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Order-disorder phenomena in $MgAl_2O_4$ spinel

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ABSTRACT

The distribution of Al between octahedral and tetrahedral sites in $MgAl_2O_4$ spinel has been determined on quenched samples by high-resolution ^{27}Al NMR spectroscopy. The degree of inversion, x (atomic fraction of Al in tetrahedral positions), increases from 0.21 ± 0.02 at 700°C to 0.39 ± 0.04 at 900°C. The cation distribution has been reversed at 715, 800, and 850°C. Samples quenched from above 900°C all have x values of about 0.38, probably because of reordering to the 900°C distribution during cooling.

The large degree of inversion implies a residual entropy of Mg-Al disorder of about 3 cal/mol·K which needs to be added to the calorimetrically measured entropy of spinel. In contrast, an analysis of reversed phase-equilibrium data constrains the residual entropy to be close to 1.0 cal/mol·K. The discrepancy must arise either from a large nonconfigurational entropy of Mg-Al exchange or from short-range Mg-Al order. The measured temperature dependence of Mg-Al disorder is inconsistent with the nonconfigurational entropy hypothesis, which implies that short-range order is responsible for the low entropy of $MgAl_2O_4$ at high temperature. Calorimetrically measured enthalpies of reordering confirm the entropy estimates based on phase-equilibrium measurements.

The effect of disorder on the unit-cell edge is extremely small. A sample with $x = 0.21$ has a cell edge of 8.0834(5) Å, whereas the same material disordered to $x = 0.39$ yields a cell edge of 8.0855(6) Å.

INTRODUCTION

Spinels are mineralogical constituents of most igneous and metamorphic rocks and, because of their wide *P-T* stability fields and compositional complexities, provide important monitors of petrogenetic processes (Sack, 1982). These properties have led to the calibration of numerous equilibria involving spinel components as geologic thermometers and barometers (e.g., Buddington and Lindsley, 1964; Sack, 1980; Gasparik and Newton, 1984). Despite the utility of such equilibria, however, difficulties arise in understanding and extrapolating spinel properties because of the variable and largely unquantified extents of cation disorder on octahedral and tetrahedral sites in the spinel structure.

In the spinel structure, metal cations occupy one-eighth of the available tetrahedral sites and one-half of the available octahedral sites so that the overall cation to anion ratio is 3:4. The general formulae of "normal" 2-3 and 2-4 spinels are $A^{2+}(B_2^{3+})O_4$ and $A^{2+}(A^{2+}B^{4+})O_4$, respectively, where the species occupying the octahedral sites are denoted by the parentheses. The "inverse" cation configurations are $B^{3+}(A^{2+}B^{3+})O_4$ and $B^{4+}(A_2^{2+})O_4$. The nature of cation distribution, "normal," "inverse," or disordered between these extremes depends on spinel composition and temperature of equilibration. Of the geologically important spinels, chromite, $Fe(Cr_2)O_4$, and ulvospinel, $Fe(FeTi)O_4$, are essentially normal whereas the high-pressure forms of olivine, $Si(Mg_2)O_4$ and $Si(Fe_2)O_4$, are completely inverse. Magnetite, $Fe^{3+}(Fe^{2+}Fe^{3+})O_4$, is almost completely inverse at low temperatures, but recent thermopower measurements have demonstrated increasing Fe^{2+}-Fe^{3+} disorder over tetrahedral and octahedral sites with increasing temperature (Wu and Mason, 1981). This disorder is such that Fe^{2+} and Fe^{3+} are completely randomly distributed over the two types of sites at 1450°C. The mineral that gives its name to the group, $Mg(Al_2)O_4$ spinel, is known from nuclear magnetic resonance (NMR; Brun and Hafner, 1962), ESR (electron spin resonance; Schmocker and Waldner, 1976), and calorimetric measurements (Navrotsky and Kleppa, 1967) to exhibit at least partial inverse character.

Navrotsky and Kleppa (1967) heated a natural spinel of close to $MgAl_2O_4$ composition at temperatures between 735 and 1300°C for 24 h, quenched the samples, and determined heats of solution in $Pb_2B_2O_5$ melt at 695°C. They found that the enthalpy of solution is constant for samples annealed at 735°C or 695°C, but about 0.9 kcal/mol lower for material annealed at 1060°C. Annealing above 1060°C produced no further effect.

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Navrotsky and Kleppa interpreted the observed enthalpy effect as being due to disordering of a completely normal $MgAl_2O_4$ spinel to an equilibrium distribution of Al and Mg at 800–900°C with approximately 0.1 tetrahedral Al atoms per formula unit. In terms of a simple nonconvergent disorder model, these data may be used to estimate the temperature dependence of tetrahedral occupancy by Al and the enthalpy of the disordering reaction by considering the equilibrium

$$Mg_{tet} + Al_{oct} = Mg_{oct} + Al_{tet}. \qquad (1)$$

Navrotsky and Kleppa assumed that 0.1 atoms of Al on tetrahedral sites give an enthalpy effect of 0.9 kcal/mol of $MgAl_2O_4$ so that the standard-state enthalpy of equilibrium was estimated to be ~9.0 kcal/mol. Using the nonconvergent disorder model, assuming random Al-Mg mixing on each sublattice and zero standard-state entropy of reaction, gives (Navrotsky and Kleppa, 1967)

$$-\frac{\Delta H^0_{dis}}{RT} = \frac{-9000}{1.99T} = \ln\left(\frac{x^2}{(1-x)(2-x)}\right), \qquad (2)$$

where x is the atomic fraction of Al on the tetrahedral sites. Thus, x is predicted to be about 0.14 at 800°C, 0.25 at 1200°C, and 0.32 at 1600°C.

Schmocker and Waldner (1976) determined the ESR spectra of natural and synthetic spinels containing small amounts of Cr^{3+} substituting for Al^{3+} in octahedral positions. They used the Cr^{3+} spectra to determine the proportion of nearest-neighbor octahedral sites occupied by Al^{3+} and the fraction containing Mg^{2+}. From stoichiometry, they were then able to calculate the degree of inversion, x. Heat treatment of two natural spinels produced an apparently increasing degree of inversion between 750 and 900°C. Untreated specimens had x of about 0.05, but this rapidly increased to approximately 0.3 with heat treatment at 900°C (Fig. 2). Experiments at above 900°C yielded no further disorder. Qualitatively, the rapid increase in inversion with temperatures above 750°C and the high-temperature "plateau" agree with the observations of Navrotsky and Kleppa (1967). In detail, however, the extents of disorder differ appreciably. Navrotsky and Kleppa's results imply a value of x of about 0.18 at 900°C, whereas Schmocker and Waldner (1976) obtained values close to 0.3. In addition, the ESR data suggest that the extent of disorder depends on composition, the two natural samples giving somewhat different results.

Wood and Holloway (1984) attempted to derive the thermodynamic properties of synthetic $MgAl_2O_4$ spinel from a combination of solution calorimetric data and phase-equilibrium results for the reaction

$$\underset{\text{enstatite}}{2Mg_2Si_2O_6} + \underset{\text{spinel}}{MgAl_2O_4} = \underset{\text{pyrope}}{Mg_3Al_2Si_3O_{12}} + \underset{\text{forsterite}}{Mg_2SiO_4}. \qquad (3)$$

They found that the experimentally determined P-T slope of Reaction 3 is inconsistent with the relatively small exchange enthalpy and large extents of disorder proposed by Navrotsky and Kleppa (1967) and Schmocker and Waldner (1976). Making the assumption that the standard-state heat capacity (ΔC^0_p) of Reaction 3 is constant between 1000 and 1873 K, Wood and Holloway (1984) concluded that the phase-equilibrium results require an exchange enthalpy (ΔH^0_{dis}) of 20 kcal/mol rather than the 9 kcal/mol proposed by Navrotsky and Kleppa. If correct, this conclusion would require a dramatically smaller degree of Mg-Al disorder in spinel than that found by Schmocker and Waldner. Wood and Holloway's results yield, for example, values of disorder parameter x of 0.01 at 800°C, 0.045 at 1200°C, and 0.09 at 1600°C.

It is clear that there are considerable discrepancies between published extents of spinel disorder based on spectroscopic, calorimetric, and phase-equilibrium data. The advent of high-resolution NMR spectroscopy using magic-angle sample-spinning (MASS) techniques has enabled the direct investigation of the coordination numbers of Al in crystalline and amorphous states via the NMR-active nucleus ^{27}Al. The purpose of this study has been to make precise determinations of the distribution of Al between octahedral and tetrahedral spinel sites using MASS NMR spectroscopy. This involved heating spinels with known extents of disorder under controlled temperature conditions at 1-atm pressure. After heat treatment, the samples were quenched to room temperature and their ^{27}Al spectra obtained.

EXPERIMENTAL PROCEDURE

Analytical grade Al_2O_3 and MgO (from $MgCO_3$) were heated overnight at 1300°C, cooled, and stored in a desiccator. They were then weighed in the stoichiometric proportions necessary to produce $MgAl_2O_4$ and ground together under acetone. Spinels were synthesized by pressing the oxide mixes into pellets and sintering at 1300 and 1425°C in a 1-atm furnace. After reacting for 48 h, the samples were cooled in air and reground, pressed, and run for an additional 7 d. No unreacted oxide was detectable by X-ray diffractometer after 48 h at 1425°C or after 9 d at 1300°C. Further syntheses were performed hydrothermally at 700°C and 1 kbar in standard cold-seal vessels. The latter also yielded no detectable phase other than spinel. Cell edges of product spinels (Table 1) were determined by X-ray diffractometer measurements of the 511 and 440 peaks using Cu$K\alpha_1$ radiation (λ = 1.5405 Å) and a metallic Si internal standard.

One-atmosphere quenching experiments were performed in a vertical tube furnace. In each experiment, about 0.2 g of single-phase spinel was sealed in a Pt capsule and suspended on a thin Pt wire next to a Pt-Rh thermocouple. Experiments were performed at temperatures of 710–1600°C for periods varying from 2 to 400 h. At the end of each experiment the thin wire was melted by passing a current through it, and the samples were quenched by dropping into water. Total quenching time to a temperature less than 100°C was about 2 s.

SPECTROSCOPIC METHODS

The partitioning of ^{27}Al between the tetrahedral and octahedral spinel sites was determined via ^{27}Al MASS NMR spectroscopy at a frequency of 130 MHz using the techniques described by Meadows et al. (1982), Kirkpatrick et al. (1985a), and Kinsey et al. (1985). The spectrometer used is homebuilt and is based on an

Table 1. $MgAl_2O_4$ unit-cell edges

#	T °C	x	Cell Edge Å
Synthesis	700	0.21	8.0834(5)
Synthesis	1300	0.37	8.0842(5)
3A	1050	0.39	8.0855(6)

Value in ( ) refers to one standard deviation

11.7-T superconducting magnet and a Nicolet 1280 computer automation system. The MASS sample probe uses Andrew-Beams-type sample-spinning rotor assemblies (Andrew, 1971). Chemical shifts are reported relative to ^{27}Al in 1 *M* $AlCl_3$ solution at room temperature. More positive chemical shifts correspond to decreased shielding.

Because ^{27}Al has a quadrupole moment, care was taken to collect the spectra under identical run conditions. Meadows et al. (1982) and Kirkpatrick et al. (1985a) have discussed the effects of second-order quadrupole interactions on MASS NMR spectra. For ^{27}Al (spin $I = 5/2$), greatest signal intensity is obtained with a pulse width of ⅓ of that which is required to produce a 90° angular flip of the spin system of ^{27}Al in solution (Fenzke et al., 1984). The pulse width is the length of time that the sample is irradiated with radio-frequency radiation to excite the nuclear spin system. The spectra reported here were all collected under MASS conditions at a pulse width of ⅓ the solution 90° pulse width (3 μs). Varying the pulse width from 0.5 to 4 μs under otherwise identical run conditions does not affect the relative peak areas, and we conclude that the peak areas, including the area of the spinning sidebands associated with that peak, yield the true relative abundances of Al(4) and Al(6) in each sample.

Figure 1 presents ^{27}Al spectra of spinel synthesized at 700°C and of the same material heat treated at 900°C. The spectrum of the sample synthesized at 700°C and 1 kbar contains a large peak at +11 ppm due to octahedral Al and a smaller peak at +72 ppm due to tetrahedral Al, together with pronounced spinning sidebands. Spectral assignments are based on comparison of the chemical shifts with those of phases in which Al is known to be tetrahedrally and octahedrally coordinated by oxygen (Kirkpatrick et al., 1985b). The positions of the peaks for both the octahedral Al and tetrahedral Al are in the range expected for oxides and aluminates. The spectrum of the 700°C spinel heated at 900°C for 185 h and then quenched contains a larger peak from tetrahedral Al and shows clearly a greater extent of inversion and tetrahedral Al occupancy (Fig. 1). The chemical shifts of neither the octahedral nor the tetrahedral Al change with heat treatment more than the ±1 ppm precision of the measurement. Estimation of octahedral-tetrahedral distribution was performed by determining the areas under tetrahedral and octahedral peaks. Areas of spinning sidebands were added into the areas of main peaks and integrated by cutting out the peaks and weighing them on a 4-place balance. Repeated measurement of the same spectrum indicates that the integration method results in an uncertainty in the Al(4)/Al(6) ratio of ±4%. Duplicate spectra were obtained on one sample, and the spectrum of another was collected three times. Determination of Al(4)/Al(6) on these five spectra indicates that cation distributions are actually reproducible to better than ±10%. The temperature dependence of the Al(4)/Al(6) ratio, discussed next, is clearly detectable using the NMR method.

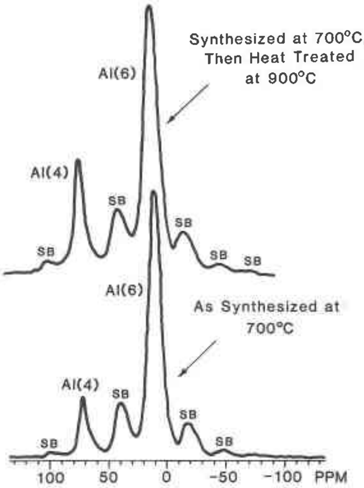

Fig. 1. High-resolution 11.7-T MASS NMR spectra of spinel synthesized at 700°C (lower) and of the same sample heat treated for 8 d at 900°C (upper). Note marked increase in intensity of major tetrahedral peak at 900°C. Al(4) denotes tetrahedral Al, Al(6) denotes octahedral Al, and SB denotes spinning sidebands.

Table 2. Experimental results

Run #	T °C	Time (hr)	X_{Al}^{tet} (initial)	X_{Al}^{tet} (final)
Synthesis	700	24	-	0.21
Synthesis	1300	215	-	0.37
Synthesis	1425	220	-	0.39
7	710	2	0.39	0.28
5	710	15	0.39	0.26
4A	715	370	0.21	0.24
4B	715	370	0.39	0.26
11	800	3	0.37	0.32
9A	800	210	0.21	0.32
9B	800	210	0.37	0.30
8A	850	70	0.21	0.35
8B	850	70	0.36	0.35
6A	900	185	0.21	0.39
3A	1050	400	0.21	0.39
3B	1050	400	0.37	0.36
1	1200	210	0.39	0.37

TEMPERATURE DEPENDENCE OF INVERSION

The measured fractions of tetrahedral sites occupied by Al are given in Table 2, and the temperature dependence of inversion illustrated in Figure 2. From these data it may be seen that the degree of inversion increases from about 0.2 at 700°C to 0.4 at 900°C and that all experiments between 900 and 1425°C yield the same amount of inversion. The form of the curve and the nature of the high-temperature "plateau" agree well with those observed by Schmocker and Waldner (1976), as do the extents of disorder at high temperatures. Unlike the earlier data on natural spinels, however, our results refer to direct measurements of octahedral and tetrahedral Al. Gobbi et al. (1984) found extents of Mg-Al disorder in synthetic $MgAl_2O_4$ similar to those those reported here, but they were unable to disorder natural spinels even at temperatures above 900°C. This could imply that the *x* values measured in synthetic spinels do not refer to equilibrium states of order, a suggestion that we have tested by reversal experiments. The Al(4)/Al(6) ratio has been reversed at 715, 800, and 850°C by running previously synthesized spinel of known x, quenching, and then redetermining x. As can be seen from Table 2, spinels with high (0.37) and low (0.21) initial values of x produced final site occupancies that are virtually identical. It appears, therefore, that the results at these three temperatures refer to equilibrium states of Al-Mg disorder in synthetic $MgAl_2O_4$.

Quenching after different times at 710 and 800°C indicates that complete re-equilibration takes place in less than 3 h at the latter temperature and that considerable reordering occurs in 2 h at 710°C (Table 2). In view of the rapid rates of rearrangement at these low temperatures, it appears likely that the high-temperature "plateau" does not refer to equilibrium ordering states. It is more likely that the plateau is a quenching phenomenon and that the equilibrium inversion cannot be quenched from temperatures above about 900°C. Inferences bearing on the thermodynamic properties of spinel can only, therefore, be drawn from site occupancies corresponding to temperatures below 900°C.

VOLUME-DISORDER RELATIONS

Unit-cell edges of three spinels with known extents of disorder have been measured by the X-ray method discussed earlier. The volume effect of Al-Mg disorder appears to be extremely small. Spinels synthesized at 700°C (hydrothermally) and at 1300°C (dry) gave results (Table 1) that are indistinguishable from one another. Since small nonstoichiometries can affect cell edge, a better test of the effect is provided by a disordering experiment (run number 3A) performed on the spinel previously synthesized at 700°C. An increase in disorder parameter from 0.21 to 0.39 produces a small increase in cell edge from 8.0834 to 8.0855 Å. This corresponds to a volume increase of only +0.03 cm^3 and is opposite in sign to that predicted from the spinel model of O'Neill and Navrotsky (1983). The latter requires a decrease in volume of 0.06 cm^3, as the extent of disorder increases from 0.21 to 0.39. The data obtained in this study (and the O'Neill-Navrotsky model) require that the pressure effect on Mg-Al disorder is minute. Using the Navrotsky-Kleppa model, we may take, for example, the cation distribution at 700°C and calculate the enthalpy change due to disorder caused by raising temperature or pressure

$$H^{\mathrm{dis}}_{\mathrm{T}_2} - H^{\mathrm{dis}}_{\mathrm{T}_1} = \Delta H^0_{\mathrm{dis}}(x_{\mathrm{T}_2} - x_{\mathrm{T}_1})$$

$$H^{\mathrm{dis}}_{x_1P} - H^{\mathrm{dis}}_{x_2P} = (P - 1)(V_{x_1} - V_{x_2}).$$

This approximate treatment indicates that an increase in pressure of 400 kbar is equivalent, in terms of disordering enthalpy, to a decrease in temperature of about 1°C. The volume effect may clearly be ignored when performing phase-equilibrium calculations involving spinel disorder.

PHASE EQUILIBRIA AND DISORDERING ENTROPY

The data of Figure 2 indicate that $MgAl_2O_4$ spinel is about 23% disordered at 700°C and 40% disordered at 900°C. This disordering should add substantial configurational entropy to spinel and hence have considerable impact on its thermodynamic properties. Given the cation populations on each of the two sublattices, the configurational entropy may be calculated by assuming random mixing on tetrahedral sites and random mixing on octahedral sites. This yields an "ideal" configurational entropy given by

$$S_{\mathrm{conf}} = -R\{x \ln x + (1 - x)\ln(1 - x) + x\ln(x/2) + (2 - x)\ln[1 - (x/2)]\}. \quad (4)$$

In Equation 4, x is the disorder parameter that is equal to the atomic fraction of Al on tetrahedral sites. The 700°C data imply an S_{conf} of about 2.5 cal/mol·K, and the increased disorder at 900°C increases S_{conf} to 3.3 cal/mol·K.

The configurational entropy term only needs to be added explicitly to calorimetric data if it is not detected in heat-capacity measurements. The definitions of enthalpy and entropy changes induced by a temperature increment dT are, of course, $dH = C_P dT$ and $dS = (C_P/T)dT$. Heat capacities (C_P) are measured by dropping samples from a known temperature into a calorimeter at some other known temperature (usually 25°C). If the sample has the equilibrium state of order at the fixed temperature and if it then rearranges to the equilibrium state of order at the temperature of the calorimeter, the differential heat, C_P, and entropy effects are all accounted for. If, on the other hand, the sample quenches to some metastable state of order, there are residual enthalpy, C_P, and entropy effects that have not been measured.

The data of Figure 2 imply that dropping of any sample from temperatures less than about 850°C into a calorimeter at 25°C will produce a spinel with an ordering state corresponding to the initial rather than final temperature. Clearly, therefore, there are residual enthalpy and entropy terms that need to be added to spinel properties measured in the temperature range 273–850°C. Heat-content measurements made above 850–900°C will, on the other hand, produce quenching to a state of order appropriate to 850–900°C, so that the enthalpy difference $H_T - H_{1173}$ (T in kelvins) and hence the heat capacity C_P will be correct at temperatures above 900°C. Therefore, the tabulated heat capacities of spinel should be correct at temperatures above 850–900°C and too small at lower temperatures. In terms of entropy, the high-temperature entropies of $MgAl_2O_4$ need a term added to them to take account of any residual disorder that has not been measured calorimetrically. This corresponds to the configurational entropy S_{conf} appropriate for the quenched Mg-Al disorder in the temperature range 850–900°C.

Precise phase-equilibrium measurements on fluid-absent reactions may be used to test this model of residual entropy. Reaction 3 (2 enstatite + spinel = pyrope + for-

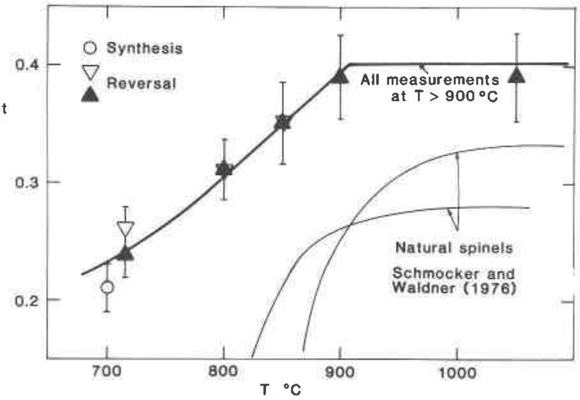

Fig. 2. Measured degree of inversion of $MgAl_2O_4$ spinel as a function of temperature. Note that all experiments at $T > 900°C$ give the same amount of tetrahedral Al (0.39 approx., Table 1). Open and closed triangles refer, respectively, to equilibrium approached from high X^{tet}_{Al} and low X^{tet}_{Al}. Data of Schmocker and Waldner are ESR measurements of Cr^{3+}-bearing natural spinels (see text).

sterite) has been studied in the pressure and temperature ranges of 18–30 kbar and 900–1600°C (Fig. 3). The calorimetric data of Table 3 indicate that, at 1 atm and 1000 K, Reaction 3 has standard entropy and heat-capacity changes of +1.83 cal/K and −5.25 cal/K, respectively, neglecting any residual terms in spinel. Extrapolation of the data to higher temperatures is hindered by the lack of heat-capacity data for pyrope and enstatite. There are several reasonable approximations that may be made, however. First, it is necessary to add an entropy term for quenched spinel disorder, which, from the previous discussion, is estimated to be on the order of 2.3–3.3 cal/K. Second, the heat capacities of enstatite and pyrope in the range 1000–1873 K must be estimated or the heat capacity of reaction assumed fixed at the 1000 K value. Enstatite and pyrope heat capacities at high temperatures were estimated using the Debye model with data from Kieffer (1980) and calorimetric Debye temperatures of 620 and 1080 K, respectively. The latter were obtained by fitting the measured heat capacities at 1000 K. Any errors in this approximation tend to cancel, because there are 20 atoms on each side of Reaction 3 for which estimates were employed. A combination of estimated heat capacities and the measured values for spinel and forsterite yield a heat-capacity change of Reaction 3 of

$$\Delta C_P = -14.3 + 0.009T \, (1000 \leq T \leq 1873 \text{ K}).$$

Adding the configurational and measured calorimetric terms yields, for this equilibrium:

$$\Delta S_T = 1.83 + S_{\text{conf}} - 14.3 \ln(T/1000) + 0.009(T - 1000).$$

The slope of the reaction on a P-T diagram may now be calculated from the measured volumes of the reactants and products, taking account of the solubility of $MgAl_2SiO_6$ in the pyroxene in the manner described by Wood and Holloway (1984).

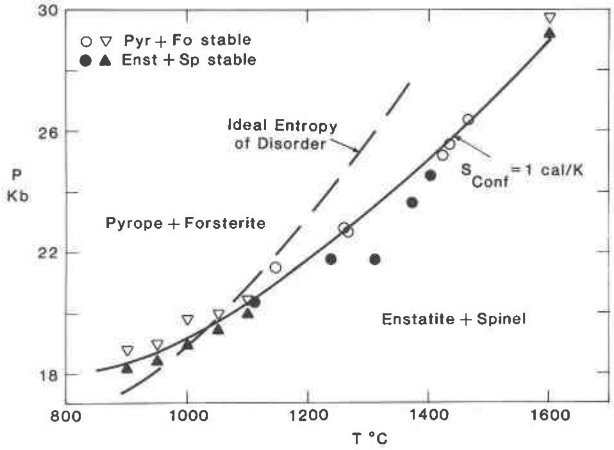

Fig. 3. Experimental data on the reaction enstatite + spinel = pyrope + forsterite. ○ ● Perkins et al. (1981). ▽ ▲ Danckwerth and Newton (1978) (900–1100°C) and Gasparik and Newton (1984) (1600°C). Open symbols, Pyr + Fo stable; solid symbols, Enst + Sp stable. Curve labeled "ideal entropy of disorder" assumes a residual entropy of 2.6 cal/K. Solid curve is calculated for a residual entropy of 1 cal/K.

Figure 3 illustrates a comparison between the calculated P-T curve for Reaction 3 and the experimental data of Danckwerth and Newton (1978), Perkins et al. (1981), and Gasparik and Newton (1984). It may readily be seen that the ideal random configurational entropy of spinel of 2.6 cal/K drastically overestimates the P-T slope of the reaction. A much better fit is obtained if a quenched entropy contribution of only about 1 cal/K is used (Fig. 3). The slope of the reaction is extremely sensitive to the assumed residual entropy contribution and is, therefore, a very sensitive monitor of the macroscopic properties of spinel. This can be seen even more clearly on Figure 4, which is a plot of standard-state free-energy change ΔG^0_3 for Reaction 3 as a function of temperature at 1 atm. The phase-equilibrium data place extremely strong constraints on the temperature dependence of ΔG^0_3 and hence on the entropy of spinel disorder.

The high-temperature heat-capacity approximation that we have made also affects the best-fit value of configu-

Table 3. Thermodynamic data at 1000 K and 1 atm

Mineral	H* (cal)	S (cal/K)	C_P (cal/K)
enstatite	-16840	93.51	60.28
spinel	-5380±180**	63.21	42.61
pyrope	-20300	185.83	116.01
forsterite	-15140	66.23	41.91

* enthalpy of formation from oxides
** Charlu et al. (1975)
Data from compilation of Wood and Holloway (1984)

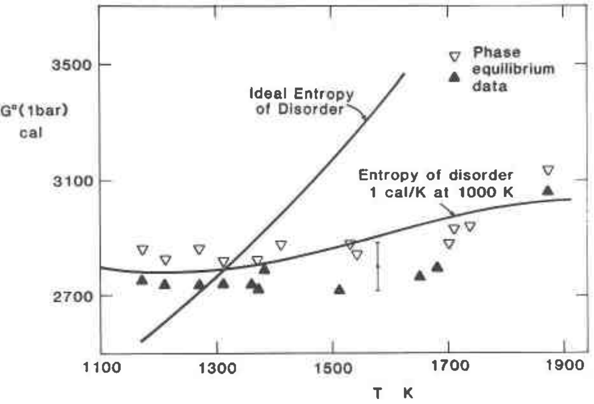

Fig. 4. Same experimental data as Fig. 4 recalculated to $\Delta G^0_{1\ \mathrm{bar}}$ for Reaction 3. Arrows indicate direction of "true" $\Delta G^0_{1\ \mathrm{bar}}$ at the temperature of interest. Error bar gives approximate uncertainty in ΔG values derived from high-pressure experiments. About 1 cal/K of residual disorder is required by the experimental data.

rational entropy. If the Debye approximation is discarded and the heat capacity of reaction assumed constant at the 1000 K value of −5.25 cal/K, the best-fit residual entropy term would diminish to about 0.3 cal/K. Under either set of assumptions, therefore, the residual entropy is much smaller than would be predicted on the basis of random mixing using Equation 4. Therefore, the entropy of Mg-Al mixing must be much less than the ideal value for a given value of the disorder parameter, x. There are two possible mechanisms by which the disordering entropy may be lowered: short-range ordering or nonconfigurational entropy contributions to the free energy of the Mg-Al exchange reaction.

NONIDEAL ENTROPY EFFECTS

Consider the Mg-Al exchange (Reaction 1) involving octahedral and tetrahedral spinel sites. With a given extent of disorder, x, the free energy of the spinel will be changed through the enthalpy ($\Delta H^0_{\mathrm{dis}}$), configurational entropy (S_{conf}), and nonconfigurational entropy ($\Delta S^0_{\mathrm{dis}}$) terms as follows:

$$(G_{\mathrm{sp}})_{x=x} - (G_{\mathrm{sp}})_{x=0} = x\Delta H^0_{\mathrm{dis}} - T(x\Delta S^0_{\mathrm{dis}} + S_{\mathrm{conf}}). \quad (5)$$

The nonconfigurational entropy term is a contribution derived from the standard-state properties of completely normal and completely inverse spinel. It reflects changing vibrational properties of the mineral with degree of inversion. This term is usually regarded as being subordinate in magnitude to the configurational term and was assumed to be zero by Navrotsky and Kleppa (1967). In order to reduce the unmeasured, residual entropy of spinel from about 3 cal/K to 1 cal/K at x of 0.35, a value of $\Delta S^0_{\mathrm{dis}}$ of approximately −6 cal/K would be required. Although this seems extremely large for a cation-exchange reaction, it cannot be entirely ruled out, since site-population data on Fe_3O_4 suggest a negative exchange entropy in that phase. Wu and Mason (1981) determined the temperature dependence of the disordering equilibrium in magnetite using thermopower measurements. Their results may be interpreted either as indicating a composition-dependent exchange enthalpy or a moderate (−3.2 cal/K) negative entropy of cation exchange (O'Neill and Navrotsky, 1983). The possibility of a negative entropy of Al-Mg exchange in spinel can be tested by considering the temperature-dependence of the disorder parameter, x.

If the order-disorder data are fitted to a simple, nonconvergent disorder model (Eq. 2) and adding a nonconfigurational entropy term of the type discussed above, we obtain

$$\frac{-\Delta H^0_{\mathrm{dis}} + T\Delta S_{\mathrm{dis}}}{RT} = \ln \frac{x^2}{(1-x)(2-x)}. \quad (6)$$

Substituting values of x appropriate to 700°C (0.23) and 900°C (0.4) yields a result for $\Delta S^0_{\mathrm{dis}}$ of +10.5 cal/K, which is completely inconsistent with that derived from the phase-equilibrium experiments (−6 cal/K). This means either that the nonconfigurational entropy explanation is wrong or that the enthalpy of Al-Mg exchange has a complex composition dependence (O'Neill and Navrotsky, 1983). The most likely explanation is that the entropy of disorder is actually reduced by short-range Mg-Al order rather than by a large nonconfigurational entropy of exchange.

There are a number of possible ways in which short-range ordering could reduce the entropy of a nominally disordered spinel. The tetrahedral Al atoms may, for example, tend to cluster in discrete, but randomly distributed regions of the structure. Alternatively, a tendency toward preserving local charge balance may necessitate short-range ordering whereby tetrahedral Mg is accompanied by octahedral Al and vice versa. Although we cannot distinguish between these and other possibilities, it is of interest to examine the "local charge-balance" model to determine the extent of order required to reduce the residual entropy term to about 1 cal/K. If, for illustrative purposes, we assume a quenched x of about 0.25 (corresponding to 730°C, Fig. 2), then the ideal configurational entropy for this spinel (with no charge-balance constraints) from Equation 4 would be 2.62 cal/mol·K. Preservation of local charge balance on a small number of formula units could require that any two formula units chosen at random in the structure have the stoichiometric formula $Mg_2Al_4O_8$ or any four formula units $Mg_4Al_8O_{16}$ and so on. This is in contrast to an ideal disordered spinel in which any two formula units chosen at random can have formulae $MgAl_5O_8$, Al_6O_8, $Mg_3Al_3O_8$, and so on. Entropies in the locally charge-balanced cases can be calculated in the conventional way from the Boltzmann formula,

$$S_{\mathrm{conf}} = -k \ln \frac{N!}{n_{\mathrm{A}}!\ n_{\mathrm{B}}!}$$

where N, n_{A}, and n_{B} refer, respectively, to number of sites and numbers of atoms of types A and B involved in mixing. Consider, for example, x of 0.25 and local charge balance on the two-formula-unit basis. There are three possible configurations of charge-balanced $Mg_2Al_4O_8$: (Mg,

$Mg)_{tet}(Al_4)_{oct}O_8$, $(Mg, Al)_{tet}(Mg, Al_3)_{oct}O_8$, and $(Al_2)_{tet}(Mg_2Al_2)_{oct}O_8$ with probabilities of occurrence (at $x = 0.25$) of 0.5625, 0.375, and 0.0625, respectively. Applying the Boltzmann formula for 1 mol of spinel gives

$$S_{conf} = \frac{-R}{2}[0.5625 \ln 1 + 0.375(\ln 2 + \ln 4) + 0.0625 \ln 6]$$
$$= 0.89 \text{ cal/mol·K}.$$

The gas constant R is divided by two to take account of the two-formula-unit basis for ordering. Extension to three- and four-formula-unit ordering yields 1.19 and 1.37 cal/K for the configurational entropy, respectively. The implication is that in order to explain the phase-equilibrium data, spinel must exhibit extensive short-range order, equivalent to local charge balance on a two- to three-formula-unit basis. This result is supported by recent calorimetric data on the $MgAl_2O_4$-$Al_{8/3}O_4$ spinel join (Navrotsky et al., 1986). A combination of enthalpy and phase-equilibrium data on this join requires that the partial molar entropy of mixing of the defect $Al_{8/3}O_4$ spinel component be very close to zero at all mole fractions and much less than required by "ideal" disordered models. Extensive short-range Al-Mg or Al-defect ordering is the most likely explanation (Navrotsky et al., 1986).

Additional information on the enthalpy and entropy of spinel disorder may be obtained from the calorimetric data of Osborne and Navrotsky (1984). These authors determined the heat absorbed when $MgAl_2O_4$ samples previously quenched from high temperature were dropped into a calorimeter at 700°C. By comparing their results with those for annealed spinel samples, they found that the enthalpy of reordering at 700°C is 260 ± 147 cal/mol. It may be seen from Table 1 that a quenched sample with initial X_{Al}^{tet} of 0.37–0.39 will reorder to some extent in the calorimeter at 700°C. In the 1 h or so over which most calorimetric measurements are made, a reduction in X_{Al}^{tet} of 0.07–0.1 might be expected. Because the total entropy of disorder is about 1.0 cal/K at X_{Al}^{tet} of 0.25 to 0.33, the increase in entropy of Mg-Al disorder from x of 0.23 at 700°C to x of 0.4 at 900°C is approximately 0.5 cal/K. Thus we have

$$\frac{C_P^{dis}}{T} = \frac{dS_{dis}}{dT} = \frac{0.5}{200} = 2.5 \times 10^{-3}$$
$$C_P^{dis} = 2.5 \text{ cal/mol·K}.$$

Therefore, the heat effect on rearranging from the quenched configuration to one that corresponds to x of about 0.3 corresponds to the integrated heat effect on reordering through about 100°C (Fig. 2). Thus the calculated heat effect is approximately 250 cal/mol, in excellent agreement with Osborne and Navrotsky's results.

CONCLUSIONS

MASS NMR spectroscopy is a precise method for determining the distribution of ^{27}Al between octahedral and tetrahedral sites in $MgAl_2O_4$ spinel. The spectra of samples quenched from high temperature indicate that the fractional occupancy of tetrahedral sites by Al increases from 0.23 at 700°C to 0.39 at 900°C. Experiments at higher temperatures (1050–1600°C) produce degrees of inversion that are indistinguishable from those at 900°C. In view of the ease of reordering at low temperatures, it is likely that the latter results reflect an inability to quench configurations more disordered than the 900°C one.

The way in which measurements of heat capacity and entropy are made result in there being residual disorder that is unaccounted for calorimetrically at temperatures below 850–900°C. Assuming that, for a given degree of inversion, Mg and Al are readily mixed on tetrahedral and on octahedral sites, the residual entropy is approximately 3 cal/K. The random model has been tested using phase-equilibrium measurements on Reaction 3, 2 enstatite + spinel = pyrope + forsterite. The calorimetrically measured entropy and heat-capacity changes of this reaction are very small, so that its calculated P-T slope is extremely sensitive to the residual disorder term. The phase-equilibrium experiments are not consistent with a residual disorder term as large as 3 cal/K, however. They constrain it to be close to 1 cal/K. Based on measured unit-cell edge as a function of inversion, pressure should not have a significant effect on the amount of tetrahedral Al at any given temperature.

The discrepancy between "phase equilibrium" and "spectroscopic" measurements of residual entropy requires either that there is a large nonconfigurational entropy of Mg-Al exchange or that there is substantial short-range Mg-Al order in partially inverse spinel. The sign of the required nonconfigurational entropy of exchange is, however, opposite to that obtained from the temperature dependence of the inversion parameter so that short-range order is the most likely explanation. This conclusion is supported by enthalpy and phase-equilibrium measurements on the $MgAl_2O_4$-$Al_{8/3}O_4$ spinel join (Navrotsky et al., 1986).

Recent calorimetric measurements of the enthalpy of Mg-Al reordering at 700°C confirm our deduction of a relatively small entropy of Mg-Al disorder. Osborne and Navrotsky (1984) obtained a heat effect of 260 ± 147 cal/mol which, on the basis of the experiments performed here, corresponds to a lowering of x from 0.38 to about 0.30. The small effect is in good agreement with our value of 1.0 cal/K of residual entropy, which would yield an enthalpy of reordering of about 250 cal/mol. From the point of view of phase-equilibrium calculations, it appears that the calorimetrically measured enthalpy and entropy of spinel may be used at high temperature provided that the 1.0 cal/K of residual disorder is added.

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REFERENCES

Andrew, E.R. (1971) The narrowing of NMR spectra of solids by high-speed specimen rotation and the resolution of chemical shift and spin multiplet structures for solids. Progress in Nuclear Magnetic Resonance Spectroscopy, 8, 1–39.

Brun, E., and Hafner, S. (1962) Die elektrische quadrupolaufspaltung von Al^{27} in Spinell $MgAl_2O_4$ und Korund Al_2O_3. I. Paramagnetische Kernresonanz von Al^{27} und Kationenverteilung in Spinell. Zeitschrift für Kristallographie, 117, 37–62.

Buddington, A.F., and Lindsley, D.H. (1964) Iron-titanium oxide minerals and their synthetic equivalents. Journal of Petrology, 5, 310–357.

Danckwerth, P.A., and Newton, R.C. (1978) Experimental determination of the spinel peridotite to garnet peridotite reaction in the system MgO-Al_2O_3-SiO_2 in the range 900–1100°C and Al_2O_3 isopleths of enstatite in the spinel field. Contributions to Mineralogy and Petrology, 66, 189–201.

Fenzke, D., Freude, D., Frohlich, T., and Hasse, J. (1984) NMR intensity measurements of half-integer quadrupolar nuclei. Chemical Physics Letters, 111, 171–175.

Gasparik, T., and Newton, R.C. (1984) The reversed alumina contents of orthopyroxene in equilibrium with spinel and forsterite in the system MgO-Al_2O_3-SiO_2. Contributions to Mineralogy and Petrology, 85, 186–196.

Gobbi, G.C., Christoffersen, R., Otten, M.T., Miner, B., Buseck, P.R., Kennedy, G.J., Fyfe, C.A., and Roy, R. (1984) Determination of Mg-Al order-disorder in spinel by high resolution Al-27 magic angle spinning (MAS) NMR. EOS, 65, 1144.

Kieffer, S.W. (1980) Thermodynamics and lattice vibrations of minerals: 4. Application to chain and sheet silicates and orthosilicates. Reviews of Geophysics and Space Physics, 18, 862–886.

Kinsey, R.A., Kirkpatrick, R.J., Hower, J., Smith, K.A., and Oldfield, E. (1985) High-resolution aluminum-27 and silicon-29 nuclear magnetic resonance spectroscopic study of layer silicates, including clay minerals. American Mineralogist, 70, 537–548.

Kirkpatrick, R.J., Kinsey, R.A., Smith, K.A., Henderson, D.M., and Oldfield, E. (1985a) High resolution solid-state sodium-23, aluminum-27, and silicon-29 nuclear magnetic resonance spectroscopic reconnaissance of alkali and plagioclase feldspars. American Mineralogist, 70, 106–123.

Kirkpatrick, R.J., Smith, K.A., Schramm, S., Turner, G., and Yang, W.-H. (1985b) Solid-state nuclear magnetic resonance spectroscopy of minerals. Annual Review of Earth and Planetary Sciences, 13, 29–48.

Meadows, M.D., Smith, K.A., Kinsey, R.A., Rothgeb, T.M., Skarjune, R.P., and Oldfield, E. (1982) High-resolution solid-state NMR of quadrupolar nuclei. National Academy of Sciences Proceedings, 79, 1351–1355.

Navrotsky, A., and Kleppa, O.J. (1967) The thermodynamics of cation distributions in simple spinels. Journal of Inorganic and Nuclear Chemistry, 29, 2701–2714.

Navrotsky, A., Wechsler, B.A., Geisinger, K., and Seifert, F. (1986) Thermochemistry of $MgAl_2O_4$-$Al_{8/3}O_4$ defect spinels. American Ceramic Society Journal, in press.

O'Neill, H.St.C., and Navrotsky, A. (1983) Simple spinels: Crystallographic parameters, cation radii, lattice energies, and cation distribution. American Mineralogist, 68, 181–194.

Osborne, M.D., and Navrotksy, A. (1984) A calorimetric study of $MgFe_2O_4$-$MgAl_2O_4$, $ZnFe_2O_4$-$ZnAl_2O_4$ solid solutions. Geological Society of America Abstracts with Programs, 16, 615.

Perkins, D., Holland, T.J.B., and Newton, R.C. (1981) The Al_2O_3 contents of enstatite in equilibrium with garnet in the system MgO-Al_2O_3-SiO_2 at 15–40 kbar and 900–1600°C. Contributions to Mineralogy and Petrology, 78, 99–109.

Sack, R.O. (1982) Spinels as petrogenetic indicators: Activity-composition relations at low pressure. Contributions to Mineralogy and Petrology, 71, 169–186.

Schmocker, U., and Waldner, F. (1976) The inversion parameter with respect to the space group of $MgAl_2O_4$ spinels. Journal of Physics C: Solid State Physics, 9, L235–237.

Wood, B.J., and Holloway, J.R. (1984) A thermodynamic model for subsolidus equilibria in the system CaO-MgO-Al_2O_3-SiO_2. Geochimica et Cosmochimica Acta, 48, 159–176.

Wu, C.C., and Mason, T.O. (1981) Thermopower measurements of cation distribution in magnetite. American Ceramic Society Journal, 64, 520–522.

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