Abstract
High-resolution solid-state $^{27}$Al NMR spectra have been obtained from ALON, $\beta'$-sialon and yttrium aluminate phases. The usefulness of $^{27}$Al magic-angle spinning NMR in phase characterization is shown by comparing different preparations of the yttrium aluminates. The sensitivity of the $^{27}$Al resonance position to the local environment means different units (e.g. AlN$_4$, AlO$_4$, AlO$_6$) can readily be distinguished allowing oxynitride structures, containing elements of similar scattering factor, to be refined. This is exemplified for the $\beta'$-sialon phase. For quadrupolar nuclei (nuclear spin, $I \geq 1$) such as $^{27}$Al ($I = \frac{1}{2}$), interaction with the local electric-field gradient can cause extensive broadening of the resonance such that the NMR spectrum may not precisely quantify the aluminium distribution.

1. Introduction
High-resolution NMR in the solid state is becoming increasingly used as an aid to structural characterization since the NMR frequency is influenced by small changes in the electronic environment of the nucleus. The technique of magic-angle spinning (MAS) (Andrew, 1981) produces high-resolution NMR spectra which readily distinguish different local aluminium coordination units (Muller, Gessner, Behrens & Scheler, 1981). This has been particularly useful where techniques such as X-ray diffraction (XRD) provide little information about the aluminium distribution due either to the similarity in scattering factors of the constituent elements or to the lack of long-range order. $^{27}$Al MAS-NMR has been performed on a wide variety of inorganic solids including aluminates (Muller, Gessner & Scheler, 1983; Muller, Gessner, Samoson, Lippmaa & Scheler, 1986), zeolites (Klinowski, 1984, and references therein), oxynitrdes (Butler, Dupree & Lewis, 1984), spinels (Gobbi et al., 1985; Dupree, Lewis & Smith, 1986; Wood, Kirkpatrick & Montez, 1986) and amorphous solids (Muller, Berger, Grunze, Ladwig, Hallas & Haubenreisser, 1983; Dupree, Farnan, Forty, El-Mashri & Bottyan, 1985).

The most important structural feature influencing the chemical-shift position is the local coordination, with octahedral AlO$_6$ resonating between $+15$ and $-30$ p.p.m., the much less common AlO$_5$ group resonating between $+40$ and $+25$ p.p.m. while tetrahedral AlO$_4$ groups typically resonate between $+80$ and $+50$ p.p.m., all relative to $[\text{Al(H}_2\text{O)}_6]^3^+$. Unlike spin $-\frac{1}{2}$ nuclei there are a number of factors which complicate the interpretation of spectra from quadrupolar ($I \geq 1$) nuclei owing to the interaction of these nuclei with the local electric-field gradient (e.g.). The size of this interaction in most materials means only the $-\frac{1}{2} \leftrightarrow \frac{1}{2}$ transition is observed since unlike the other transitions (e.g. $\frac{1}{2} \leftrightarrow \frac{3}{2}$) the central transition is not affected by first-order quadrupole effects (Cohen & Reif, 1957). If the e.f.g. is sufficiently large the central transition is noticeably affected by the quadrupole interaction taken to second order and MAS is only able to narrow partially this second-order broadening (Behrens & Schnabel, 1982). Useful high-resolution spectra can still be obtained but the peak positions become noticeably field dependent (Lippmaa, Samson & Magi, 1986) and spectral intensity may be lost owing to incomplete excitation of the transition (Sanz & Serratosa, 1984; Lampe, Muller, Gessner, Grimmer & Scheler, 1982; Fenkze, Freude, Frolich & Haase, 1984) once the e.f.g. becomes sufficiently large.

In this paper the use of $^{27}$Al MAS–NMR for structure refinement and monitoring phase development is assessed for a range of oxide and oxynitride phases. They are derived mainly from the Y–Si–Al–O–N system in which a number of phases are components of a new series of 'sialon' engineering ceramics. Specific phases studied in this work include the pure oxide yttrium aluminates ($Y_2AIO_3$, $YAO_3$, $Y_3AIO_12$) which have well known crystal structures and oxynitride phases (ALON, $\beta'$-, $\beta''$-sialons) whose local atomic arrangements are incompletely defined.

2. Experimental
The yttrium aluminates were prepared by direct sintering of the terminal oxides ($Y_2O_3$, $\alpha$-AIO$_3$) and also by the 'wet' chemical technique of thermal de-
composition of the nitrates or sulfates (Messier & Gazzra, 1972). For solid-state sintering stoichiometric mixtures of the oxides were dry mixed followed by compaction into pellets which were embedded in BN in a graphite crucible. The samples were heated to \( \sim 2048 \) K in a RF graphite-susceptor induction furnace for 2–3 h under a flowing nitrogen atmosphere. The decomposition technique involved taking appropriate mixtures of \( \text{Y(NO}_3\text{)}_3 \cdot 6\text{H}_2\text{O} \) and \( \text{Al(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O} \) or \( \text{NH}_4\text{Al(SO}_4\text{)}_2 \cdot 12\text{H}_2\text{O} \) so that the \( \text{Y:Al} \) ratio was correct for the final product. The powders were ground together and a small amount of distilled water added. The saturated solution was boiled off and finally thermally decomposing. The resulting solid was reground and placed in an alumina boat in an open tube resistance furnace to be heated at \( 1470 \) K for \( \sim 30 \) h.

The ALO\(_N\) phase was directly sintered from AlN and \( \gamma\text{-Al}_2\text{O}_3 \) at a range of compositions centred on \( 5\text{AlN:9Al}_2\text{O}_3 \) at 2048 K for 3 h under a flowing oxygen-free nitrogen atmosphere. The \( \beta\)-sialons were nominally single-phase specimens prepared by hot pressing. Powder X-ray diffraction was performed on all specimens with some phases additionally characterized by scanning electron microscopy.

The MAS–NMR was performed on a Bruker MSL-360 spectrometer operating at 93–83 MHz for \( ^{27}\text{Al} \). The samples were finely powdered and packed into conventional ‘mushroom’ spinners which contained \( \sim 0.5 \) g of sample and were spun at 3–5 kHz. Spinning exactly at the magic angle narrows both the central transition and the higher-order transitions, \( (\text{e.g.} \frac{3}{2} \leftrightarrow \frac{1}{2}) \) with the extensive manifold of side bands associated with the higher-order transitions complicating spectral interpretation [compare Fig. 2(a) where octahedral side bands obscure the tetrahedral site with Fig. 2(c)]. However, the slight variability of the spinning axis usually results in only the central transition being efficiently narrowed. Spectra were accumulated using short, \( 0.5–1 \) \( \mu \)s, intense \( (B_1 \sim 5 \) mT) pulses with suitable delays (\( \sim 1 \) s) to prevent saturation for \( \sim 500 \) scans. Unless otherwise stated, dead-time delays of \( \sim 4 \) \( \mu \)s before acquisition were employed such that components broader than \( \sim 250 \) kHz were not recorded in the time domain signal. All spectra were referenced to an external standard of \( [\text{Al(H}_2\text{O)}_6]^{3+} \) in dilute aqueous aluminium nitrate. The chemical shifts stated generally correspond to the peak position rather than the true isotropic chemical shift (Muller, 1982). No artificial smoothing was used except for the \( \beta\)-sialons where 100 Hz exponential broadening was employed. A standard spectrum of reagent-grade \( \alpha\text{-Al}_2\text{O}_3 \) was accumulated under the same conditions, to enable a quantitative determination of the fraction of \( ^{27}\text{Al} \) nuclei detected by MAS–NMR.

3. NMR spectroscopy

3.1. Yttrium aluminates

The \( \text{Y}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3 \) system is known to contain three crystalline phases, \( \text{Y}_4\text{Al}_3\text{O}_9 \) (\( Y_2A \)), \( \text{YAlO}_3 \) (\( YA \)) and \( \text{Y}_3\text{Al}_5\text{O}_{12} \) (\( Y_3A_5 \)) (Cockayne, 1985). The crystal structures and hence aluminium coordinations of these phases are well known. The monoclinic \( Y_2A \) contains two \( \text{AlO}_4 \) tetrahedra joined by a bridging oxygen while \( Y_2A_5 \) contains both tetrahedrally and octahedrally coordinated aluminium in the ratio 3:2. \( YA \) is believed to have two forms, a high-temperature orthorhombic phase with octahedral aluminium and a low-temperature hexagonal form (\( \leq 1223 \) K) containing the aluminium in a distorted pentacoordinate environment. Single crystals of \( YA \) and especially \( Y_3A_5 \), which is the easiest to fabricate, are commercially important solid-state laser materials when doped with neodymium.

3.1.1. \( Y_2A \). Sintering at 2048 K produced single-phase \( Y_2A \) according to XRD. A MAS–NMR accumulation with 20 \( \mu \)s dead time surprisingly gave a peak corresponding only to octahedral aluminium (Fig. 1b). The minor resonance at \( \sim 114 \) p.p.m. must be some very low impurity phase, possibly AlN formed by nitrogen pick up from the sintering atmosphere. A smaller dead time (\( \sim 4 \) \( \mu \)s cf. \( \sim 20 \) \( \mu \)s) and larger \( B_1 \) clearly reveals the presence of a much broader component (Fig. 1c) showing that the octahedral aluminium is due to a minor phase (\( YA \), Table 1) whose presence cannot be detected by XRD. The peak integrals show that the broad and narrow components account for 50 and 4\% of the total aluminium content respectively, with the rest undetected. Preparation of \( Y_2A \) by crystallization of the nitrate decomposition product at 1470 K for 30 h gave a complex mixture of \( Y_2A \), orthorhombic \( YA \) and \( Y_3A_5 \) according to XRD with the MAS–NMR spectrum (Fig. 1a) confirming the presence of both \( YA \) and \( Y_3A_5 \).

3.1.2. \( Y_3A_5 \). A comparison is made between three different \( Y_3A_5 \) samples produced by direct sintering (Fig. 2a), a commercially made sample (Johnson–Matthey) (Fig. 2b) and by thermal decomposition of the nitrates (Fig. 2c) with all samples being single phase according to both XRD and NMR. The spectra clearly show the two aluminium coordinations 0-8 \% (peak position of \( \text{AlO}_6 \) unit) and 740 p.p.m. (isotropic shift of the \( \text{AlO}_4 \) unit). A spectral simulation (Fig. 2d) agrees with the form of the experimental spectra (see Discussion). These two sites can only partially be resolved in a static spectrum (Fig. 2e) owing to the increased line width. Only 75\% of the aluminium (when compared with \( \gamma\text{-Al}_2\text{O}_3 \)) is recorded in the MAS–NMR spectra and, as expected in this situation, the ratio of the peak integrals of the two sites [\( \text{AlO}_4/(\text{AlO}_6 \sim 0.7(3)] \) does not agree with the value from crystallography (\( \text{AlO}_4/\text{AlO}_6 = 1.5 \)).
3.1.3. \( \text{YA} \). XRD of the directly sintered \( \text{YA} \) composition shows orthorhombic \( \text{YA} \) as the major phase with some \( \text{Y}_2\text{A} \) and a small amount of \( \text{Y}_3\text{A}_5 \). The \( \text{YA} \) peak at +9.4 p.p.m. (peak maximum) (Fig. 3a) is in agreement with the aluminium in this phase being octahedrally coordinated. Immediately after thermal decomposition the nitrate mixture was completely amorphous according to XRD. The MAS–NMR spectrum (Fig. 3d) agrees with this as both the octahedrally (~0 p.p.m.) coordinated and tetrahedrally coordinated (~65 p.p.m.) aluminium sites have greatly increased line widths, an indication of the increased disorder that is present in the system at this stage. After heat treatment (Fig. 3c) crystallization has occurred resulting in a complex mixture of phases, with \( \text{YA} \) the principal phase but appreciable amounts of \( \text{Y}_2\text{A} \) and \( \text{Y}_3\text{A}_5 \) are also formed according to XRD. The hexagonal form of \( \text{YA} \) has previously been synthesized from the thermal decomposition of yttrium nitrate and ammonium alum (Bertaut & Mareschal, 1963). After only 2 h at 1170 K the amorphous decomposition product shows extensive crystallization with the XRD showing \( \text{Y}_2\text{O}_3 \), orthorhombic \( \text{YA} \), \( \text{Y}_3\text{A}_5 \), \( \text{Y}_2\text{A} \) and some hexagonal \( \text{YA} \). MAS–NMR can detect signals from orthorhombic \( \text{YA} \) and \( \text{Y}_3\text{A}_5 \) (Fig. 3b) with an underlying broad component. We were unable to obtain single-phase hexagonal \( \text{YA} \) with the heat treatments used.

At 2048 K, \( \text{Y}_3\text{A}_5 \), orthorhombic \( \text{YA} \) and \( \text{Y}_2\text{A} \) are all stable. The \( \text{Y}_3\text{A}_5 \) is the easiest to form as a single-phase product by all the methods of preparation. Although the sinterings at 2048 K may not be at true equilibrium it does appear possible to produce nearly single-phase products of all three phases. This agrees with the latest phase-equilibrium studies as opposed to early work on this system which suggested \( \text{YA} \) decomposed into \( \text{Y}_2\text{A} \) and \( \text{Y}_3\text{A}_5 \) below ~2098 K (Cockayne, 1985). The formation of these phases by the thermal decomposition of the nitrates does allow appreciable phase formation at much lower temperatures, where direct sintering produces almost zero...
Table 1. The $^{27}\text{Al}$ peak position chemical shift and the observed fraction of the aluminium content from MAS-NMR spectra at $B_0 = 8.45T$

<table>
<thead>
<tr>
<th>Composition</th>
<th>Preparation</th>
<th>Observed peak position (p.p.m.) ± 0.5 p.p.m. with respect to $\text{Al}[\text{H}_2\text{O}]^3$</th>
<th>Total fraction of aluminium content observed in the MAS-NMR spectrum relative to $\alpha$-$\text{Al}_2\text{O}_3$ ± 0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-$\text{Al}_2\text{O}_3$</td>
<td>11-5(1)</td>
<td>1</td>
<td>0.1</td>
</tr>
<tr>
<td>$\gamma$-$\text{Al}_2\text{O}_3$</td>
<td>66(0.25), 8(0.75)</td>
<td>1</td>
<td>0.2</td>
</tr>
<tr>
<td>AIN</td>
<td>113(0.65)</td>
<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td>$Y_4\text{Al}_2\text{O}_9$, ($Y_2\text{A}$)</td>
<td>Direct sinter, 2048 K, 2.5 h</td>
<td>9-4(0.04), 114(0.01)</td>
<td>0.5</td>
</tr>
<tr>
<td>$Y_3\text{Al}<em>5\text{O}</em>{12}$, ($Y_3\text{A}_5$)</td>
<td>Direct sinter, 2048 K, 2.5 h</td>
<td>9-4(0.05), 0.8(0.03)</td>
<td>0.7</td>
</tr>
<tr>
<td>$\text{YN}<em>4\text{A}</em>{12}\text{O}_{47}$, ($Y_2\text{A}$)</td>
<td>Direct sinter, 2048 K, 2.5 h</td>
<td>74*(NM), 0.8(NM)*</td>
<td>0.7</td>
</tr>
<tr>
<td>$\text{YN}_3\text{Al}<em>5\text{O}</em>{12}$, ($Y_3\text{A}_5$)</td>
<td>Direct sinter, 2048 K, 3 h</td>
<td>74*(0.35), 0.8(0.45)</td>
<td>0.8</td>
</tr>
<tr>
<td>Commercial sample</td>
<td>Nitrate decomposition, 1473 K, 30 h</td>
<td>74*(NM), 0.8(NM)*</td>
<td>0.7</td>
</tr>
<tr>
<td>$\text{YN}_2\text{Al}<em>4\text{O}</em>{11}$, ($Y_2\text{A}$)</td>
<td>Direct sinter, 2048 K, 3 h</td>
<td>9-4(0.06), 0.8(0.02)</td>
<td>0.7</td>
</tr>
<tr>
<td>$\text{YN}_3\text{Al}<em>5\text{O}</em>{12}$, ($Y_3\text{A}_5$)</td>
<td>Direct sinter, 2048 K, 3 h</td>
<td>9-4(0.05), 0.8(0.06)</td>
<td>0.75</td>
</tr>
<tr>
<td>$\text{YN}_3\text{Al}<em>5\text{O}</em>{12}$, ($Y_3\text{A}_5$)</td>
<td>Direct sinter, 2048 K, 3 h</td>
<td>9-4(0.05), 0.8(0.08)</td>
<td>0.75</td>
</tr>
<tr>
<td>$\text{YN}_2\text{Al}<em>4\text{O}</em>{11}$, ($Y_2\text{A}$)</td>
<td>Direct sinter, 2048 K, 3 h</td>
<td>114(0.03), 65(0.04), 12(0.08)</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Reaction, owing to the intimate mixing of the components in the amorphous decomposition product, although the final product is generally a more complex phase mixture.

3.2. ALON phase

The ALON phase is a result of the stabilization of the defective spinel structure of $\gamma$-$\text{Al}_2\text{O}_3$ at high temperatures by the introduction of nitrogen, with a range of compositional stability centred around 35-7 mol % ALN (McCauley & Corbin, 1979). It may be expected that the aluminium will have a range of local tetrahedral and octahedral environments including mixed anion (i.e. nitrogen and oxygen) coordinations allowing comparison with the expected environments in $\beta'$-sialons.

Various mixtures of AIN and $\gamma$-$\text{Al}_2\text{O}_3$ in the region 27-40 mol % AIN sintered at 2048 K for 3 h produced almost single-phase ALON according to XRD. The MAS-NMR of 9$\text{Al}_2\text{O}_3$:5AIN (Fig. 4) shows three distinct peaks at 114, 65 and 120 p.p.m. (Table 1) which can be compared with AIN (113.0 p.p.m.), $\gamma$-$\text{Al}_2\text{O}_3$ (66, 8 p.p.m.) and $\alpha$-$\text{Al}_2\text{O}_3$ (11.5 p.p.m.). As XRD shows only minor levels of the reactants and as the NMR spectrum represents ~40% of the aluminium nuclei present compared to $\alpha$-$\text{Al}_2\text{O}_3$, some of these peaks have to be from the ALON phase despite their close agreement with the peak positions of the reactants. Since not all the aluminium is present in the MAS-NMR spectra the various possibilities of oxygen/nitrogen ordering cannot be distinguished. However, for all schemes (i.e. from strictly ordered AIO$_4$, AIN$_4$ partitioning to a random distribution), AIO$_4$ tetrahedra would dominate over AlN$_4$ tetrahedra. Hence the peak at 114 p.p.m. is AIN, estimated to be 3% of the total aluminium content, which is just detectable by XRD. Since $\gamma$-$\text{Al}_2\text{O}_3$ and ALON are isostructural it is quite likely that the AlO$_4$ position may be very similar in these two materials.

3.3. $\beta'$-Sialons

$\beta'$-Sialon $\text{Si}_{3-x}\text{Al}_x\text{O}_{2x}\text{N}_{4-x}$ (0 ≤ x ≤ 2) is an important phase in high-temperature ceramics, derived by aluminium and oxygen substitution in $\beta$-$\text{Si}_3\text{N}_4$. Previous structural studies by infrared spectroscopy (Wild, Elliot & Thompson, 1978; Takase, Umebayashi & Kishi, 1982) and neutron diffraction (Gillot, Cowlam & Bacon, 1981; Roult, Braissart, Labbe & Goursat, 1986) have demonstrated the isostructural nature of the substitutional crystal but have been able to say little about the local coordination changes which occur across this series. The aluminium is expected to have a range of tetrahedral coordinations,
AlO$_2$N$_4$-$_x$ ($0 \leq x \leq 4$). The metastable $\beta''$-sialon has the same crystal structure as $\beta$-Si$_3$N$_4$ with magnesium and aluminium replacement of silicon and is much enriched in oxygen (Wild, Leng-Ward & Lewis, 1981).

The $^{27}$Al NMR spectra (Fig. 5) from a series of $\beta'$-sialons ($x = 0.5$ to $x = 2$) and $\beta''$-sialon show some narrower components (Figs. 5a–d) on top of a much broader one [Fig. 5(e), $x = 2$]. The sialon spectra (Figs. 5a–d) have had the first few points of the time domain ($\sim 20$ $\mu$s) omitted which removes the broad (rapidly decaying) part of the signal, leaving the narrower components. The amount of aluminium represented by these spectra, including the broad components is $\sim 50\%$ ($x = 2$) decreasing to $\sim 10\%$ ($x = 0.5$) when compared with $\alpha$-Al$_2$O$_3$ collected under the same conditions. Thus the narrow components represent a relatively small fraction of the aluminium content. The spectra do indicate that there are two relatively symmetric environments in these materials which cannot be assigned to the reactants (see Table 1). These peaks are tentatively assigned to AlN$_4$ (103 p.p.m.) and AlO$_4$ (66 p.p.m.). As $x$ increases the dominant AlN$_4$ peak for $x = 0.5$ becomes the minor peak compared with AlO$_4$ for $x = 2$. With increasing $x$ there is a small increase in the AlN$_4$ peak position from 103 p.p.m. ($x = 0.5$) to 109 p.p.m. ($x = 2$). In the $x = 2$ sample there is also a small reproducible octahedrally coordinated aluminium peak at $\sim 4$ p.p.m. The octahedral peak may be explained either as a very low level impurity phase which cannot be detected by...
other techniques or alternatively at high substitution levels there may be some tendency for aluminium to go into an octahedral coordination in the \( \beta' \) structure. In \( \beta'' \)-sialon (Fig. 5d) (Mg₆Al₃Si₃O₁₁N), the major narrow component at 67 p.p.m. is consistent with AlO₄ units in agreement with this phase being more oxygen rich than \( \beta' \)-sialon.

4. Discussion

4.1. Quantification of solid-state \( ^{27} \text{Al} \) NMR spectra

The interaction of aluminium nuclei with the local electric-field gradient produced by nearest neighbours can often cause severe line broadening even of the \( ( - \frac{1}{2} \leftrightarrow \frac{1}{2} ) \) transition which in the present field (8.45T) cannot be narrowed by MAS nor effectively excited resulting in some lost intensity. From the comparison of the resonance peak integrals from the sample with our arbitrary \( \alpha \)-Al₂O₃ standard it is clearly demonstrated that some spectra represent an incomplete picture of the aluminium distribution.

MAS–NMR effectively narrows the central transitions in \( YA \) and \( Y₃A₅ \) where the quadrupole interaction strengths determined from single-crystal studies are for \( YA \), \( e^2qQ/h \approx 3 \text{MHz} \) (Grochulski & Zbieranowski, 1979), and for \( Y₃A₅ \), \( e^2qQ/h \approx 0.6 \text{MHz} \) (octahedral), \( e^2qQ/h \approx 6 \text{MHz} \) (tetrahedral) (Brog, Jones & Verber, 1966). A computer simulation of the powder pattern of \( Y₃A₅ \) (Fig. 2d) agrees with a quadrupole interaction strength \( e^2qQ/h \approx 6 \text{MHz} \) and \( \eta \approx 0 \) (quadrupole asymmetry parameter) for the tetrahedral site. Spectral integration gives the ratio AlO₄/AlO₆ \( \approx 0.7(3) \) which is smaller than the 1.5 expected from crystallography but is consistent with a larger loss of signal from the site with the larger quadrupole interaction. Since no narrow component at all could be detected from \( Y₂A \), the AlO₄ tetrahedra of this phase must have a much larger quadrupolar interaction than the other aluminate phases \( (i.e. > 7 \text{MHz}) \) giving rise to a broad component which cannot be narrowed by MAS–NMR at this field and rotation frequency. No single-crystal measurements have been made of the quadrupole interaction in \( Y₂A \) and no accurate bond-length data could be located to confirm this explanation. The same is probably the case for the pentacoordinate aluminium in hexagonal \( YA \).

When mixed local environments \( (e.g. \text{AlO}_₄\text{N}_₄\text{O}_₋₄) \) occur it is expected that the quadrupolar broadening will become more severe (Delpeuch, 1983). For both the ALON and \( \beta' \)-sialons the missing signal may be attributed to the mixed types of environment. The basis of the assignment of the \( \beta' \)-sialon spectral peaks to AlO₄ and AlN₄ is the belief that intermediate members \( (\text{AlO}_₃\text{N}, \text{AlO}_₂\text{N}_₂ \text{and AlO}_₃\text{N}_₃) \) are severely broadened since they are also expected to exist in ALON, yet are not evident.

4.2. Structural models for \( \beta' \)-sialons

As NMR studies of the local coordination of both the \( ^{29}\text{Si} \) (Dupree, Lewis, Leng-Ward & Williams, 1985) and \( ^{27}\text{Al} \) have now been carried out on the same specimens a model of the local structure may be proposed. The \( ^{29}\text{Si} \) resonance showed very little change across the whole substitution range. The invariant peak position, at \( -48.5 \text{p.p.m.} \) (with respect to Me₄Si) suggests that SiN₄ units are present throughout by analogy with \( \beta' \)-sialon, \( -49 \text{p.p.m.} \) (with respect to Me₄Si). There was a gradual increase in the line width (FWHM 280 → 440 Hz) from \( x = 0.5 \) to \( x = 2 \). This increase in line width was attributed to a small spread of bond lengths and angles, owing to a range of next-nearest aluminium neighbours (Dupree, Lewis, Leng-Ward & Williams, 1985). The \( ^{27}\text{Al} \) spectra show a distinct change in the relative numbers of aluminium nuclei which are associated with AlN₄ and AlO₄ environments with AlN₄ being dominant at \( x = 0.5 \) while for \( x = 2 \) AlO₄ is the principal symmetric environment. It should be emphasized for these samples that a large fraction of the aluminium \( (\geq 50\%) \) is not present in the spectra and it is supposed that this is due to aluminium with some mixed type of local

Fig. 6. Schematic representation of a possible structure for \( x = 2 \) \( \beta' \)-sialon consistent with the MAS–NMR data. Atoms in columns 1, 4 and 6 are above the plane of the paper, 3 below with 2 and 5 in the plane. The planes of atoms carry on in the same form perpendicular to the paper and parallel to a with the repeat unit along c between the lines × are defects within the layers.
coordination (e.g. AlO$_3$N). A structural model constrained by these NMR results allows only silicon in SiN$_4$ coordination while the aluminium has a range of coordinations AlO$_x$N$_{4-x}$ (0 ≤ x ≤ 4) with AlO$_4$ dominant over AlN$_4$ at x = 2 and vice versa at x = 0.5.

A purely random distribution model is clearly not feasible as both the silicon and aluminium local environments would be dominated by mixed local coordinations. This is clearly not so for the silicon and even for the aluminium where these units may exist the coordinations. This is clearly not so for the silicon and environments would be dominated by mixed local feasible as both the silicon and aluminium local

strained by these NMR results allows only silicon in AIO$_4$ coordination while the aluminium has a range of SiNg coordination while the aluminium has a range of coordinations A1OxNg_x (0 ≤ x ≤ 4) with A10$_4$ dominate over A1Ng at x = 2 and vice versa at x = 2.

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gests a more ordered model which is in fact generally implicit in these materials since the ability of alu-

minum and oxygen to replace silicon and nitrogen number of AIO$_4$ units would not be expected to dominate over AlN$_4$ for any composition. This sug-

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References

5. Concluding remarks
Provided that the aluminium coordination is symmetric enough for MAS–NMR effectively to narrow the central transition, very low levels (≤ 1%) of phases can be detected which would not be possible by other techniques. These phases may be identified by matching the chemical shifts with those of phases which are likely to be present. Determination of unknown coordinations present in specimens is straightforward once the resonance has been detected because the different coordination units lie in reasonably well defined chemical-shift ranges. This is especially true of amorphous samples since the NMR depends only on the local order in the sample. Information about the local coordination has allowed a layered structure model to be proposed for β'-silicon.

Changes in the relative amounts of phases present can be seen directly from the changes of the ratios of the peak integrals of the spectra. However, it is inadvisable to perform quantitative analysis on a single spectrum unless some check is made on the amount of aluminium represented by the spectrum. The quadrupole broadening resulting from distorted aluminium environments can result in severely broadened lines. It would be extremely informative to perform the same study at much higher magnetic fields where quantitative analysis would become more accurate. Once the limitations of $^{27}$Al MAS-NMR have been realized this technique is a powerful aid to characterization of the solid state.

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