American Mineralogist, Volume 77, pages 44–52, 1992

Temperature dependence of cation disorder in $MgAl_2O_4$ spinel using ^{27}Al and ^{17}O magic-angle spinning NMR

ROBERTA L. MILLARD, RONALD C. PETERSON
Department of Geological Sciences, Queen's University, Kingston, Ontario K7L 3N6, Canada
BRIAN K. HUNTER
Department of Chemistry, Queen's University, Kingston, Ontario K7L 3N6, Canada

ABSTRACT

The disorder of Mg^{2+} and Al^{3+} cations between the tetrahedral and octahedral sites in $MgAl_2O_4$ spinel has been determined by ^{27}Al magic-angle spinning (MAS) NMR spectroscopy for synthetic powders quenched from temperatures between 700 and 1400 °C. Disorder, measured by the fraction of Al in the tetrahedral site and described by the inversion parameter, x, increased with temperature from $x = 0.22$ (± 0.03) at 700 °C to $x = 0.29$ (± 0.03) at 1000 °C. This temperature-dependent increase in disorder is significantly lower than that reported in a previous ^{27}Al MAS NMR study by Wood et al. (1986) as a result of a more appropriate choice of instrument parameters for acquisition of the ^{27}Al MAS NMR spectra.

Cation disorder in $MgAl_2O_4$ was also investigated by ^{17}O MAS NMR on ^{17}O-enriched samples quenched from 700 and 1400 °C. The disorder increased from $x = 0.16$ (± 0.02) at 700 °C to $x = 0.24$ (± 0.03) at 1400 °C. This temperature-dependent increase in disorder was similar in magnitude but systematically lower than that obtained by ^{27}Al MAS NMR.

INTRODUCTION

The ability of the spinel structure to incorporate many cation species of different valence states into octahedral and tetrahedral sites lends stability to the spinel structure over a wide range of temperature, pressure, and composition. This has led to their utility as petrogenetic indicators of temperature and pressure (Buddington and Lindsley, 1964; Gasparik and Newton, 1984; Jamieson and Roeder, 1984; Mattioli and Wood, 1988).

Despite the utility of systems containing spinels, the study of mineral equilibria involving spinel is complicated by cation disorder in the spinel structure. For most spinels, the cation order-disorder behavior has not yet been well characterized (Sack, 1982; Mattioli and Wood, 1988; Nell et al., 1989).

The systematics of the spinel structure have been reviewed by Blasse (1964) and Hill et al. (1979). The majority of spinels show some degree of disorder, having a cation distribution somewhere between two end-member cation distributions: normal $^{[4]}A^{[6]}B_2O_4$ and inverse $^{[4]}B^{[6]}(AB)O_4$ (Barth and Posnjak, 1932). This disorder can be expressed by the general formula $^{[4]}(A_{1-x}B_x)^{[6]}(B_{2-x}A_x)O_4$ where x is referred to as the "degree of inversion."

Cation distribution in both natural and synthetic $MgAl_2O_4$ is well known to be partially disordered from calorimetric (Navrotsky and Kleppa, 1967), ESR (Schmocker and Waldner, 1976), NMR (Brun and Hafner, 1962; Gobbi et al., 1985; Wood et al., 1986), and neutron diffraction (Peterson et al., 1991) studies. Wood et al. (1986) have used high-field ^{27}Al MAS NMR spectra to determine the temperature dependence of cation disorder in quenched samples of synthetic powdered $MgAl_2O_4$. They measured an increase in disorder from $x = 0.21$ (± 0.02) at 700 °C to $x = 0.39$ (± 0.03) at 900 °C. The degree of disorder they obtained at high temperature, however, was inconsistent with Schmocker and Waldner's (1976) ESR data for heat-treated natural samples. Schmocker and Waldner determined the disorder in two heat-treated natural samples to increase to about $x = 0.3$ at 900–950 °C.

Recently, Peterson et al. (1991) measured the cation distribution in the synthetic $MgAl_2O_4$ sample of Wood et al. (1986) by neutron diffraction at temperatures between 600 and 1000 °C. They could not duplicate the high degree of disorder found by Wood et al. (1986). The present ^{27}Al MAS NMR study was undertaken to reinvestigate the temperature dependence of disorder in $MgAl_2O_4$, to reconcile the degree of disorder found by ^{27}Al MAS NMR to that found by other methods.

Potential for ^{17}O MAS NMR of spinels

The study of structure and bonding in minerals by ^{17}O NMR has only recently been systematically applied to the study of minerals (see Kirkpatrick, 1988). The ^{17}O MAS NMR technique is useful in the study of spinels, which contain isolated tetrahedra, because chemical shifts in ^{17}O MAS NMR spectra of O in such structures is sensitive to substitution by both octahedral and tetrahedral cations (Timken et al., 1987). The present ^{17}O MAS NMR study was undertaken to investigate the potential of ^{17}O MAS NMR for determining cation ordering as a function of temperature in spinels. The ^{17}O MAS NMR will give a

0003–004X/92/0102–0044$02.00

TABLE 1. Thermal history and final inversion parameter (x) for $MgAl_2O_4$ spinel

Sample no.	^{17}O *	Synthesis T (±5 °C)	Synthesis t (h)	Equilibrations 1 T (±5 °C)	Equilibrations 1 t (h)	Equilibrations 2 T (±5 °C)	Equilibrations 2 t (h)	x (±0.03)
RLM104	*	1300	60	—	—	—	—	—
RLM105	*	1300	60	700	409	—	—	0.22
RLM106	*	1300	60	1401	29	—	—	0.29 0.30
RLM107		1298	129	—	—	—	—	0.26
RLM108A		1298	129	1202	71–87	—	—	0.29
RLM108B		1298	129	1202	220	—	—	0.30
RLM109		1298	129	1402	42	—	—	0.30
RLM110		1298	129	1004	186	—	—	0.29
RLM111		1298	129	807	180	—	—	0.25
RLM112		1298	129	1402	42	902	528	0.27
RLM150		1298	129	800	498	—	—	0.26
RLM151		1298	129	800	498	1201	138	0.28
RLM152		1298	129	800	498	1002	166	0.29
RLM153		1298	129	800	498	902	471	0.25

* Denotes samples containing ^{17}O.

unique perspective on cation ordering in spinels and allow a second estimate of cation disorder for comparison to ^{27}Al MAS NMR results from the same samples.

EXPERIMENTAL METHODS

Syntheses

One batch of synthetic $MgAl_2O_4$ was prepared by sintering an equimolar mixture of dried commercial analytical grade Al_2O_3 (Aldrich, Milwaukee) and MgO (Aesar, Toronto) at 1300 °C in air for 129 h with three regrindings. Samples were heated in a vertical tube furnace (Deltech Inc., Denver).

A second batch of $MgAl_2O_4$ was prepared as above except 15–20% ^{17}O-enriched Al_2O_3 was used. This Al_2O_3 was prepared in two steps. First, the ^{17}O-enriched bayerite [$Al(OH)_3$] was prepared by reaction of triethylaluminum [$Al(C_2H_5)_3$] (Ethyl Corp.) with 26.8% ^{17}O-enriched H_2O (MSD Isotopes, Montreal) according to the reaction

$$Al(C_2H_5)_3\ (l) + 3H_2O\ (l) \rightarrow Al(OH)_3\ (s) + 3C_2H_6\ (g). \quad (1)$$

A slight excess of 26.8% ^{17}O-enriched H_2O (1.7 mL) was added to 150 mL dry hexane containing 3.4 mL triethylaluminum, at a rate of one drop per minute, under positive N_2 pressure on a Schlenk line. The mixture was stirred during the addition of H_2O and for about 1 h afterward.

The precipitate of ^{17}O-enriched $Al(OH)_3$ was dried and heated for 2 h in air at 1200–1250 °C to produce ^{17}O-enriched α-Al_2O_3. $MgAl_2O_4$ was then prepared from ^{17}O-enriched Al_2O_3 by sintering with MgO for 60 h under N_2 (g) with one regrinding.

Synthetic Al_2O_3 and spinel were examined by powder X-ray diffraction and found to be single phase, and the stoichiometry was checked by determination of the lattice parameters. The a cell edges for selected samples of synthetic $MgAl_2O_4$ were $a = 8.083(1)$ Å and $a = 8.081(1)$ Å for $MgAl_2O_4$ enriched and nonenriched in ^{17}O, respectively. These are within the range of values previously reported for synthetic $MgAl_2O_4$ (Yamanaka and Takéuchi, 1983; Singh et al., 1975) and are typical of stoichiometric (MgO-Al_2O_3) spinel (Chiang and Kingery, 1989).

Cation equilibration experiments

All synthetic spinels were heated at 800, 900, 1000, 1200, or 1400 °C for various periods of time, as outlined in Table 1. Samples equilibrated at 700, 800, and 900 °C were heated in a muffle furnace for several days in air and then removed and quenched in liquid N_2. The quench time was estimated at 5–10 s. Samples equilibrated at 1000, 1200, and 1400 °C were heated in a vertical tube furnace. Samples containing ^{17}O were heated under N_2 (g), whereas others were heated in air. After heating, the pellets were drop quenched into liquid N_2. Quench time was estimated at approximately 2 s. The attainment of equilibrium cation distribution was verified at 900, 1000, and 1200 °C by bringing samples to these temperatures from both higher and lower initial temperatures (see Table 1).

NMR SPECTROSCOPY

Instrumentation

The ^{27}Al and ^{17}O spectra were acquired at 104.2 MHz and 52.2 MHz, respectively, on a narrow-bore AM-400 NMR spectrometer (Bruker Spectrospin, Milton, Ontario), equipped with a 9.4 T magnet, and a variable-frequency Doty magic-angle spinning solids probe (Doty Scientific Inc., Columbia, South Carolina). Spectra were acquired using a Bloch decay or "one-pulse" experiment during magic-angle spinning (MAS). Powdered samples were rotated in zirconia rotors at the angle of 54°44′ to the magnetic field vector at spinning speeds of 10 to 11 kHz.

Parameters for ^{27}Al MAS NMR spectra

The ^{27}Al MAS NMR spectra were collected at room temperature using a pulse width of 0.8 μs or about $\pi/34$ relative to the solution $\pi/2$ (90°) pulse width (13–14 μs) [measured using 0.2 M $Al(NO_3)_3$ (aq)]. A delay of 5 s was allowed between pulses. However, there was no change

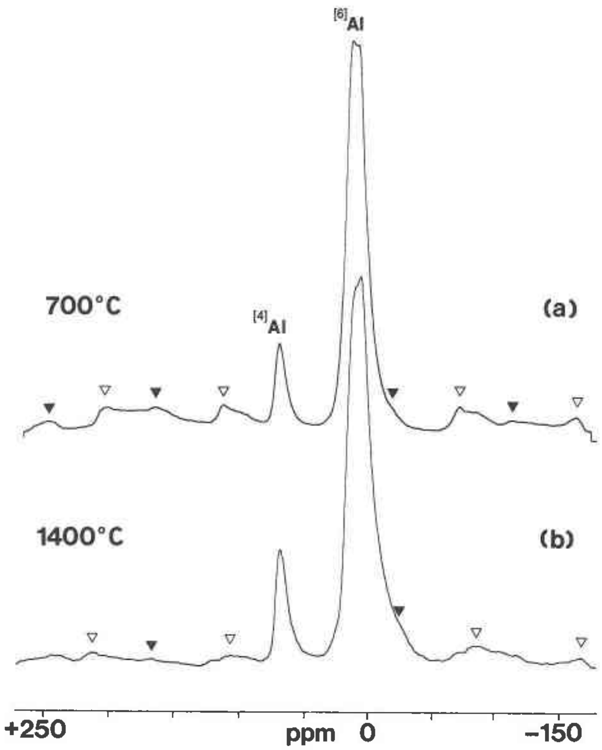

Fig. 1. High-resolution 9.4 T ^{27}Al MAS NMR spectra of synthetic $MgAl_2O_4$ quenched from (a) 700 °C and (b) 1400 °C. The peaks corresponding to Al in octahedral and tetrahedral coordination are denoted by $^{[6]}Al$ and $^{[4]}Al$, respectively. Note the increase in intensity of the $^{[4]}Al$ peak with increase in quench temperature. Open and solid triangles denote spinning sidebands associated with $^{[6]}Al$ and $^{[4]}Al$ center peaks, respectively. Samples were spinning at 10–11 kHz.

in inversion parameter determined from spectra acquired with relaxation delays of 0.1, 5.0, or 30 s. This is consistent with the observation that ^{27}Al in both the octahedral and tetrahedral environments in $MgAl_2O_4$ has the same spin-lattice relaxation time constant [T_1 = 24 (± 1) s]. T_1 was determined by saturation recovery (Fukushima and Roeder, 1981).

The spectra were collected in the time domain, as free-induction-decays (FIDs), using a spectral width of 50000 Hz and 4096 or 8192 data points. Between 64 and 200 FIDs were acquired and added to produce each spectrum. FIDs were Fourier transformed to spectra in the frequency domain after exponential multiplication with 100-Hz line broadening. Chemical shifts are reported relative to $[Al(H_2O)_6]^{3+}$ in 0.2 *M* aluminum nitrate $[Al(NO_3)_3]$ (aq). Rolling base lines in spectra were corrected by quadratic base-line correction. Horizontal base lines were then estimated, and inversion parameters were determined by cutting and weighing the center peaks. The ^{27}Al MAS NMR spectra of $MgAl_2O_4$ yielded well-separated peaks for octahedral and tetrahedral ^{27}Al, but spectra were complicated by multiple spinning sidebands (see Fig. 1). This made base line estimation difficult, resulting in an estimated error of ±0.03 in *x*.

Integration was done using center peaks only, but *x* values were not systematically different when the first pair of sidebands was included with each center peak. The small tetrahedral sideband overlapping the octahedral peak at about −20 ppm (see Fig. 1) has not been subtracted from the overall intensity of the octahedral peak; however, the systematic error in *x* involved in not making this correction was estimated to be small (+0.002) compared with the overall error (± 0.03) estimated for the technique.

Reproducibility in measuring *x* was checked on two samples of $MgAl_2O_4$. NMR spectra of one sample were acquired four times, and two NMR spectra were acquired for another sample. Inversion parameters calculated for these samples (using center peaks only) agreed to within ±0.01 and ±0.02, respectively.

Parameters for ^{17}O MAS NMR spectra

The ^{17}O MAS NMR spectra of the ^{17}O-enriched $MgAl_2O_4$ spinels were acquired at room temperature using a B_1 pulse width of 1.0 μs or $\pi/27$ relative to the solution $\pi/2$ (90°) pulse width (13.5 μs) (measured using 26.8% ^{17}O-enriched H_2O). The spectra were collected using a spectral width of 20000 Hz and 2048 data points, and a delay of 5 s between pulses. Between 128 and 512 FIDs were collected and added to produce each spectrum. FIDs were Fourier transformed after zero filling to 4096 data points and exponential multiplication using 200-Hz line broadening. Spectra were plotted after quadratic base-line correction. Chemical shifts are reported relative to 26.8% ^{17}O-enriched H_2O.

The ^{17}O spectra of $MgAl_2O_4$ were integrated by curve fitting using the Glinfit line fitting program (Bain, 1989), using Lorentzian lines. Curve fitting was necessary to resolve overlapping peaks in the NMR spectrum. Each ^{17}O spectrum could be fitted with a two-line calculated spectrum with under 7% RMS error in the agreement between the observed and the calculated spectrum. A 7% RMS error in the calculated line intensities corresponds to a maximum error of ±0.03 for *x*.

RESULTS AND DISCUSSION FOR ^{27}Al MAS NMR

The ^{27}Al MAS NMR spectra

Typical ^{27}Al MAS NMR spectra of $MgAl_2O_4$ quenched from 700 and 1400 °C are shown in Figure 1. The ^{27}Al MAS NMR spectra of $MgAl_2O_4$ contain a low field peak at 68 ppm [from $Al(NO_3)_3$] and a high field peak at 7 ppm, corresponding to AlO_4 tetrahedra ($^{[4]}Al$) (Müller et al., 1986) and AlO_6 octahedra ($^{[6]}Al$) (Fyfe et al., 1982; Lippmaa et al., 1986), respectively.

The spectra are consistent with those of previous workers for $MgAl_2O_4$ (Gobbi et al., 1985; Dupree et al., 1986; Wood et al., 1986). The ^{27}Al MAS NMR chemical shifts of $MgAl_2O_4$ are compared with literature values in Table 2. The chemical shifts in the spectra of Gobbi et al. (1985), at the same applied field as the present study, vary slightly

TABLE 2. The ^{27}Al MAS NMR chemical shifts of synthetic $MgAl_2O_4$

Chemical shifts			
$^{[4]}$Al (ppm)	$^{[6]}$Al (ppm)	Reference	Field strength (Tesla)
68	7	this study	9.4
69.7	9.8	Gobbi et al. (1985)	9.4
72	11	Wood et al. (1986)	11.7

from those reported here, probably because of uncertainty in the position of their peaks due to complication of spectra by spinning sidebands. The observed chemical shifts in our spectra of $MgAl_2O_4$ (at 9.4 T) are systematically 4 ppm to high field of those reported by Wood et al. (1986) at 11.6 T, probably because of an increase in the field-dependent quadrupolar shift of the signal at the lower applied field used in this study. The chemical shifts reported by us as well as previous workers (Table 2) are center-of-gravity shifts only and have not been corrected for field-dependent quadrupolar shift effects (see Akitt, 1989).

Calculation of the inversion parameter

The inversion parameter (x) was calculated from the ratio of Al in the octahedral ($^{[6]}$Al) and tetrahedral ($^{[4]}$Al) sites in the spinel. From the general formula $^{[4]}(Mg_{1-x}Al_x)^{[6]}(Al_{2-x}Mg_x)O_4$, the ratio of octahedral to tetrahedral Al is $^{[6]}Al/^{[4]}Al = (2 - x)/x$ or $x = 2/[1 + (^{[6]}Al/^{[4]}Al)]$.

Cation disorder as a function of temperature

The inversion parameters for synthetic $MgAl_2O_4$ spinel quenched from various equilibration temperatures between 700 and 1400 °C are listed in Table 1. The inversion parameter (x) is plotted against equilibration temperature in Figure 2. Disorder in $MgAl_2O_4$ was found to increase from $x = 0.22$ (± 0.03) at 700 °C to $x = 0.29$ (± 0.03) at 1000 °C. The attainment of equilibrium cation distribution was confirmed at 900 and 1000 °C when samples approaching equilibrium from both higher and lower initial temperatures gave final inversion parameters that were equal within experimental error.

There was no change in x for samples equilibrated at temperatures higher than 1000 °C before quenching. This plateau in the slope has been attributed to cation reordering during quenching (Wood et al., 1986). The inversion parameter determined for the synthesis experiment (1300 °C) is lower than those determined for the other samples quenched above 1000 °C (see Fig. 2) because the synthesis experiment was not quenched. This lower inversion is due to cation reordering during the relatively slower cooling of these samples (minutes) as compared with the quenched samples (seconds).

Comparison with previous studies of disorder in $MgAl_2O_4$

The present correlation between inversion parameter and temperature is compared with previous studies for $MgAl_2O_4$ in Figure 2. There is general agreement among all curves in form; each shows an increase in x with temperature. Also, the curves in both this study and Wood et al. (1986) exhibit a high-temperature plateau attributed to quench effects (Wood et al., 1986). This effect is absent in the study by Peterson et al. (1991) because their work was done at elevated temperature.

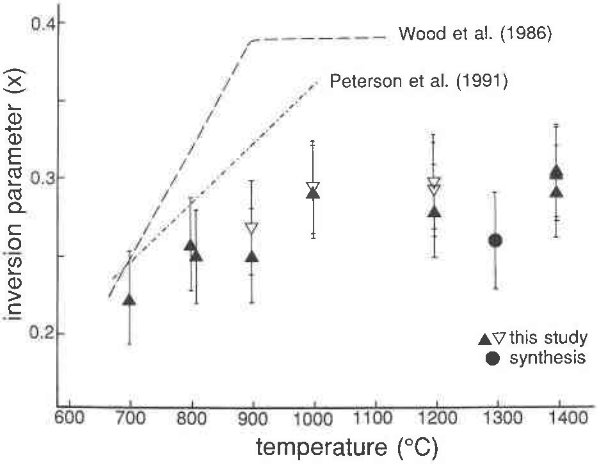

Fig. 2. The degree of inversion x as a function of equilibration temperature for synthetic $MgAl_2O_4$. Triangles denote data from this study. Open triangles (pointing down) denote samples approaching equilibrium cation disorder from a previously higher temperature, whereas solid triangles (pointing up) denote samples approaching equilibrium from a previously lower equilibration temperature. Trends of data from previous studies are also indicated. Wood et al. (1986) (dashed line) performed ^{27}Al MAS NMR on quenched samples. Peterson et al. (1991) (dot-dash) performed in situ neutron diffraction on the sample of Wood et al.

Our data differ substantially from the ^{27}Al MAS NMR data reported by Wood et al. (1986). At low temperature (700 °C), the inversion parameter measured in this study is similar to that determined by Wood et al. [$x = 0.22$ (± 0.03) vs. $x = 0.21$ (± 0.02), respectively]. However, the disorder in $MgAl_2O_4$ spinel increased more slowly with temperature in this study, reaching a maximum quenchable disorder of $x = 0.29$ (± 0.03), which is significantly lower than the maximum quenchable disorder of $x = 0.39$ (± 0.03) determined by Wood et al. We have shown that this discrepancy in x has resulted primarily because our ^{27}Al MAS NMR data and the ^{27}Al MAS NMR data of Wood et al. (1986) were collected using different NMR acquisition parameters. In particular, these are sample spinning speed and spectrometer B_1 pulse width.

Spinning speed and complication of spectra

The most obvious difference between our ^{27}Al MAS NMR experiment and those of Gobbi et al. (1985), Dupree et al. (1986), and Wood et al. (1986) is the sample spinning speed, as illustrated in Figure 3. The spectrum labeled a in Figure 3 resembles those in the previous work. It clearly shows spinning sideband intensity contained under the

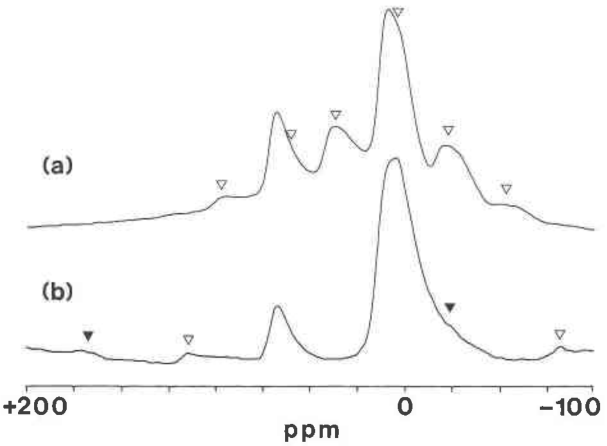

Fig. 3. The ^{27}Al MAS NMR spectra of one sample of $MgAl_2O_4$ (RLM106) at different spinning speeds. For the spectrum labeled a, the sample was spinning at 3–3.5 kHz. The spectrum is similar to those obtained by Gobbi et al. (1985), Dupree et al. (1986), and Wood et al. (1986), showing spinning sidebands (triangles) overlapping both the octahedral and tetrahedral peaks. For the spectrum labeled b, the sample was spinning at 10–11 kHz. Open and solid triangles denote spinning sidebands associated with $^{[6]}Al$ and $^{[4]}Al$ peaks, respectively. Most of the spinning sidebands are well separated from the center peaks.

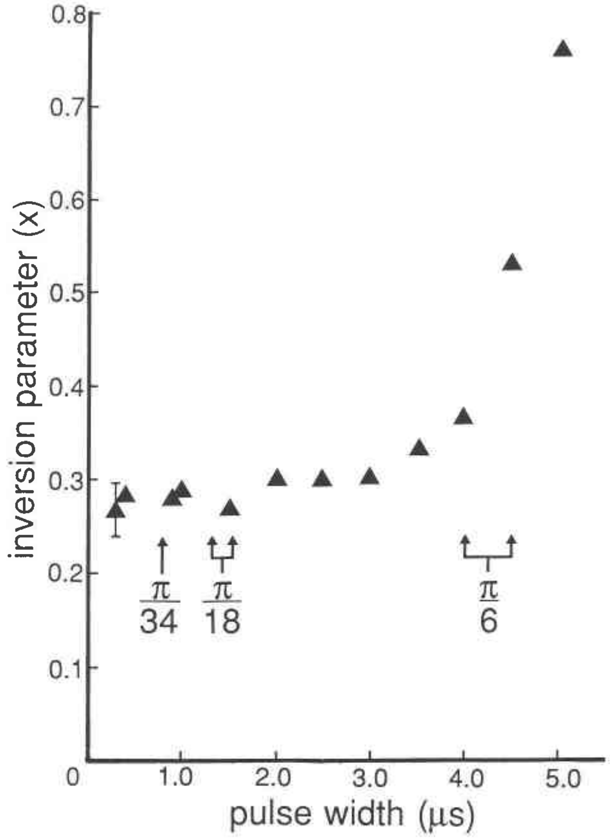

Fig. 4. The apparent inversion parameter, x, of $MgAl_2O_4$ quenched at 1400 °C (RLM106), as determined by peak ratios in the ^{27}Al MAS NMR spectrum, increases with increase in the pulse width used for spectral acquisition. The $\pi/34$ is the pulse width (0.8 μs) used for acquisition of the spectra in this study. The $\pi/18$ is the maximum pulse width recommended by Lippmaa et al. (1986) for acquisition of quantitative ^{27}Al MAS NMR spectra. The $\pi/6$ is the pulse width used by Wood et al. (1986) for acquisition of their ^{27}Al MAS NMR spectra. The error bar indicates the estimated error in determining x from ^{27}Al MAS NMR spectra.

center peaks, making it difficult to determine relative peak intensities. Our samples were spinning three times faster than those of the previous workers (see Fig. 3, spectrum b). The faster spinning speed has moved the spinning sidebands away from the center peaks, minimizing overlap between the center peaks and the spinning sidebands and making integration more straightforward.

Spectrometer B_1 pulse width

The spectrometer pulse width is the duration of the radiofrequency field (B_1) used for excitation of the nuclear spin system. It is well known that relative peak intensities of different central lines in the MAS NMR spectra of half-integer quadrupolar nuclei, such as ^{27}Al, are dependent on pulse width (Samoson and Lippmaa, 1983; Fenzke et al., 1984; Lippmaa et al., 1986; Fernandez et al., 1988). The inversion parameter, which is determined from relative peak intensities in the MAS NMR spectrum, should also be dependent on pulse width. We have shown this to be the case. As shown in Figure 4, the apparent inversion parameter (x), determined from a series of ^{27}Al MAS NMR spectra of one $MgAl_2O_4$ sample acquired at various pulse widths, shows a clear dependence on pulse width.

Lippmaa et al. (1986) suggested that center line intensities are only quantitative within 5% accuracy for pulse widths shorter than that required to tip the magnetization by an angle of $\pi/[6(I + 1/2)]$ radians. Accordingly, the recommended maximum tip angle for ^{27}Al ($I = 5/2$) becomes $\pi/18$. The pulse width necessary to produce a $\pi/18$ tip angle is referred to as the $\pi/18$ pulse width. The position of the $\pi/18$ pulse width has been indicated in Figure 4. Note in Figure 4 that x remains constant for pulse widths shorter than the recommended $\pi/18$ pulse width but increases rapidly as pulse widths are increased above the recommended range.

The ^{27}Al MAS NMR spectra used in the present study were acquired using a pulse width of 0.8 μs, or $\pi/34$ (where the solution $\pi/2$ pulse width is 13–14 μs). This value is well below the recommended maximum pulse width for quantitative ^{27}Al NMR spectra (Lippmaa et al., 1986) and occurs in the region where x is independent of pulse width (see Fig. 4).

The ^{27}Al MAS NMR spectra reported by Wood et al. (1986) were acquired using a pulse width of $\pi/6$, which is longer than the $\pi/18$ pulse width recommended by Lippmaa et al. (1986) and occurs in the region where x is strongly dependent on pulse width (see Fig. 4).

The spectra of $MgAl_2O_4$ quenched from 1400 °C yielded

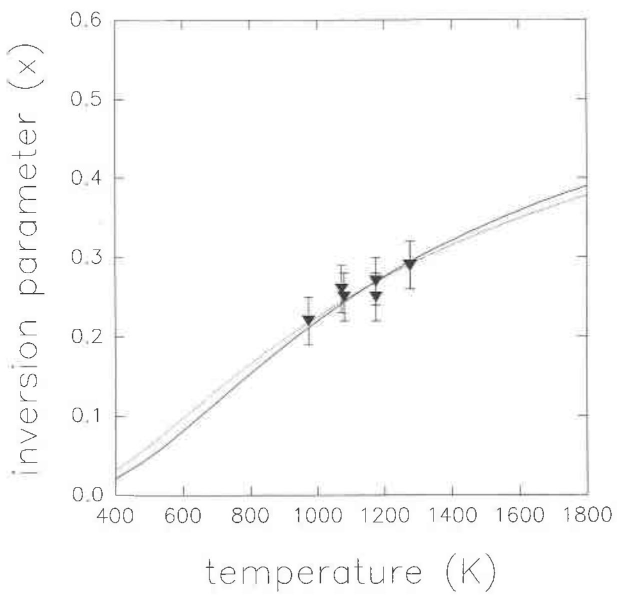

Fig. 5. Temperature dependence data for disorder in $MgAl_2O_4$ including only samples for which equilibrium cation distribution could be quenched (973–1273 K). The data were fitted using the Navrotsky-Kleppa (1967) thermodynamic model to give the solid curve and fitted using the O'Neill-Navrotsky (1983) model to give the dotted curve.

$x = 0.29$ when acquired using short pulse widths (below $\pi/18$) but gave $x \approx 0.35–0.5$ when using pulse widths approximating $\pi/6$. Therefore, by using the B_1 pulse width reported by Wood et al. (1986), we produce an overestimated degree of disorder for $MgAl_2O_4$.

IMPLICATION TO THERMODYNAMIC MODELS

Enthalpy of disordering

The temperature-dependent behavior of cation disorder in several spinels has been related to enthalpy of disorder by O'Neill and Navrotsky (1983) using a thermodynamic model based on quadratic dependence of enthalpy on disorder

$$\Delta H_D = \alpha x + \beta x^2 \quad (2)$$

where ΔH_D is the change in enthalpy on disordering. Our data, when fitted with the O'Neill-Navrotsky model (Eq. 2), gave $\alpha = 25$ (± 5) kJ and $\beta = 5.8$ (± 9.5) kJ (dotted curve, Fig. 5).

The temperature dependence of x determined in this study could be fitted equally well by the simpler equation of Navrotsky and Kleppa (1967)

$$\ln K = \ln[x^2(2 - x)^{-1}(1 - x)^{-1}] = -\Delta H_D/RT. \quad (3)$$

The Navrotsky-Kleppa (1967) model (Eq. 3) fitted to our data yields $\Delta H_D = 28$ (± 1) kJ (solid curve, Fig. 5). Considering the similarity between the two calculated curves, our data do not warrant use of the more complicated O'Neill-Navrotsky model (1983) over the temperature range studied.

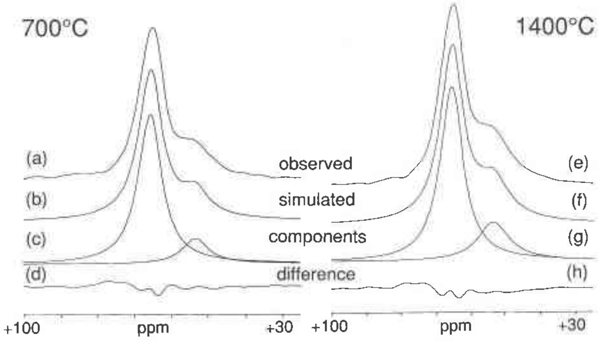

Fig. 6. High-resolution 9.4 T ^{17}O MAS NMR spectra and simulated spectra of $MgAl_2O_4$ quenched at 700 °C (left) and 1400 °C (right). Note the increase in the intensity of the small peak as cation disorder increases with increase in temperature. This is best seen by comparing the component spectra (c and g).

Configurational entropy

Wood et al. (1986) measured a higher degree of disorder from their ^{27}Al MAS NMR spectra than expected from configurational entropy considerations applied to phase equilibrium data. They suggested that, despite the large disorder they observed in their ^{27}Al MAS NMR experiment, the configurational entropy of $MgAl_2O_4$ must have remained low because the cations on either sublattice were undergoing short-range ordering. The present study showed that cation disorder in $MgAl_2O_4$ is not as extensive as that found by Wood et al. (1986). Therefore, short-range ordering within the spinel structure does not have to be as extensive as suggested by Wood et al. (1986) for disorder in $MgAl_2O_4$ to be compatible with phase equilibrium data.

RESULTS AND DISCUSSION FOR ^{17}O MAS NMR

The ^{17}O MAS NMR spectra

The ^{17}O MAS NMR spectra and simulated spectra for samples of ^{17}O-enriched $MgAl_2O_4$ quenched from 700 and 1400 °C are shown in Figure 6. Chemical shifts and peak widths are given in Table 3. Both spectra can be fitted with two peaks. The large, low field peak at 66 ppm (from $H_2{}^{17}O$) is considered to be due to O in an environment of normal cation distribution because $MgAl_2O_4$ is a normal spinel (20–30% disordered). The smaller, high field peak at 54 ppm is considered to result from disorder.

TABLE 3. The ^{17}O MAS NMR parameters* for ^{17}O-enriched $MgAl_2O_4$, at 9.4 T

		NMR parameters			
		O (normal)		O (disorder)	
Sample no.	Equil. T (±5 °C)	δ_{obs} (ppm)	$\Delta\nu_{1/2}$ (Hz)	δ_{obs} (ppm)	$\Delta\nu_{1/2}$ (Hz)
RLM105	700	66	420	54	500
RLM106	1401	66	430	54	600

* Chemical shifts (δ_{obs}) have not been corrected for field-dependent quadrupole effects; $\Delta\nu_{1/2}$ is peak width at half-height.

TABLE 4. Probabilities of the eight cation combinations around O in disordered $MgAl_2O_4$ spinel

	Cation probabilities				
No.	Tetrahedral site	Octahedral sites			O site probability
1	Al (x)	Al $1 - (x/2)$	Al $1 - (x/2)$	Al $1 - (x/2)$	= product
2	Al (x)	Mg ($x/2$)	Mg ($x/2$)	Mg ($x/2$)	= product
3	Al (x)	Al $1 - (x/2)$	Mg ($x/2$)	Mg ($x/2$)	= 3 × product
4	Al (x)	Al $1 - (x/2)$	Al $1 - (x/2)$	Mg ($x/2$)	= 3 × product
5	Mg $(1 - x)$	Al $1 - (x/2)$	Al $1 - (x/2)$	Al $1 - (x/2)$	= product
6	Mg $(1 - x)$	Mg ($x/2$)	Mg ($x/2$)	Mg ($x/2$)	= product
7	Mg $(1 - x)$	Al $1 - (x/2)$	Mg ($x/2$)	Mg ($x/2$)	= 3 × product
8	Mg $(1 - x)$	Al $1 - (x/2)$	Al $1 - (x/2)$	Mg ($x/2$)	= 3 × product

In fully ordered normal $MgAl_2O_4$, each O anion is surrounded by one tetrahedral Mg and three octahedral Al cations. In the disordered spinel, however, there are eight possible distributions of four nearest-neighbor cations around O (Table 4). However, the statistical probability of occurrence of these eight cation distributions around O is weighted and is dependent on the degree of disorder, x, in the spinel as outlined in Table 4. For example, in a spinel disordered to $x = 0.3$, five environments would contribute the majority of intensity to the NMR signal. These are $^{[4]}$Mg-O-3$^{[6]}$Al (43%), $^{[4]}$Mg-O-(2$^{[6]}$Al,$^{[6]}$Mg) (23%), $^{[4]}$Al-O-3$^{[6]}$Al (18%), $^{[4]}$Al-O-(2$^{[6]}$Al,$^{[6]}$Mg) (10%), and $^{[4]}$Mg-O-($^{[6]}$Al,2$^{[6]}$Mg) (4%). Each of these five probable local environments around O in the disordered spinel could potentially yield a distinct peak in the ^{17}O MAS NMR spectrum. However, the spectra exhibit only two peaks.

Most likely, fewer peaks are seen in the ^{17}O MAS NMR spectrum than predicted above because some of the existing O sites experience similar electronic shielding, and the resulting NMR peaks overlap. We assume that the chemical shifts of the two resolved peaks in the ^{17}O MAS NMR spectrum result from substitution of Al for Mg at the tetrahedral site bonded to O (Walter and Oldfield, 1989). For $MgAl_2O_4$ spinel, the large normal peak in the ^{17}O MAS NMR spectrum may be assigned to O bonded to Mg at the tetrahedral site. The smaller peak can be assigned to O having Al substituted for Mg at the tetrahedral site. The ^{17}O MAS NMR peak assignment based on tetrahedral site occupancy has been done previously by Walter and Oldfield (1989) in their assignment of the ^{17}O MAS NMR spectra of γ-Al_2O_3 and η-Al_2O_3, which have defect spinel structures. In these structures, both the octahedral and tetrahedral sites are occupied by Al, with numerous vacancies in the tetrahedral positions (Dupree et al., 1985). Walter and Oldfield (1989) assigned the peaks in their ^{17}O MAS NMR spectra as due to either Al or a vacancy at the tetrahedral site.

An alternative interpretation of the ^{17}O MAS NMR spectra in Figure 6 is that the position of the small peak may be dominated by a quadrupole-induced shift to high field, as a result of the break from axial symmetry at the O site, on substitution of Mg for Al at one or more of the octahedral sites. Although the direction of shift of the smaller peak is consistent with a quadrupole-induced shift, the peak does not appear to show any second-order quadrupolar splitting or singularities in profile typical of peaks influenced by second-order quadrupole interaction. Therefore, peak positions are more likely to be due to electronic shielding effects than quadrupole effects.

Cation disorder deduced from ^{17}O MAS NMR spectra

The degree of inversion, x, was calculated from the ^{17}O MAS NMR spectrum as the fraction of the total NMR peak intensity occupied by the small peak (due to disorder). Peak intensities were measured from the simulated spectra for $MgAl_2O_4$ (Fig. 6, spectra c and g). The degree of inversion was determined to be $x = 0.16$ ($\pm$ 0.02) and $x = 0.24$ ($\pm$ 0.03) for samples quenched from 700 and 1400 °C, respectively. The x values derived from ^{17}O MAS NMR spectra are systematically lower than those measured by ^{27}Al MAS NMR of the same samples. However, the increase in disorder between 700 and 1400 °C is of the same magnitude in both studies.

This systematic error in x determined from ^{17}O MAS NMR spectra may have resulted because peak profiles and intensities in the ^{17}O MAS NMR spectrum have not been adequately represented by simple curve fitting. The ^{17}O MAS NMR spectra may be further complicated by quadrupole effects. Work using dynamic-angle spinning (DAS) (Mueller et al., 1990) and double rotation (DOR) (Wu et al., 1990) is presently underway to help resolve these spectra.

Another reason for the discrepancy between ^{27}Al and ^{17}O MAS NMR spectra may be that each nucleus is affected differently by a second ordering process that may be occurring in $MgAl_2O_4$ spinel. Such a process has been suggested by Fiske and Stebbins (1989).

SUMMARY AND CONCLUSIONS

The ^{27}Al MAS NMR and disorder in $MgAl_2O_4$

The observed maximum disorder in synthetic $MgAl_2O_4$ spinel determined by ^{27}Al MAS NMR spectroscopy was found to be significantly less than that reported in a previous ^{27}Al MAS NMR study by Wood et al. (1986). The discrepancy arises because of the dependence of the apparent inversion parameter on pulse width. Wood et al. (1986) acquired spectra using a longer B_1 pulse width than has been recommended for quantitative central-transition spectra (Lippmaa et al., 1986), which has resulted in a systematic overestimation of the degree of disorder in their $MgAl_2O_4$ samples.

The temperature-dependent behavior of cation disorder determined in this study was better fitted by the simple Navrotsky-Kleppa (1967) thermodynamic model than by the more complicated O'Neill-Navrotsky (1983) model. Also, the lower degree of disorder measured in this study decreases the extent to which short range ordering in $MgAl_2O_4$ spinel is necessary to bring ordering data into compatibility with phase equilibrium studies.

The ^{17}O MAS NMR and cation disorder in spinels

The temperature dependence of cation disorder in synthetic ^{17}O-enriched $MgAl_2O_4$ spinel was observable by ^{17}O MAS NMR, with spectra showing an increase in disorder of the same magnitude as that measured by ^{27}Al MAS NMR. However, the degree of disorder determined by ^{17}O MAS NMR is systematically lower than that obtained by ^{27}Al MAS NMR, and further investigation is in progress.

The ^{17}O NMR is a potentially useful independent measure of x in spinels containing NMR-active cations, such as ^{27}Al. When the ^{17}O MAS NMR spectra of $MgAl_2O_4$ spinel are more completely understood, this technique will extend the use of NMR, as a direct measure of cation ordering, to spinels without NMR-active cations, which were previously not accessible for study by this method.

ACKNOWLEDGMENTS

We would like to thank J.S. Hartman and J.A. Ripmeester for their help in obtaining our preliminary ^{27}Al and ^{17}O MAS NMR spectra and R.D. Heyding for determining the cell constants for selected spinel samples. We also thank P.L. Roeder for use of his laboratory and furnaces for mineral synthesis. This research was funded by a Natural Sciences and Engineering Research Council of Canada operating grant to R.C.P. and postgraduate scholarship to R.L.M. R.J. Kirkpatrick and an anonymous referee are thanked for their useful reviews.

REFERENCES CITED

Akitt, J.W. (1989) Multinuclear studies of aluminum compounds. Progress in NMR Spectroscopy, 21, 1–149.

Bain, A.D. (1989) GLINFIT. Bruker Spectrospin, Milton, Ontario, Canada.

Barth, T.F.W., and Posnjak, E. (1932) Spinel structures: With and without variate atom equipoints. Zeitschrift für Kristallographie, 82, 325–341.

Blasse, G. (1964) Crystal chemistry and some magnetic properties of mixed metal oxides with spinel structures. Philips Research Reports, Supplements, 3, 1–139.

Brun, E., and Hafner, S. (1962) Die elektrische quadrupolaufspaltung von Al^{27} in spinell $MgAl_2O_4$ und korund Al_2O_3. Zeitschrift für Kristallographie, 117, 37–62.

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

Chiang, Y.-M., and Kingery, W.D. (1989) Grain-boundary migration in non-stoichiometric solid solutions of magnesium aluminate spinel: I. Grain growth studies. Journal of the American Ceramic Society, 72, 271–277.

Dupree, R., Farnan, I., Forty, A.J., El-Mashri, S., and Bottyan, L. (1985) A MAS NMR study of the structure of amorphous alumina films. Journal de Physique (Paris), Colloque, C8, 113–117.

Dupree, R., Lewis, M.H., and Smith, M.E. (1986) A study of the vacancy distribution in non-stroichiometric spinels by magic-angle spinning NMR. Philosophical Magazine A, 53, L17–L20.

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

Fernandez, C., LeFebvre, F., Nagy, J.B., and Derouane, E.G. (1988) Quantitative analysis of aluminium in zeolites by ^{27}Al NMR: Determination of extra-framework and framework species. In P.J. Grobet, Ed., Innovation in zeolite materials science, p. 223–230. Elsevier, Amsterdam, The Netherlands.

Fiske, P.S., and Stebbins, J.F. (1989) Evidence for multiple mechanisms of disorder in $MgAl_2O_4$ spinel: An ^{27}Al NMR study. Eos, 70, 1375.

Fukushima, E., and Roeder, S.B.W. (1981) Experimental pulse NMR—A nuts and bolts approach, 539 p. Addison-Wesley, Reading, Massachusetts.

Fyfe, C.A., Gobbi, G.C., Hartman, J.S., Klinowski, J., and Thomas, J.M. (1982) Solid-state magic-angle spinning aluminum-27 nuclear magnetic resonance studies of zeolites using a 400-MHz high-resolution spectrometer. Journal of Physical Chemistry, 86, 1247–1250.

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., and Fyfe, C.A. (1985) Direct determination of cation disorder in $MgAl_2O_4$ spinel by high-resolution ^{27}Al magic-angle-spinning NMR spectroscopy. Chemistry Letters, 6, 771–774.

Hill, R.J., Craig, J.R., and Gibbs, G.V. (1979) Systematics of the spinel structure type. Physics and Chemistry of Minerals, 4, 317–339.

Jamieson, H.E., and Roeder, P.L. (1984) The distribution of Mg and Fe^{2+} between olivine and spinel at 1300 °C. American Mineralogist, 69, 283–291.

Kirkpatrick, R.J. (1988) MAS NMR spectroscopy of minerals and glasses. In Mineralogical Society of America Reviews in Mineralogy, 18, 341–403.

Lippmaa, E., Samoson, A., and Mägi, M. (1986) High-resolution ^{27}Al NMR of aluminosilicates. Journal of the American Chemical Society, 108, 1730–1735.

Mattioli, G.S., and Wood, B.J. (1988) Magnetite activities across the $MgAl_2O_4$-Fe_3O_4 spinel join, with application to thermbarometric estimates of upper mantle oxygen fugacity. Contributions to Mineralogy and Petrology, 98, 148–162.

Mueller, K.T., Sun, B.Q., Chingas, G.C., Zwanziger, J.W., Terao, T., and Pines, A. (1990) Dynamic-angle spinning of quadrupolar nuclei. Journal of Magnetic Resonance, 86, 470–487.

Müller, D., Gessner, W., Samoson, A., Lippmaa, E., and Scheler, G. (1986) Solid-state aluminium-27 nuclear magnetic resonance chemical shift and quadrupole coupling data for condensed AlO_4 tetrahedra. Journal of the Chemical Society, Dalton Transactions, 1277–1281.

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

Nell, J., Wood, B.J., and Mason, T.O. (1989) High-temperature cation distributions in Fe_3O_4-$MgAl_2O_4$-$MgFe_2O_4$-$FeAl_2O_4$ spinels from thermopower and conductivity measurements. American Mineralogist, 74, 339–351.

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.

Peterson, R.C., Lager, G.A., and Hitterman, R. (1991) A time-of-flight neutron powder diffraction study of $MgAl_2O_4$ at temperatures up to 1273 K. American Mineralogist, 76, 1455–1458.

Sack, R.O. (1982) Spinels as petrogenetic indicators: Activity-composition relations at low pressures. Contributions to Mineralogy and Petrology, 79, 169–186.

Samoson, A., and Lippmaa, E. (1983) Excitation phenomena and line intensities in high-resolution NMR powder spectra of half-integer quadrupolar nuclei. Physical Review B, 28, 6567–6570.

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–L237.

Singh, H.P., Simmons, G., and McFarlin, P.F. (1975) Thermal expansion of natural spinel, ferroan gahnite, magnesiochromite and synthetic spinel. Acta Crystallographica A, 31, 820–822.

Timken, H.K.C., Schramm, S.E., Kirkpatrick, R.J., and Oldfield, E. (1987) Solid-state oxygen-17 nuclear magnetic resonance spectroscopic studies of alkaline earth metasilicates. Journal of Physical Chemistry, 91, 1054–1058.

Walter, T.H., and Oldfield, E. (1989) Magic angle spinning oxygen-17 NMR of aluminum oxides and hydroxides. Journal of Physical Chemistry, 93, 6744–6751.

Wood, B.J., Kirkpatrick, R.J., and Montez, B. (1986) Order-disorder phenomena in $MgAl_2O_4$ spinel. American Mineralogist, 71, 999–1006.

Wu, Y., Sun, B.Q., Pines, A., Samoson, A., and Lippmaa, E. (1990) NMR experiments with a new double rotor. Journal of Magnetic Resonance, 89, 297–309.

Yamanaka, T., and Takéuchi, Y. (1983) Order-disorder transition in $MgAl_2O_4$ spinel at high temperatures up to 1700 °C. Zeitschrift für Kristallographie, 165, 65–78.

Manuscript received August 20, 1990
Manuscript accepted September 16, 1991