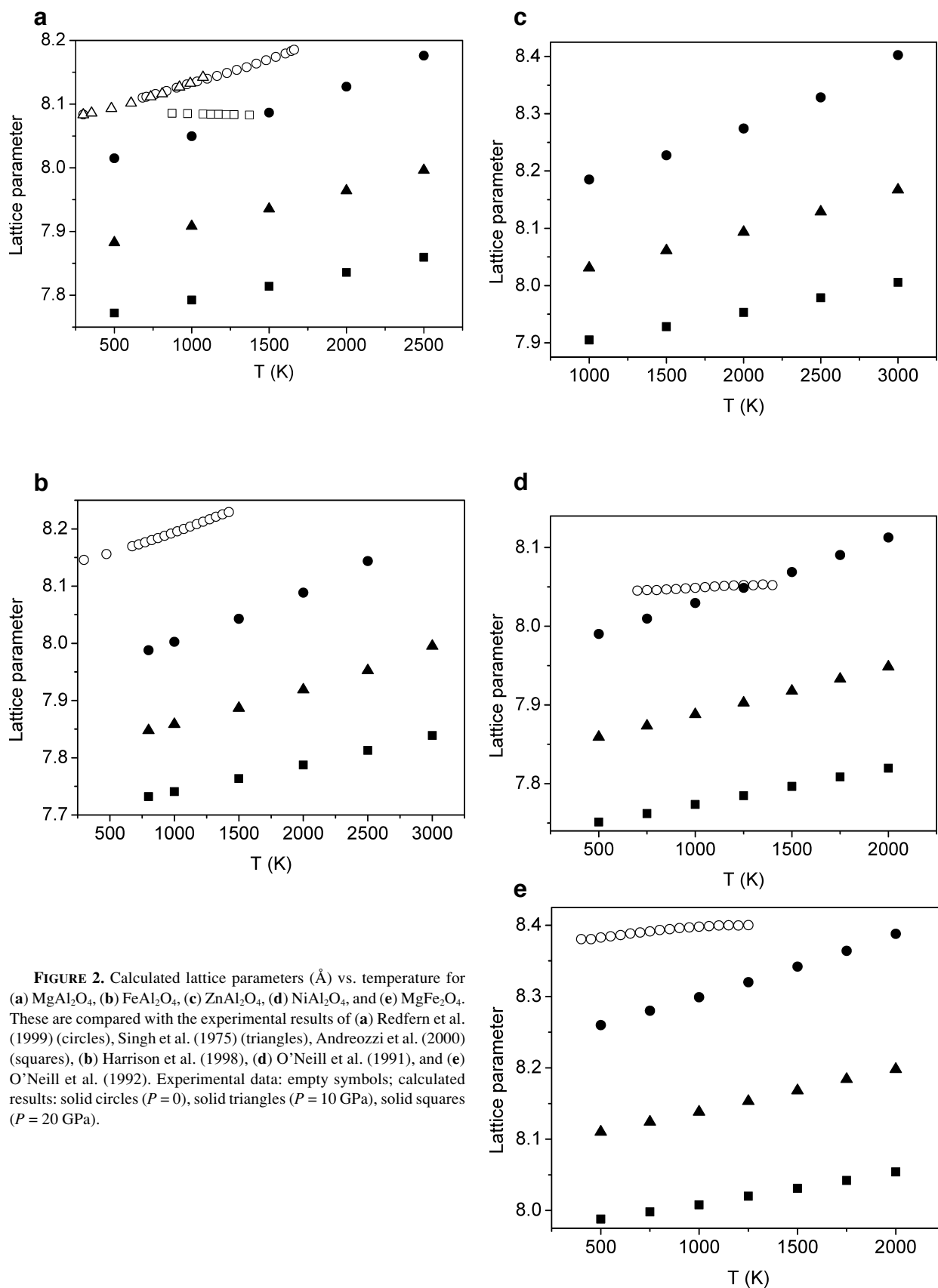


FIGURE 2. Calculated lattice parameters (\AA) vs. temperature for (a) MgAl_2O_4 , (b) FeAl_2O_4 , (c) ZnAl_2O_4 , (d) NiAl_2O_4 , and (e) MgFe_2O_4 . These are compared with the experimental results of (a) Redfern et al. (1999) (circles), Singh et al. (1975) (triangles), Andreozzi et al. (2000) (squares), (b) Harrison et al. (1998), (d) O'Neill et al. (1991), and (e) O'Neill et al. (1992). Experimental data: empty symbols; calculated results: solid circles ($P = 0$), solid triangles ($P = 10$ GPa), solid squares ($P = 20$ GPa).

TABLE 3. Calculated and experimental values of the lattice parameters and linear expansion coefficients of the five spinels studied

System	Lattice parameter (Å) (calculated at 1000 K)	Lattice parameter (Å) (experimental)	Linear expansion coefficient α (10^{-6} K^{-1}) (calculated at 1000 K)	Linear expansion coefficient α (10^{-6} K^{-1}) (experimental)
Spinel (MgAl_2O_4)	<i>8.050</i>	8.0834 (973 K, Wood et al. 1986) 8.13564 (1035 K, Redfern et al. 1999)	8.7	9.2 (299–1662 K, Redfern et al. 1999)
Hercynite (FeAl_2O_4)	8.003	8.19571 (1023 K, Harrison et al. 1998)	8.3	9.1 (298–1423 K, Harrison et al. 1998)
gahnite (ZnAl_2O_4)	8.185	8.0883 (1000 K, Waerenborgh et al. 1994) 8.089; 8.110 (773 K, Revel et al. 2000)	8.7	–
NiAl_2O_4	8.030	8.0451 (Tabira and Withers 1999) 8.0452 (973 K, O'Neill et al. 1991)	10.1	1.2 (973–1673 K, O'Neill et al. 1991)
Magnesioferrite (MgFe_2O_4)	8.299	8.3914 (1023 K, O'Neill et al. 1992)	10.0	3.8 (673–1073 K, O'Neill et al. 1992)

Note: The entry in italics is a fitted value (see Table 1a).

2a, to the results of Singh et al. (1975) and those of Redfern et al. (1999). Singh et al. (1975) concluded that the linear thermal expansion coefficient α increases from $5.9 \times 10^{-6} \text{ K}^{-1}$ at 299 K to $12.73 \times 10^{-6} \text{ K}^{-1}$ at 1073 K for synthetic spinel (of stoichiometric content) and report similar values of α for a natural nonstoichiometric spinel with 7 at% of Mg replaced by Fe. Results reported by Redfern et al. (1999) give an average value of α over the range 299–1662 K of $9.2 \times 10^{-6} \text{ K}^{-1}$. Finally, in the recent study of Suzuki et al. (2000), α is given as $8.59 \times 10^{-6} \text{ K}^{-1}$ at 998 K, in excellent agreement with our calculations, which give $\alpha = 8.7 \times 10^{-6} \text{ K}^{-1}$ at 1000 K, increasing with temperature to $12.7 \times 10^{-6} \text{ K}^{-1}$ at 2000 K. We see no negative thermal expansion over the range 500–2000 K.

Calculated values of α for all the systems studied are presented in Table 3, together with average experimental values where experimental data for α were available over a wide temperature range. Our calculated values are in good agreement for the normal spinels MgAl_2O_4 and FeAl_2O_4 , but agreement is poorer for the inverse spinels NiAl_2O_4 and MgFe_2O_4 , for which experimental data suggests values which are smaller by a factor of 3–10. This discrepancy requires further investigation; however, in this context it is worth mentioning the agreement between our results for MgFe_2O_4 and the calculations of Hazen and Yang (1999), who predicted an α value of $8 \times 10^{-6} \text{ K}^{-1}$ for the fully inverse structure.

Bulk modulus

We now turn to the pressure dependence of the volume. We also plot in Figure 2 the calculated variation of the lattice parameter with temperature at 10 GPa and 20 GPa as well as at zero pressure. For the isothermal bulk modulus of MgAl_2O_4 , our calculated values of K_T are 178.3 GPa at 1000 K and 187.8 GPa at 500 K, extrapolating to 191.6 GPa at room temperature and to 197 GPa at $T = 0$. These results are in very good agreement with recent measurements by Suzuki et al. (2000), who reported values of 179.592 GPa at 996 K and 191.986 GPa at 496 K, and in good agreement with earlier experiments by Askarpour et al. (1993), who gave 198.93 GPa at ambient temperature, extrapolating to 180.8 GPa at 1000 K, and by Yoneda (1990), who found K_T to be 196.5 GPa at ambient temperature. Hartree-Fock calculations of Catti et al. (1994) gave 227 GPa

at $T = 0$, overestimating the experimental value of Suzuki et al. (2000) by ~ 20 GPa. The agreement is substantially better in our atomistic simulations.

Ordering

For each spinel we have calculated the order parameter, Q , over a broad temperature range, as shown in Figure 3. This figure also compares our calculated values of Q at zero pressure with experimental data (Redfern et al. 1999; Andreozzi et al. 2000; Harrison et al. 1998; Waerenborgh et al. 1994; O'Neill et al. 1991, 1992). The calculated value of Q for the normal spinels gradually decreases on heating. Above approximately 900–1000 K our results show excellent agreement with the experiments. Below this temperature kinetic effects, which are not included in our calculations, become increasingly important. Our results for MgAl_2O_4 display similar features to those calculated using a parameterized Hamiltonian (Warren et al. 2000). This is not unexpected due to the similar nature of the computational technique, even though that of Warren et al. (2000) does not include thermal effects. Note that the two experimental studies of MgAl_2O_4 (Redfern et al. 1999; Andreozzi et al. 2000) shown in Figure 3a differ substantially, which indicates difficulties in preparing stoichiometric samples and in the experimental determination of the order parameter. The variation of Q with temperature, if not the absolute value of Q itself, is similar in the two studies. Of the three normal spinels studied, ZnAl_2O_4 shows the weakest temperature dependence of the order parameter (Q changes from 1 to 0.72 between 1000 and 3000 K). In contrast to the normal spinels, the calculated value of Q for the inverse spinels increases with temperature. Our calculated values are not in as good agreement with the experimental data as for the normal spinels, but are nevertheless able to provide qualitative and quantitative information. For example, our simulations consistently give lower Q (more inverse order) for NiAl_2O_4 than for MgFe_2O_4 , in agreement with experimental data. The derivative $\partial Q/\partial T$ is similar for both compounds, according to our simulations, while experimental data suggests higher value for MgFe_2O_4 . It is worth noting in this context that earlier experiments (Tellier 1967; Faller and Birchenall 1970) gave lower values of $\partial Q/\partial T$, in better agreement with our simulations. Finally, it is worth noting that in-

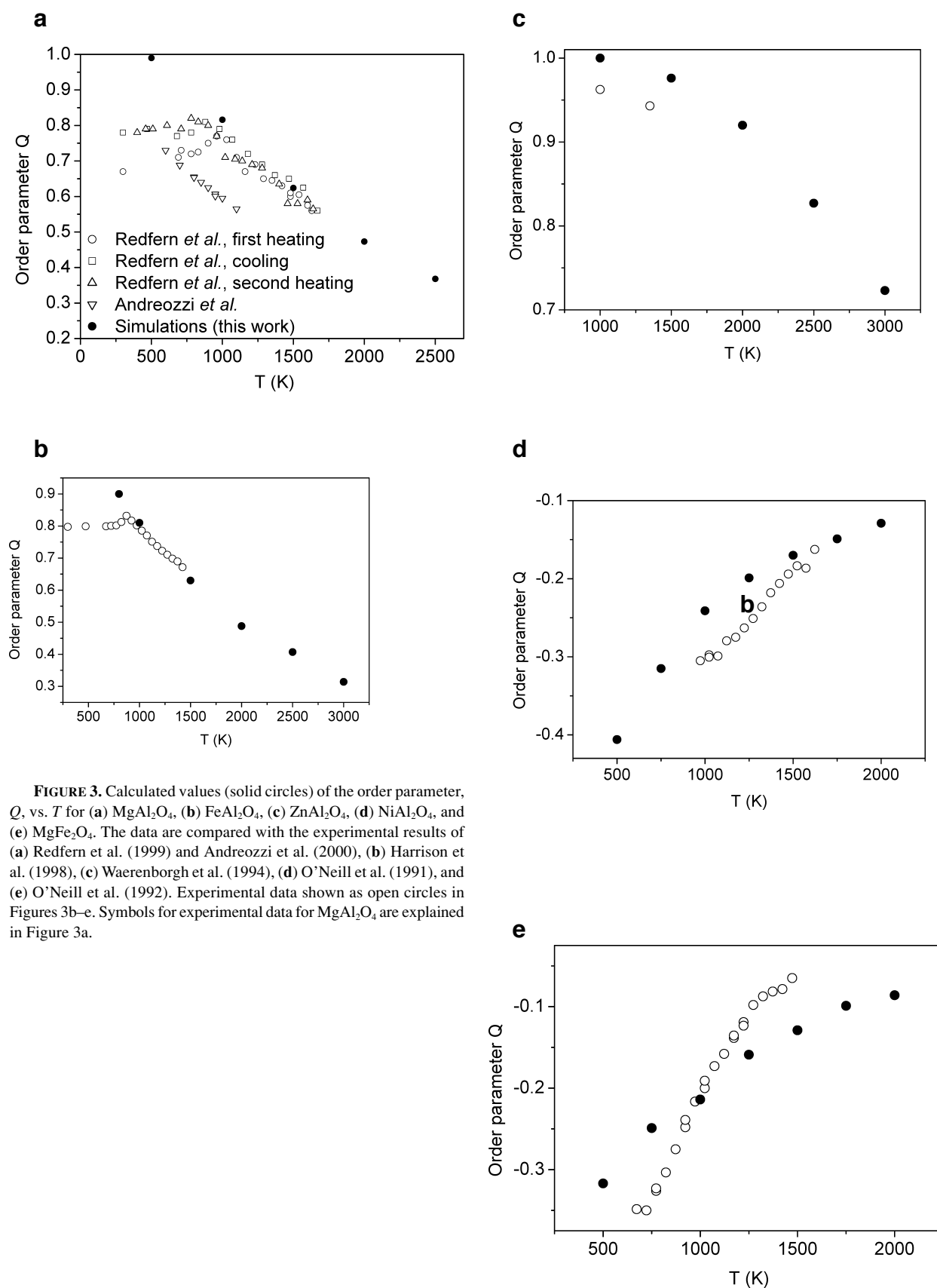


FIGURE 3. Calculated values (solid circles) of the order parameter, Q , vs. T for (a) $MgAl_2O_4$, (b) $FeAl_2O_4$, (c) $ZnAl_2O_4$, (d) $NiAl_2O_4$, and (e) $MgFe_2O_4$. The data are compared with the experimental results of (a) Redfern *et al.* (1999) and Andreozzi *et al.* (2000), (b) Harrison *et al.* (1998), (c) Waerenborgh *et al.* (1994), (d) O'Neill *et al.* (1991), and (e) O'Neill *et al.* (1992). Experimental data shown as open circles in Figures 3b–e. Symbols for experimental data for $MgAl_2O_4$ are explained in Figure 3a.

creasing temperature to 2000 K leads to an almost random arrangement of cations ($Q \approx -0.1$) in inverse spinels, while for all normal spinels studied, a large degree of order remains even at this temperature ($0.5 \leq Q \leq 0.9$).

The Monte Carlo technique allows us to investigate the dependence of the bulk modulus and thermal expansion coefficient on the order parameter. Recently, Hazen and Yang (1999) (see also Smyth et al. 2000) have derived equation-of-state parameters, such as compressibility and thermal expansion, for spinels from bond distances, bond compressibilities, and bond thermal expansivities, which, in turn, are estimated from crystal chemical systematics. They propose that the degree of cation order-disorder strongly affects both the bulk modulus and the thermal expansion, and in particular their calculations suggest that the compressibilities for normal (fully ordered) and completely inverse variants may differ by as much as 17% (Mg_2TiO_4), with linear thermal expansivities differing by 15% (MgAl_2O_4 , MgFe_2O_4). We therefore performed calculations for (completely) normal and (completely) inverse spinels at 1000 K and zero pressure. During the simulation, the value of Q was kept constant (i.e., 1 for normal and -0.5 for inverse spinel), so that the normal spinel is completely ordered and exchanges between cations are prohibited, while in the inverse spinel, exchanges between A- and B-type cations at octahedral sites are still possible. The results are collected together in Table 4. Our results indicate that the bulk modulus and the linear expansion coefficient exhibit a marked dependence on Q . The biggest difference between normal and inverse spinels is for the calculated thermal expansion coefficient, which is as large as 21% for NiAl_2O_4 and MgFe_2O_4 . For the bulk modulus, the largest difference is for NiAl_2O_4 (9%). Our conclusions for the expansion coefficient agree with those of Hazen and Yang (1999) in that normal MgAl_2O_4 and MgFe_2O_4 have larger expansion coefficients than the inverse structures. However, Hazen and Yang (1999) also suggest the bulk modulus is larger for the normal structures, whereas our simulations suggest the contrary. This discrepancy is possibly due to the values of bond compressibility used by Hazen and Yang (1999), which were taken from high-pressure structure studies and cannot be directly applied at zero pressure. In addition, their results for the inverse structure depend on the procedure chosen to average bond distances and the derivatives of these quantities with respect to pressure.

Finally, in this section we turn to how the order parameter varies with pressure. This dependence is related to the change of volume accompanying the interchange of cations between tetrahedral and octahedral sites. Quantitatively, as shown in the Appendix, the pressure dependence of the equilibrium value of the order parameter is related to the variation of volume with Q by

$$\left(\frac{\partial Q_{\text{eq}}}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial Q}\right)_{P,T} / \left(\frac{\partial^2 G}{\partial Q^2}\right)_{P,T} \quad (5)$$

Since the second derivative ($\partial^2 G / \partial Q^2$)_{P,T} is positive for the system in equilibrium, ($\partial V / \partial Q$)_{P,T} and ($\partial Q_{\text{eq}} / \partial P$)_T are opposite in sign, in agreement with Le Châtelier's principle.

TABLE 4. Calculated bulk moduli and thermal expansion coefficients for normal and inverse spinels at 1000 K

System	Type of ordering	Bulk modulus (GPa)	Linear expansion coefficient (10^{-6} K^{-1})
spinel (MgAl_2O_4)	Normal	170	8.8
	Inverse	180	8.1
hercynite (FeAl_2O_4)	Normal	166	9.8
	Inverse	181	8.4
gahnite (ZnAl_2O_4)	Normal	158	10.3
	Inverse	161	9.3
NiAl_2O_4	Normal	165	10.0
	Inverse	180	8.3
magnesianferrite (MgFe_2O_4)	Normal	144	11.6
	Inverse	155	9.6

TABLE 5. Calculated difference in volume between normal and inverse spinel and the change of order parameter Q resulting from an increase in pressure from 0 to 10 GPa

System	$V(\text{normal}) - V(\text{inverse})$, $10^{-6} \text{ m}^3 / \text{mol}$	$Q(P=10 \text{ GPa}) - Q(P=0)$
Spinel (MgAl_2O_4)	0.0196	-0.009
Hercynite (FeAl_2O_4)	0.0123	-0.014
Gahnite (ZnAl_2O_4)	-0.0071	0.002
NiAl_2O_4	0.1022	-0.120
Magnesianferrite (MgFe_2O_4)	0.0422	-0.010

Note: All results are at 1000 K except for ZnAl_2O_4 , where the variation in Q with pressure is calculated at 1500 K (Q is too close to zero at 1000 K for a reliable answer).

In Table 5 we compare the calculated change of volume accompanying the transition from inverse to normal (i.e., when Q increases from -0.5 to 1) for all five spinels. This table shows that ($\partial V / \partial Q$)_{P,T} has the opposite sign to ($\partial Q / \partial P$)_T over the pressure range 0–10 GPa. For the normal spinels we predicted that the order parameter is almost independent of pressure (Figure 4). Increasing the pressure leads to a slight decrease of the order parameter for MgAl_2O_4 and hercynite FeAl_2O_4 , and to a very small increase in Q for gahnite ZnAl_2O_4 . The results for MgAl_2O_4 appear to be consistent with the known resistance of this material to void swelling under neutron radiation, which, it has been suggested, is linked to a small volume change accompanying interchange of the Mg and Al ions (Sickafus et al. 2000). The pressure effect is more pronounced for inverse spinels, and especially for NiAl_2O_4 . For both inverse spinels, the degree of inversion for a given temperature increases with increasing pressure.

Kinetics

Lastly we briefly discuss how a knowledge of the thermodynamic properties of spinel is useful for modeling the kinetics of the cation ordering process. The time dependence of the order parameter can be derived from the statistical mechanics of small steps (Metiu et al. 1976; Salje 1988) and is given by

$$\frac{dQ}{dt} = \frac{\gamma \exp(-\Delta G^* / RT)}{2RT} \frac{\partial \Delta G}{\partial Q} \quad (6)$$

where γ is a frequency factor, ΔG^* the free energy of activation, and ΔG the free energy (see also Harrison and Putnis 1999).

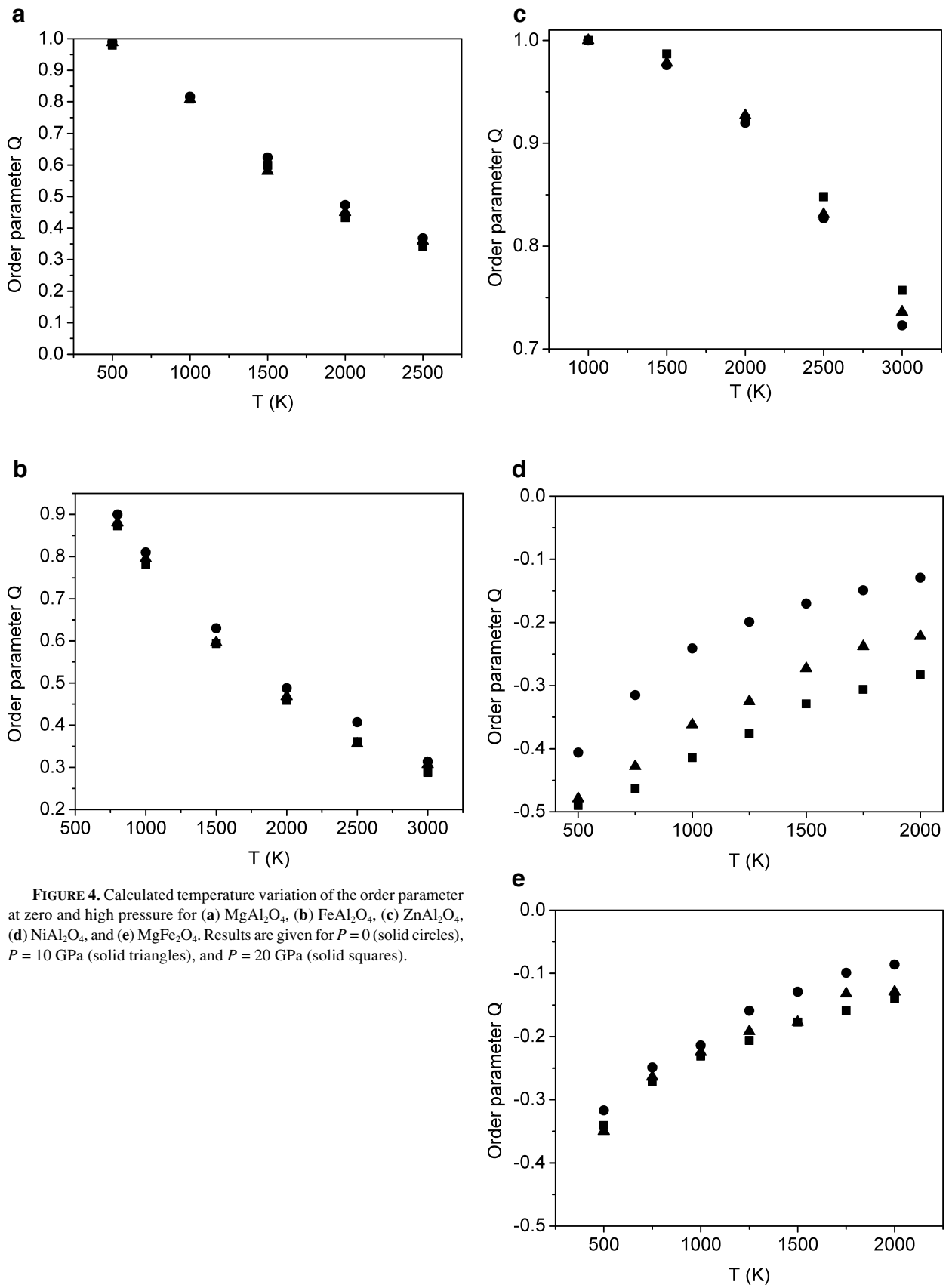


FIGURE 4. Calculated temperature variation of the order parameter at zero and high pressure for (a) MgAl_2O_4 , (b) FeAl_2O_4 , (c) ZnAl_2O_4 , (d) NiAl_2O_4 , and (e) MgFe_2O_4 . Results are given for $P = 0$ (solid circles), $P = 10$ GPa (solid triangles), and $P = 20$ GPa (solid squares).

To date, $\Delta G(Q)$ has been described using phenomenological models (Carpenter and Salje 1994; Harrison and Putnis 1999), putting $\Delta G(Q)$ equal to zero at $Q = 0$ (fully disordered state). The excess free energy due to ordering is then given by

$$\Delta G = -hQ + \frac{1}{2}a(T - T_c)Q^2 + \frac{1}{6}cQ^6 \quad (7)$$

where parameters h , a , T_c , and c are determined from experimental data relating to the temperature dependence of Q . Empirical values of γ and ΔG^* are usually chosen so as to obtain the best overall agreement between the experimental and calculated time dependence of Q . The choice of values for γ and ΔG^* clearly depends strongly on $\Delta G(Q)$. We can calculate directly the dependence of ΔH on Q from simulations in which Q is not allowed to change. In the simplest approximation, the entropy term can be taken to be purely configurational and ideal and, using $\Delta G(Q) = \Delta H(Q) - T\Delta S_{\text{conf}}(Q)$, we can calculate $\partial\Delta G/\partial Q$ from theory rather than from experiment. As a first step, we calculated $\Delta G(Q)$ for MgAl_2O_4 at 1000 K and compare our results with those of Carpenter and Salje (1994) and Harrison and Putnis (1999) in Figure 5. Our results differ somewhat from these authors; Eqn. (7) and our fitted parameters give the $\Delta G(Q)$ curve shown as the full line in Figure 5 [$h = 21.847$ kJ/mol; $a(1000 - T_c) = 11.878$ kJ/mol (we are unable to determine both a and T_c from results for one temperature); $c = 36.378$ kJ/mol]. The magnitudes of $\Delta G(Q)$ and of the derivative $f\Delta G/fQ$ are larger in our calculations. Consequently, the value of the product $\gamma \exp(-\Delta G^*/RT)$, obtained by fitting to the experimental ordering data, is lower than that obtained previously. In this context it is worth noting also that the minimum of $\Delta G(Q)$ at 1000 K obtained by Carpenter and Salje (1994) ($Q_{\text{min}} = 0.607$), is at a much smaller value of Q than suggested by the experimental data of Redfern et al. (1999) ($Q = 0.77$), but very close to the results of Andreozzi et al. (2000) ($Q = 0.595$).

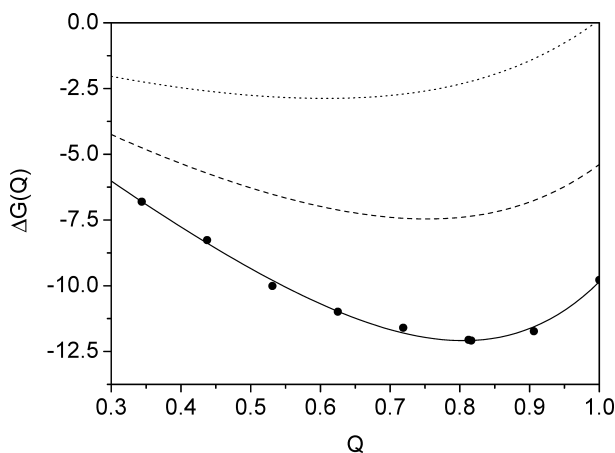


FIGURE 5. $\Delta G(Q)$ vs. Q . The results of Carpenter and Salje (1994) (dotted line), Harrison and Putnis (1999) (dashed line), and our simulations (filled circles) together with a fit of our results according to Equation 7 (solid line).

ACKNOWLEDGMENTS

This research was funded by EPSRC grant GR/M53899 and computational facilities were provided by two HEFCE JREI awards.

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APPENDIX

Our starting point is the general expression for the free energy of a system as a function of pressure, temperature, and arbitrary internal variable Q :

$$G = G(P, T, Q) \quad (A.1)$$

At equilibrium at given pressure and temperature, the free energy is minimized with respect to Q and stability requires that its second derivative is positive:

$$\left(\frac{\partial G}{\partial Q}\right)_{P,T} = 0 \quad (A.2)$$

$$\left(\frac{\partial^2 G}{\partial Q^2}\right)_{P,T} > 0 \quad (A.3)$$

Equation A.2 defines the equilibrium value of Q : $Q_{eq}(P, T)$. The change of the function $(\partial G/\partial Q)_{P,T}$ under arbitrary changes of P and Q is as follows:

$$\Delta\left(\frac{\partial G}{\partial Q}\right)_{P,T} = \left(\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial Q}\right)_{P,T}\right) \cdot \Delta P + \left(\frac{\partial^2 G}{\partial Q^2}\right)_{P,T} \cdot \Delta Q \quad (A.4)$$

If the system remains in equilibrium after an arbitrary change of pressure, then $\Delta Q = \Delta Q_{eq}(P, T)$, and the total change in $(\partial G/\partial Q)_{P,T}$, according to (Eq. A.2), is zero:

$$\left(\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial Q}\right)_{P,T}\right) \cdot \Delta P + \left(\frac{\partial^2 G}{\partial Q^2}\right)_{P,T} \cdot \Delta Q_{eq} = 0 \quad (A.5)$$

Changing the order of differentiation in the first term and recognizing $(\partial G/\partial P)_{T,Q}$ as the volume V of the system at given P , T and Q , we can rewrite (Eq. A.5) as

$$\left(\frac{\partial V}{\partial Q}\right)_{P,T} \cdot \Delta P + \left(\frac{\partial^2 G}{\partial Q^2}\right)_{P,T} \cdot \Delta Q_{eq} = 0 \quad (A.6)$$

In the limit of infinitely small changes of pressure and Q_{eq} , we arrive at the final expression:

$$\left(\frac{\partial Q_{eq}}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial Q}\right)_{P,T} / \left(\frac{\partial^2 G}{\partial Q^2}\right)_{P,T} \quad (A.7)$$

As the sign of $(\partial^2 G/\partial Q^2)_{P,T}$ is always positive (Eq. A.3), we see that the derivatives $(\partial Q_{eq}/\partial P)_T$ and $(\partial V/\partial Q)_{P,T}$ indeed have different signs.