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DIRECT DETERMINATION OF CATION DISORDER IN $MgAl_2O_4$ SPINEL BY HIGH-RESOLUTION ^{27}Al MAGIC-ANGLE-SPINNING NMR SPECTROSCOPY

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^{27}Al MAS NMR is shown to be a valuable tool in probing the coordination of aluminum in $MgAl_2O_4$ spinels, enabling the extent of Mg/Al order in the structure to be determined directly. From the relative intensities of the NMR peaks, assigned to octahedrally and tetrahedrally coordinated aluminum, the inversion parameter, i, was calculated to be 0.36±0.03 for a $MgAl_2O_4$ spinel synthesized at 1400 °C, and 0.12±0.06 for a natural spinel.

The structure of the spinel group is remarkably simple and was first investigated by Bragg[1] in 1915. It consists of a nearly cubic close-packed arrangement of oxygens, with one-eighth of the tetrahedral and one-half of the octahedral interstices occupied by various cations. There are 32 oxygens and 24 cations in the unit cell; 8 of the cations are tetrahedrally coordinated, and 16 are octahedrally coordinated. The general formula of a binary spinel may thus be represented as AB_2O_4, or $A_8B_{16}O_{32}$ per unit cell. Despite their deceptively simple structure, many spinels exhibit complex disordering phenomena involving the two cation sites; such ordering has important consequences both for their thermochemical and for their physical properties.[2]

For spinel minerals, the distribution of cations between the tetrahedral and octahedral sites varies between two limiting cases:[3] the "normal" distribution $(A)[B_2]O_4$ and the "inverse" distribution, $(B)[AB]O_4$, where the parentheses () and [] denote tetrahedral and octahedral sites, respectively. In order to describe an intermediate distribution, it is convenient to define an additional parameter, i, the inversion parameter, which is the fraction of tetrahedral sites occupied by B cations. The structural formula now becomes $(A_{1-i}B_i)[A_iB_{2-i}]O_4$, where the inversion parameter, i, is equal to 0, 2/3, and 1 for the normal, statistically random

(completely disordered), and inverse spinel, respectively. The distribution of the cations between octahedral and tetrahedral sites may vary with spinel composition, temperature, and thermal history.[4)]

Currently, there is interest in determining the degree of inversion in magnesium aluminate spinel, $MgAl_2O_4$. Although the basic structure is known, the atomic contents of both cation sites cannot be established directly by X-ray refinement because Mg^{2+} and Al^{3+} ions possess similar X-ray scattering powers. Efforts have been made during the last 25 years[2,5-14)] to characterize further the structural properties of spinel and, in particular, to determine accurately the cation distribution in $MgAl_2O_4$ using a variety of analytical techniques. Nevertheless there still remains uncertainty, discrepancy, and consequently controversy regarding the results that have been obtained.

It has been recently demonstrated that ^{27}Al magic angle spinning NMR (MAS NMR) readily distinguishes tetrahedrally and octahedrally coordinated aluminum in a variety of polycrystalline aluminates[15)] and zeolites.[16)] Thus the technique is potentially of value for studies of the cation distribution in $MgAl_2O_4$ spinels, and the present investigation aims to determine the feasibility of ^{27}Al MAS NMR for this system.

Magnesium aluminate spinel was prepared by heating a finely ground mixture of MgO and α-Al_2O_3 (1:1 molar ratio) in air at 1400 ^{o}C for 36 hours, and the product was characterized by X-ray powder diffraction. ^{27}Al MAS NMR spectra were obtained at a magnetic field strength of 9.4 T using previously described[17)] equipment on a narrow-bore Bruker WH 400 spectrometer.

The 104.2 MHz ^{27}Al MAS NMR spectrum of the synthetic $MgAl_2O_4$ sample is shown in Fig. 1A and consists of two main peaks (each flanked by a series of spinning sidebands) attributable to octahedrally coordinated aluminum, [Al], (chemical shift δ =9.8 ppm) and tetrahedrally coordinated aluminum, (Al), (δ=69.7 ppm). Considering the formula of the spinel as $(Mg_{1-i}Al_i)[Mg_iAl_{2-i}]O_4$, a value for the inversion parameter i can be determined, given that r=(2-i)/i or i=2/(r+1), where r is the ratio of octahedral to tetrahedral aluminum in the ^{27}Al NMR spectrum. Since r has a value of 4.5±0.4 (calculated from a computer deconvolution of the main peaks and their spinning sidebands), the experimentally determined inversion parameter for this sample is 0.36±0.03, indicating the presence of significant Mg,Al inversion. A comparison of the spinel's ^{27}Al MAS NMR spectral intensity with that of a reference sample containing a known number of resonant nuclei reveals, within experimental

error, that virtually all of the aluminum in the spinel is being detected, and the data should thus be quantitatively reliable.

Natural $MgAl_2O_4$ spinels that are cooled through geologic times are essentially normal[6b,10b] ($i \approx 0$) and Fig. 1B depicts the ^{27}Al MAS NMR spectrum of a spinel from Thailand ($i=0.12\pm0.06$). The natural specimen was characterized by powder X-ray diffraction, and EDX (energy-dispersive X-ray analysis) yielded a formula of $Mg_{1.00}Al_{1.98}Cr_{0.01}Fe_{0.01}O_4$.

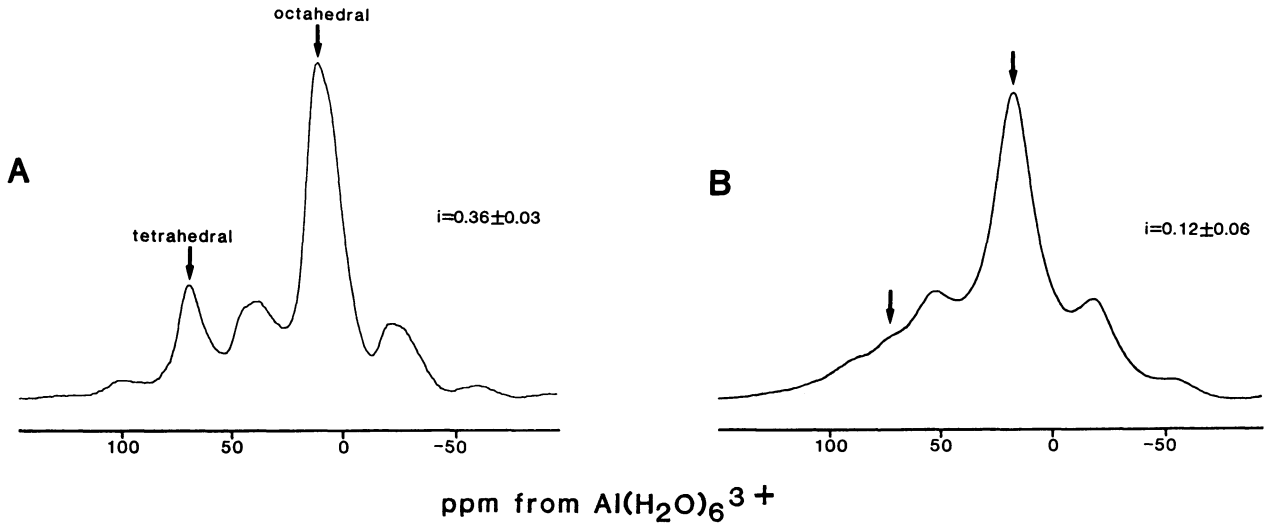

Fig. 1. ^{27}Al (104.2 MHz) MAS NMR spectra of:
A. $MgAl_2O_4$ spinel synthesized at 1400 °C ($i=0.36\pm0.03$). The peak at $\delta=69.7$ ppm is due to tetrahedrally coordinated aluminum, (Al), while the one at $\delta=9.8$ ppm is attributed to octahedrally coordinated aluminum, [Al]. Spinning sidebands occur at approximately 3.3 kHz intervals from the central resonances.
B. Natural spinel from Thailand ($i=0.12\pm0.06$).

The cation distribution seems to depend on the thermal history of the spinel and additional samples, both natural and synthetic, are currently being investigated in order to determine the temperature dependence of the inversion parameter.[18] A fuller treatment of the results, along with further details of how MAS NMR spectroscopy may be used quantitatively to monitor the site occupancy changes (via the inversion parameter) during solid state order/disorder transformations of spinel, will be given elsewhere.

In conclusion, we have shown that ^{27}Al MAS NMR is a powerful tool for the detection and characterization of aluminum ordering in $MgAl_2O_4$ spinel, thereby allowing an accurate determination of the inversion parameter.

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