Triple-Quantum Two-Dimensional $^{27}$Al Magic-Angle Spinning Nuclear Magnetic Resonance Spectroscopic Study of Aluminosilicate and Aluminate Crystals and Glasses

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Abstract: A new two-dimensional magic-angle spinning NMR experiment$^{1,2}$ using multiple-quantum coherences of half-integer quadrupolar nuclei was used to study $^{27}$Al sites in crystalline samples of leucite (KAlSi$_2$O$_6$), anorthite (CaAl$_2$Si$_2$O$_8$), and kyanite (Al$_2$SiO$_5$), as well as CaAl$_2$Si$_2$O$_8$ glass and a magnesium aluminoborate glass. In the crystals, multiple sites are partially resolved and new results for isotropic chemical shifts and quadrupolar parameters are derived, using data collected at a single magnetic field. Data for both leucite and anorthite are consistent with previous results that correlate chemical shifts with mean intertetrahedral bond angle. Signal can be obtained from sites with quadrupolar coupling constants as large as 9 MHz, but intensities are reduced. In the aluminoborate glass, peaks for sites with different Al coordination numbers are well separated. The lack of such features in CaAl$_2$Si$_2$O$_8$ glass rules out the presence of significant quantities of AlO$_3$ and AlO$_5$ groups.

Introduction

Aluminum-containing oxide crystals and glasses are abundant in nature as well as being among the most commonly used technological materials. Understanding the structures of these materials is thus fundamental to many problems in earth and in materials sciences. High resolution solid-state NMR is becoming increasingly important in resolving such problems, particularly in quantifying the extent and nature of disorder. $^{27}$Al NMR is taking on increasing importance in resolving such problems, particularly in materials sciences. High resolution solid-state NMR is becoming increasingly important in resolving such problems, particularly in quantifying the extent and nature of disorder. $^{27}$Al NMR holds great potential, but results from simple MAS spectra have been limited by the low resolution generally caused by second-order quadrupolar broadening. Several approaches have been taken to eliminate or reduce such effects, including dynamic angle spinning (DAS),$^3$ double rotation (DOR),$^7,^8$ and the observation of spinning sidebands for satellite transitions,$^{10,12}$ although DAS NMR has generally been unfeasible for $^{27}$Al because of short spin–lattice relaxation times and strong homonuclear dipolar couplings.

The most recent development in this effort has been to exploit multiple quantum coherences in two-dimensional MAS experiments (“MQMAS”).$^{13}$ Double-quantum spectra under magic angle spinning conditions were previously observed for $^2$H in solids.$^{14}$ A variant of this experiment, involving triple quantum coherence (“3QMAS”), has been documented as being particularly effective for spin $5/2$ nuclides such as $^{23}$Na and $^{87}$Rb, as well as for spin $7/2$ $^{27}$Al.$^{1,2,15,16}$ Applications of this new approach, to complex, multisol crystals and to amorphous materials, have been very limited thus far, however. Very recently, the analogous five-quantum experiment has been found useful for enhancing resolution for $^{27}$Al in aluminophosphate molecular sieve materials.$^{17}$ In this paper we explore the utility, and the limitations, of the two-dimensional, triple-quantum MAS experiment in several crystalline aluminosilicates and in several alumina-rich oxide glasses. We show that the additional information in a 2D 3QMAS experiment may be used to extract quadrupolar parameters and isotropic chemical shifts. In favorable cases, at least, such information can thus be obtained without acquiring spectra at a second magnetic field and without additional NMR experiments.

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Theory

The theory of 3QMAS has been previously presented in the literature and will not be extensively reviewed here.\(^1\) The fundamental concept in second-order averaging techniques (DAS, DOR, MQMAS) is that additional degrees of freedom need to be brought to bear on the quadrupolar interaction. In DAS and DOR the additional degree of freedom comes in rendering the spinning angle time dependent. This time dependence is exploited to remove both the \(P_2\) and \(P_4\) (second and fourth rank spatial tensors) dependant terms in the Hamiltonian. In the MQMAS experiment, the degree of freedom that is beneficially manipulated is coherence order. Normally, half-odd integer quadrupolar nuclei are studied using a \(p = \pm 1\) coherence (corresponding to \(m = \frac{1}{2} \pm \frac{1}{2}\) transition). For MQMAS the \(p = \pm 3\) or \(\pm 5\) coherences are used as a second degree of freedom. Since evolution frequency has different spatial dependences under different coherence orders, it is possible to average the second rank terms with the rapid sample spinning and the fourth rank terms with multiple quantum coherence mixing. Note that both second- and fourth-order spatial terms cannot be averaged simultaneously using only multiple quantum coherences, that is to say spinning is essential.

Experimental Methods

Samples. The sample of the natural framework silicate mineral leucite (KAISiO\(_3\), from the Roman volcanic province) has been previously studied in detail by \(^2\)Si MAS NMR.\(^1\) Several samples of crystalline anorthite (CaAl\(_2\)Si\(_2\)O\(_8\), also a framework silicate) were prepared by the method described in a detailed study of Si/Al disorder.\(^1\) A glass of this composition was prepared by melting the constituent oxides at 1650 °C for about 1 h followed by air quenching. Several portions of the glass were then crystallized by annealing at 1400 °C for either 4 min (sample 1) or 65 h (sample 2). Powder X-ray diffraction and \(^2\)Si MAS NMR spectra on these samples showed only anorthite to be present. \(^2\)Si MAS NMR spectra closely resemble those of Phillips et al.\(^1\) for samples crystallized for 15 min and 179 h, respectively, and thus have a smaller difference in the extent of disorder than expected (presumably because of vagaries of thermal history and nucleation kinetics). A sample of natural kyanite (Al\(_2\)Si\(_2\)O\(_5\), locality unknown) was also selected in order to test the relative excitation efficiencies for Al sites with widely varying quadrupolar coupling constants. A glass of composition 40 mol \% MgO, 40 mol \% B\(_2\)O\(_3\), and 20 mol \% Al\(_2\)O\(_3\) was selected because of its large concentrations of 4-, 5-, and 6-coordinated Al as determined previously by \(^27\)Al MAS NMR.\(^2\) and was also prepared by standard mixing and melting of the oxides.

NMR Spectroscopy. The MAS experiments at 9.4 T were performed on a modified Varian VXR-400S spectrometer with a 5-mm high-speed MAS probe from Doty Scientific, Inc., with spinning rates of about 11 kHz. At 11.7 T, experiments were performed on a Chemagnetics spectrometer using the same probe. In order to assure that relative peak intensities were not affected by differential spin–lattice relaxation rates, spectra were acquired with varying delay times between pulses in preliminary MAS experiments. No variations in peak shapes were observed. Spin–lattice relaxation times (\(T_1\)) were measured with the saturation-recovery method, and delay times in 3QMAS experiments were chosen to be at least 3 times \(T_1\) to assure nearly complete relaxation. The low efficiency of the triple quantum excitation and the two-dimensional data acquisition resulted in typical total acquisition times for the spectra shown here of 24 h, much longer than times typically required for 1D, single quantum MAS experiments (typically a few minutes for \(^27\)Al). Useful 3QMAS spectra can generally be obtained in somewhat shorter times of a few hours.

The pulse sequence used was the 3QMAS echo sequence described previously\(^2\) and shown in Figure 1. The first and second pulses of this sequence are hard (ideally nonselective) 360° or 720° pulses (that is they are applied with the highest allowable power). In our case, this required pulses of 15–20 µs. The third pulse was a soft (central transition selective) pulse of 180° which was approximately 15–20 µs in duration as well. The delay between the first and second pulses was the \(t_1\) period which was selected to have a dwell time equal to the desired \(t_1\) dwell time (after complete processing) multiplied by 12/31. This factor arises as the 3QMAS experiment for a spin \(\frac{5}{2}\) nucleus is mathematically equivalent to a \(k = 19/12\) DAS experiment.\(^5\) In our experiments the MAS \(t_1\) spectral width was usually 6–20 kHz while in the \(t_2\) dimension it was usually 6–15 kHz. A 10 kHz \(t_1\) dimension spectral width required the actual \(t_1\) dwell time to be set to 38.7 µs. In these experiments, usually 40–100 \(t_1\) points were required to obtain spectra without truncation artifacts. The delay between the second and third pulses was set to an integer multiple of the period of the spinning rate, \(\tau_r\). This is required to ensure that the echo is completely refocused and no additional rotational artifacts are introduced. Care must be taken, just as in a shifted-echo DAS (SEDAS) experiment, to set the echo time to an appropriate value. If it is too long, then much signal is lost; if it is too short, then the data will be truncated in the \(t_2\) dimension (remembering that whole echo in this dimension is collected). Details on setting this delay in general are discussed elsewhere.\(^2\) For our experiments it was set to values ranging from 1 to 3 ms (10–30 rotor cycles). The spinning sidebands appear in positions similar to those that would be predicted from a \(k = 19/12\) DAS experiment and the processing is identical as well.\(^2\)\(^4\)\(^7\)\(^2\)\(^2\) The only difference arises in the referencing stage, at which point the offset in the isotropic dimension (the ppm value of the center of the resulting \(t_1\) dimension spectrum) must be multiplied by \((k – 3)/(k + 1)\) or \(-17/31\).\(^2\)

The determination of the isotropic chemical shift (\(\delta_{iso}^0\)) and quadrupolar coupling product \(P_q\) (\(C_q(1 + \eta^2/3)^{1/2}\)) where \(C_q = e^2\alpha Q\hbar\) and \(\eta\) is the quadrupolar asymmetry parameter was similar to that performed in a multiple field DAS experiment, in which the isotropic shift changes with field due to the differing second-order isotropic quadrupolar shift (\(\delta_{iso}^{2Q} = (6 \times 10^{-3})P_q(2/3)\)). In the 3QMAS experiment, the isotropic shift has scaling factors that differ from those of a single quantum spectrum. Thus the separation of \(\delta_{iso}^0\) and \(\delta_{iso}^{2Q}\) can be made with a single experiment at a single field. For \(I = \frac{1}{2}\), the observed

![Figure 1. Pulse sequence used for acquisition of pure absorption phase 2D 3QMAS spectra (top) and coherence pathway used to achieve pure phase (bottom). Note that the ±3 coherences are separated in a hypercomplex fashion.](Image 334x551 to 528x734)

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The resolution in the latter is dramatically increased: separation of the 1D spectrum on top is the projection onto the isotropic dimension. The contour lines are at levels from 5 to 90% in 9.4% steps. The 2-dimensional 3QMAS spectra as described above. The 3QMAS experiment is likely to be quantitative and thus imply site occupancies that are somewhat discrepant from previous models. Given the disagreements among existing models, however, the significance of their differences with the present results is uncertain. The close similarity of the $P_q$ values for the three peaks suggests that in this case intensities in the 3QMAS experiment are likely to be quantitative and thus imply site occupancies that are somewhat discrepant from previous models. Given the disagreements among existing models, however, the significance of their differences with the present data is uncertain.

**Kyanite.** Kyanite was studied to further assess the quantitation of 3QMAS peak intensities. The mineral contains four equally populated octahedral Al sites, with $C_q$ values of 10.0, 9.4, 6.5, and 3.7 MHz. The MAS spectrum is contrasted with the isotropic projection of the 3QMAS spectrum in Figure 3. The resolution in the latter is dramatically increased: separation of the peaks in the latter is enhanced by the large range in $C_q$, and peaks are much narrower because of the full averaging of

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### Table 1. Isotropic Shifts and Quadrupolar Coupling Parameters for Leucite from 11.7 and 9.4 T 3QMAS Experiments, Derived from 3QMAS and MAS Peak Positions

<table>
<thead>
<tr>
<th>site</th>
<th>$\delta^{14T}_{\text{MAS}}$ (ppm)</th>
<th>$\delta^{14T}_{\text{3QMAS}}$ (ppm)</th>
<th>$\delta^{11T}_{\text{MAS}}$ (ppm)</th>
<th>$\delta^{11T}_{\text{3QMAS}}$ (ppm)</th>
<th>$\delta^{2Q}_{\text{iso}}$</th>
<th>$P_q$ (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>58.6 ± 2.0</td>
<td>-34.2 ± 0.2</td>
<td>59.6 ± 1.5</td>
<td>-34.0 ± 0.2</td>
<td>61.0 ± 0.7</td>
<td>2.07 ± 0.50</td>
</tr>
<tr>
<td>T2</td>
<td>59.7 ± 2.0</td>
<td>-36.4 ± 0.2</td>
<td>61.8 ± 1.5</td>
<td>-35.7 ± 0.2</td>
<td>63.9 ± 0.6</td>
<td>2.58 ± 0.50</td>
</tr>
<tr>
<td>T3</td>
<td>66.1 ± 2.0</td>
<td>-39.1 ± 0.2</td>
<td>67.2 ± 1.5</td>
<td>-38.4 ± 0.2</td>
<td>69.2 ± 0.7</td>
<td>2.34 ± 0.50</td>
</tr>
</tbody>
</table>

$^a$ Peak assignments are based on correlations between chemical shift and mean T–O–T bond angles. $P_q$ is the quadrupolar product, $C_q(1 + \eta^2/3)^{1/2}$.
the second-order quadrupolar broadening. Even sites with very large \( C_\theta \) values are excited and observed. However, it is clear that observed intensities are systematically reduced with increasing \( C_\theta \), suggesting that caution is required in materials where ranges of \( C_\theta \) are large or unknown.

**Crystalline Anorthite.** Anorthite is an excellent test for \(^{27}\)Al 3QMAS spectral resolution: it has eight crystallographically distinct tetrahedral Al sites and is fully ordered (natural samples) or nearly so (synthetic samples). \( C_\theta \) and \( \eta \) values for all sites have been reported from single crystal data,\(^{28}\) but isotropic chemical shifts are not known because \(^{27}\)Al MAS spectra are completely unresolved.

3QMAS data at 11.7 T for more ordered crystalline anorthite are shown in Figure 4 (the spectrum at 9.4 T is available in supporting information). The spectra are complex, but contain a number of significant, resolvable features. The spectra were essentially the same in overall appearance with slight shifts between the two fields. Results for the somewhat less ordered crystal are very similar, if perhaps slightly less well-resolved, and have not been analyzed in detail. We have taken two independent approaches to understanding the spectra. In both, slices through the 2D spectra at the positions of obvious spectral features were taken (Figure 4). In the first approach, the peak position in the \( \omega_1 \) dimension (\( \delta_{\text{3QMAS}} \)) and the center of gravity in the \( \omega_2 \) (MAS) dimension were determined, and \( \delta_{\text{iso}} \) and \( P_\eta \) were calculated directly as described above. Results for the two fields are shown in Tables 2 and 3, and are consistent with each other within estimated uncertainties.

MAS peak shapes in slices of the 2D spectra were also simulated as described in the Experimental Section. For example, the slice projected from \(-35.5\) to \(-36.5\) ppm in the \( \omega_1 \) dimension (which contains two distinct sites) is shown in Figure 5. The simulated spectrum agrees well, with all singularities appearing in the \( \omega_2 \) dimension of the experimental data as expected. One possible limitation of such fitting is distortion of the \( \omega_2 \) dimension (MAS) peak shape due to non-uniform excitation of nuclei in crystallites with different orientation.\(^{15}\) Results of simulations are shown in Table 4. Fits were checked independently by using the derived parameters to calculate the expected \( \omega_1 \) peak positions (\( \delta_{\text{3QMAS}} \)). The latter agree well with directly observed values, suggesting that the fits are robust. The simulations provide values for \( \eta \) as well as for \( C_\theta \) and \( \delta_{\text{iso}} \). This procedure allows assignment of at least five features in the spectra to particular crystallographic sites, based on published single crystal data (Table 4). A sixth feature (\#6 in Figure 4), at the extreme low-frequency side in \( \omega_1 \), can be simulated with parameters that are closest to those expected for the \( 0:0:0 \) site (\( C_\theta = 8.5 \) MHz), but could probably also be

**Table 2.** Isotropic Shifts and Quadrupolar Coupling Parameters for Crystalline Anorthite from 11.7 T 3QMAS Experiments, Derived from 3QMAS and MAS Peak Positions

<table>
<thead>
<tr>
<th>peak ( \omega_1 ) (ppm)</th>
<th>( \delta_{\text{3QMAS}} ) (ppm)</th>
<th>( \delta_{\text{iso}} ) (ppm)</th>
<th>( P_\eta ) (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>48.0 ± 3.0</td>
<td>-35.4 ± 0.2</td>
<td>5.43 ± 0.50</td>
</tr>
<tr>
<td>2</td>
<td>61.0 ± 1.0</td>
<td>-36.0 ± 0.2</td>
<td>2.88 ± 0.33</td>
</tr>
<tr>
<td>3</td>
<td>58.0 ± 3.0</td>
<td>-37.4 ± 0.2</td>
<td>4.26 ± 0.63</td>
</tr>
<tr>
<td>4</td>
<td>55.0 ± 3.0</td>
<td>-39.1 ± 0.2</td>
<td>5.38 ± 0.50</td>
</tr>
<tr>
<td>5</td>
<td>47.0 ± 3.0</td>
<td>-42.5 ± 0.2</td>
<td>7.37 ± 0.37</td>
</tr>
<tr>
<td>6</td>
<td>40.0 ± 5.0</td>
<td>-44.4 ± 0.2</td>
<td>8.54 ± 0.52</td>
</tr>
</tbody>
</table>

**Table 3.** Isotropic Shifts and Quadrupolar Coupling Parameters for Crystalline Anorthite from 9.4 T 3QMAS Experiments Derived from 3QMAS and MAS Peak Positions

<table>
<thead>
<tr>
<th>peak ( \omega_1 ) (ppm)</th>
<th>( \delta_{\text{3QMAS}} ) (ppm)</th>
<th>( \delta_{\text{iso}} ) (ppm)</th>
<th>( P_\eta ) (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40.8 ± 2.0</td>
<td>-37.1 ± 0.3</td>
<td>5.53 ± 0.21</td>
</tr>
<tr>
<td>2</td>
<td>59.0 ± 1.0</td>
<td>-36.2 ± 0.2</td>
<td>2.83 ± 0.20</td>
</tr>
<tr>
<td>3</td>
<td>56.0 ± 2.0</td>
<td>-37.1 ± 0.3</td>
<td>3.64 ± 0.32</td>
</tr>
<tr>
<td>4</td>
<td>51.1 ± 3.0</td>
<td>-39.1 ± 0.3</td>
<td>4.80 ± 0.36</td>
</tr>
<tr>
<td>5</td>
<td>36.6 ± 4.0</td>
<td>-45.6 ± 0.3</td>
<td>7.28 ± 0.32</td>
</tr>
<tr>
<td>6</td>
<td>25.0 ± 5.0</td>
<td>-49.0 ± 0.3</td>
<td>8.56 ± 0.33</td>
</tr>
</tbody>
</table>
shown in Table 4.

- The mean intertetrahedral (Si–O–Al) angle. As expected from previous MAS NMR studies of both 28Si and 27Al in framework aluminosilicates, δiso decreases systematically with increasing mean angle. The 3QMAS data fall close to a line previously fitted to data from ordered phases, confirming the accuracy of the new data and of the site assignments. An earlier fit that included data for disordered minerals as well agrees even more closely with the anorthite data. The agreement between the results for δiso and Pq of the two approaches to assigning spectral features is excellent.

The estimated isotropic chemical shifts for the six relatively well-constrained sites are plotted in Figure 6 as a function of the mean intertetrahedral (Si–O–Al) angle. As expected from previous MAS NMR studies of both 28Si and 27Al in framework aluminosilicates, δiso decreases systematically with increasing mean angle. The 3QMAS data fall close to a line previously fitted to data from ordered phases, confirming the accuracy of the new data and of the site assignments. An earlier fit that included data for disordered minerals as well agrees even more closely with the anorthite data. The agreement between the results for δiso and Pq of the two approaches to assigning spectral features is excellent.

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### Table 4

<table>
<thead>
<tr>
<th>peak</th>
<th>δiso (ppm)</th>
<th>δmod (ppm)</th>
<th>δiso (ppm)</th>
<th>Cq (MHz)</th>
<th>η</th>
<th>Pq (MHz)</th>
<th>site</th>
<th>mean angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-35.3</td>
<td>-37.2</td>
<td>60.6</td>
<td>5.76</td>
<td>0.45</td>
<td>5.95</td>
<td>m(0)</td>
<td>145.4</td>
</tr>
<tr>
<td>2</td>
<td>-35.9</td>
<td>-35.8</td>
<td>63.6</td>
<td>2.66</td>
<td>0.53</td>
<td>2.78</td>
<td>m(2)</td>
<td>137.9</td>
</tr>
<tr>
<td>3</td>
<td>-37.3</td>
<td>-37.9</td>
<td>64.7</td>
<td>4.39</td>
<td>0.51</td>
<td>4.58</td>
<td>0000</td>
<td>138.0</td>
</tr>
<tr>
<td>4</td>
<td>-39.1</td>
<td>-39.0</td>
<td>65.6</td>
<td>4.87</td>
<td>0.62</td>
<td>5.17</td>
<td>m(0)</td>
<td>133.5</td>
</tr>
<tr>
<td>5</td>
<td>-42.2</td>
<td>-40.3</td>
<td>66.3</td>
<td>6.58</td>
<td>0.70</td>
<td>7.10</td>
<td>0000</td>
<td>131.1</td>
</tr>
<tr>
<td>6</td>
<td>-44.0</td>
<td>-45.0</td>
<td>66.2</td>
<td>8.19</td>
<td>0.65</td>
<td>8.75</td>
<td>0000</td>
<td>132.0</td>
</tr>
</tbody>
</table>

* Uncertainties in fitted Cq values are about ±0.5 MHz; in η about ±0.2, and in δiso about ±1 to 2 ppm.

Figure 5. MAS projection from -34.5 to -36.5 ppm in the isotropic dimension of the 11.7 T 3QMAS spectrum of anorthite. The simulation of this slice was the fit and the parameters are those for peaks 1 and 2 as shown in Table 4.

attributed to 0±00 (Cq = 7.4 MHz) or to m000 (Cq = 6.3 MHz). In fact, the whole “tail” of the spectrum in this region could well be comprised of poorly resolved signal from the three peaks with largest Cq. As noted above for kyanite, peaks for sites with relatively large Cq are expected to have reduced intensities as well as greater width in the ω2 dimension, and thus are expected to be relatively difficult to observe with 3QMAS. The broad feature on the high-frequency (ω2) side of the tallest peak is also likely to be due to an unresolved peak, again possibly one of the unassigned peaks with large Cq. In general, the agreement between the results for δiso and Pq of the two approaches to assigning spectral features is excellent.

Magnesium Aluminoborate Glass. This material was chosen because it contains sub-equal concentrations of four-, five-, and six-coordinated Al, which are clearly seen as partially resolved peaks in 27Al MAS NMR spectra. The 3QMAS spectrum is shown in Figure 8, and has three well-separated peaks that can be assigned to the three coordination states, whose presence is likely to be ambiguous in MAS spectra. Estimates of isotropic chemical shifts and quadrupolar products Pq for the three AlO4 peaks can be

![Figure 6](image-url)
made by measuring the positions of the peak maxima in both dimensions as described above. For the AlO₆, AlO₅, and AlO₄ peaks respectively we obtain 4, 31, and 63 ppm for \( \delta_{\text{iso}} \) and 2, 3, and 5 MHz for \( P_q \). These results are complicated by the likelihood of overlap of signal from sites with varying parameters within each major peak, and uncertainties are at least 2 ppm and 0.5 to 1.0 MHz. The relative population of the AlO₆, AlO₅, and AlO₄ sites obtained from the total projection of the 2D spectrum is about 1:2:6. As shown before for the kyanite sample, however, the triple-quantum excitation efficiency for Al sites systematically decreases with increasing \( P_q \). Thus, the intensity observed for the AlO₄ peak is likely to be underestimated relative to the others.

The 2D spectrum is consistent with ranges of chemical shifts and coupling constants known from crystalline materials. AlO₆ sites generally have \( \delta_{\text{iso}} \) between 1 and 15 ppm and \( C_q \) between 1 and 10 MHz. Corresponding 3QMAS peak positions of \(-1\) to \(-30\) ppm in the isotropic dimension and \(-50\) to 12 ppm in the MAS dimension would be expected. Values of \( \delta_{\text{iso}} \) for AlO₅ sites typically fall between 30 and 40 ppm, with \( C_q \) between 3 and 10 MHz, giving 3QMAS peak positions ranging from \(-18\) to \(-40\) ppm in the isotropic dimension and \(-30\) to 30 ppm in the MAS dimension. Finally, AlO₃ sites typically have \( \delta_{\text{iso}} \) between 55 and 88 ppm and \( C_q \) between 1 and 10 MHz, resulting in 3QMAS peak positions from \(-30\) to \(-60\) ppm in the isotropic dimension and 0 to 80 ppm in the MAS dimension. Note that in Figure 8, each of the labeled peaks falls neatly in the center of the corresponding regions.

For the AlO₄ peak we also fitted slices along the \( \omega_2 \) dimension, as was done for the crystalline phases. Again, for a disordered material results from the fits are not unique because each slice contains unresolved intensity from sites with ranges in chemical shift and \( C_q \). However, this approach does give some estimate of the range of parameters present, about 62 to 75 ppm for \( \delta_{\text{iso}} \) and 4 to 6.5 MHz for \( C_q \).

**Conclusions**

Triple-quantum magic angle spinning (3QMAS) spectra can provide enhanced resolution for \(^{27}\text{Al}\) in aluminosilicate and aluminate materials, both crystalline and amorphous, although resolution in the isotropic dimension may still be limited by disorder and other mechanisms of residual broadening. Additional information on NMR parameters may be obtainable because the two dimensional spectra provide some separation of chemical shift and quadrupolar effects, both from simple peak position data and from fitting of MAS peak shapes in slices of the spectra. 3QMAS signal can be obtained even from sites with quadrupolar coupling constants as large as 9 MHz, but intensity is systematically reduced with increasing \( C_q \). We have derived new data for isotropic chemical shifts for five or six of the eight sites in crystalline anorthite, which agree reasonably well with previous correlations with structure. In glasses, the separation between peaks for Al in different coordination states is excellent, and provides a new and sensitive test for the presence of AlO₅ and AlO₆ sites in glasses dominated by AlO₄, although absolute quantitation may remain difficult.

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**Supporting Information Available:** The 2D triple-quantum \(^{27}\text{Al}\) MAS NMR spectrum of crystalline anorthite collected at 9.4 T (1 page). See any current masthead page for ordering and Internet access instructions.

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