on the synthetic and natural complexes show that the photodissociation initiated by pumping the Q band, as judged by the lifetime of B, takes some picoseconds to occur and depends on the heme geometry. To the extent that the photodissociation has its beginnings in the subpicosecond regime, we are in agreement with the femtosecond report of Martin et al.[6] However, in their study on CO complexes of Hb and Mb a deoxy-like species appeared with a time constant of 350 fs which had spectral characteristics that did not change for 100 ps. At the moment, we cannot explain the difference between our results and this femtosecond observation in regard to the evaluation of band shape in the transient difference spectra. Earlier picosecond work showed evidence and discussed the development of the deoxy photoproduct band shape changes that we have identified with intermediates C and D.[8] As the ligand-field level system is complex, the possibility exists that at the 307-nm pump wavelength of the femtosecond experiment a fast photodissociative channel is available that is not otherwise open with the Nd^{3+} 353- or 531-nm pump wavelengths.

Acknowledgment. We thank Andy Hutchinson and Chris Guest for their valuable assistance in the preparation and discussion of various aspects of this work. We also thank the University of Wyoming for supporting this work.

First Observation of 5-Coordinate Aluminum by MAS ^{27}Al NMR in Well-Characterized Solids[†]

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Abstract: The first magic angle spinning ^{27}Al NMR spectra of 5-coordinate aluminum in well-characterized solids are reported. Two solids containing 5-coordinate aluminum, barium aluminum glycolate and the mineral andalusite, were examined. The signal is upfield of that for tetrahedral aluminum and downfield of that for octahedral aluminum. All of the aluminum in barium aluminum glycolate is in highly distorted, AlO$_5$ trigonal bipyramids. These AlO$_5$ groups exhibit a complex line shape at δ 37 at 11.7 T. Andalusite has highly distorted AlO$_5$ and AlO$_6$ species. Even at 11.7 T, the trigonal bipyramidal AlO$_5$ species exhibits a substantial second-order quadrupole-induced broadening and upfield shift of the centerband ($e^2qQ/h = 5.9$ MHz and $\eta = 0.70$), whose center of gravity is at δ 21 (δ 35 after correction for second-order quadrupole effects). The signal for the AlO$_6$ species is extremely complex and shifted far upfield. The advantages of using MAS and VAS in studying the NMR of nonintegral spin quadrupolar nuclei in solids that exhibit complex spectra are discussed.

In the last several years, many papers have appeared on MAS ^{27}Al NMR studies of zeolites, clays, minerals, etc.[1-3] Consequently, much more is now known about the tetrahedral and octahedral aluminum in these species. In contrast, relatively few 5-coordinate aluminum species are known: the minerals andalusite, grandidierite, yoderite, augelite, and senegalite,[4] as synthesized AlPO$_4$-12,[5] as synthesized AlPO$_4$-21,[4,6] and several organic complexes.[7-13] We are unaware of any magic angle or variable angle spinning ^{27}Al NMR work that has conclusively shown the presence of 5-coordinate aluminum in a solid. However, there are at least seven reports[14-20] involving ^{27}Al NMR spectra of 5-coordinate aluminum species in liquid solutions. Where data are available,[14,15,17-20] 5-coordination results in a substantial upfield shift relative to 4-coordination. This paper reports the first examples of magic angle and off angle spinning ^{27}Al NMR spectra of species containing 5-coordinate aluminum.[21] The complex barium aluminum glycolate[13] and the mineral andalusite were chosen for study to avoid any complications that might occur in assigning the signal for 5-coordinate aluminum if atoms such as phosphorus,[24-28] nitrogen,[29,30] or boron[31] were also part of the framework. The spectra of barium aluminum glycolate and andalusite show that the signal for 5-coordinate aluminum is upfield of the signal for tetrahedral aluminum but downfield of the signal for octahedral aluminum.

Experimental Section

1. Synthesis of Barium Aluminum Glycolate (BaAlO$_8$C$_{6.75}$H$_{14.75}$).[13] A modification of the procedure of ref 13 was used.

Barium hydroxide octahydrate (31.5 g, 0.10 mol) was partially dissolved in distilled water (16.2 g, 0.90 mol), and then aluminum isopropoxide powder (40.8 g, 0.20 mol) was added to ethylene glycol (248 g, 4.0 mol). The barium hydroxide suspension was added to the alu-

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[†] However, see Note Added in Proof. Except for this note, the manuscript reflects our knowledge when the manuscript was initially submitted (February 1986).

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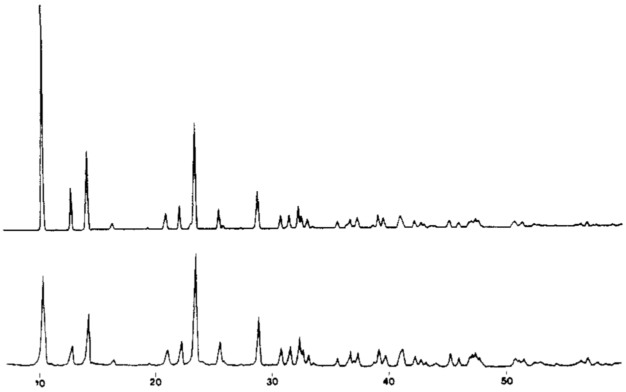

Figure 1. Top: simulated X-ray powder diffraction pattern of barium aluminum glycolate. Bottom: Experimental X-ray powder diffraction pattern.

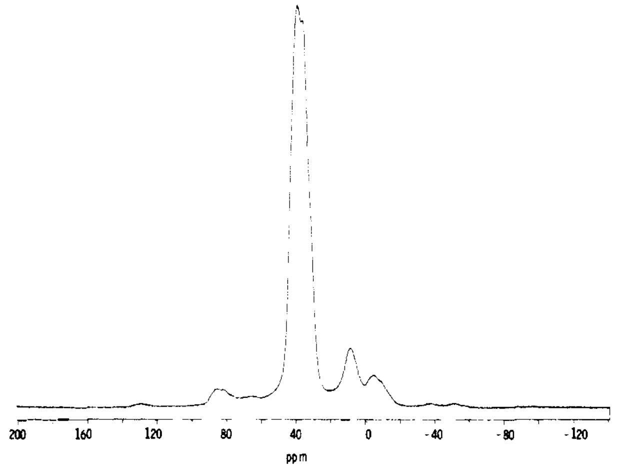

Figure 2. 130.3-MHz ^{27}Al NMR spectrum of barium aluminum glycolate (see text).

minum isopropoxide/ethylene glycol, stirred together for 30 min at room temperature, then heated in a 600-cm^3 stirred autoclave to 200 °C, and stirred at 350 rpm under autogeneous pressure for 2 weeks. The crystalline product appeared as large plates ~5 × 10 μ, many of which appeared to have shattered into pieces. The product was filtered with vacuum, air dried for 30 min at room temperature, and stored in a desiccator. The X-ray powder diffraction pattern of this solid was identical with the simulated X-ray powder diffraction pattern based upon the atomic coordinates of barium aluminum glycolate[13] (Figure 1).

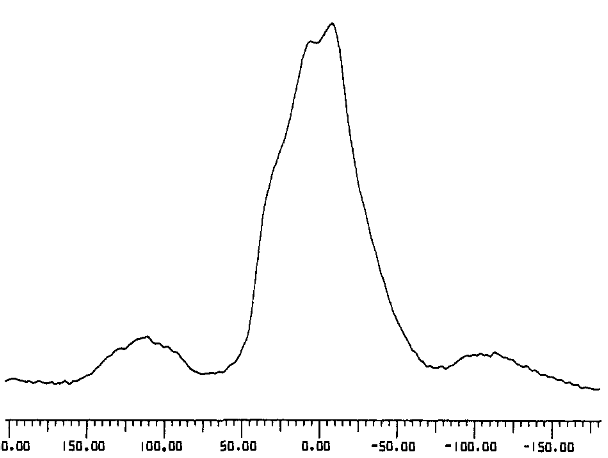

Figure 3. 51.9-MHz ^{27}Al NMR spectrum of barium aluminum glycolate (same sample as in Figure 2).

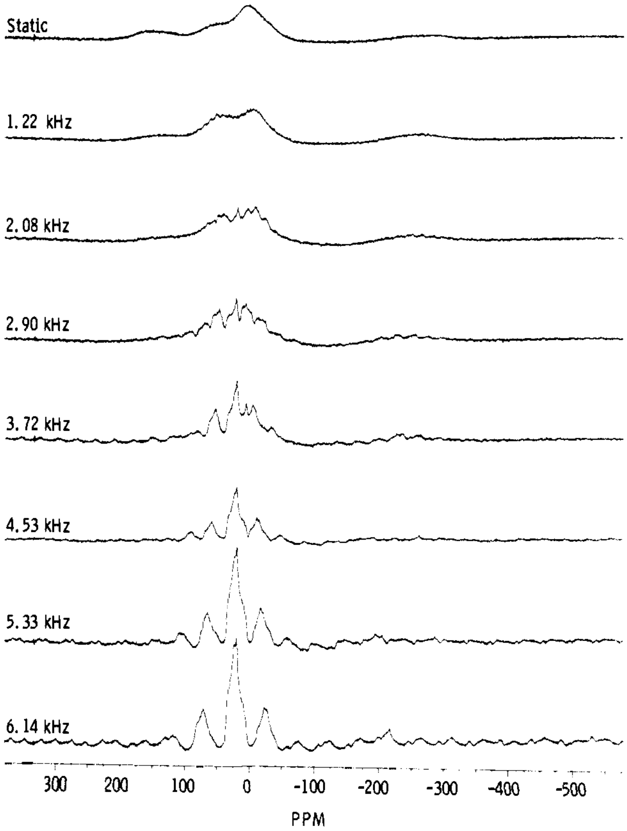

Figure 4. Scaled, 130.3-MHz ^{27}Al NMR spectra of static andalusite and at various spinning rates at the magic angle.

2. Instrumental Techniques. Standard X-ray powder diffraction techniques were followed by using a θ-2θ Norelco goniometer and Cu Kα X-radiation (1.5418 Å). The simulated X-ray powder diffraction pattern for the barium aluminum glycolate was calculated by using a modified version of POWD2.[32]

A Bruker AM-500 NMR spectrometer was used to obtain ^{27}Al NMR spectra at ν_L = 130.3 MHz. Samples were usually spun slightly off angle to suppress any signals for the noncentral transitions.[33-35] The 90° pulse for Al(NO$_3$)$_3$ (aqueous) was 10.5 μs. Other parameters for barium aluminum glycolate (Figure 2) were as follows: 271 mg, spinning rate (ν_r) = 6 kHz, pulse width (t_p) = 1.5 μs, 4 K data points in the time domain (TD) zero-filled to 8 K data points in the frequency domain (SI), spectral width (SW) = 50 kHz, filter width (FW) = 62.5 kHz, preacquisition delay (DE) = 15μs, acquisition time (AQ) = 41 ms, relaxation

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[21] After completing this study, we became aware of two reports[22,23] that both speculate on the possible presence of AlO$_5$ species in solids that have undergone some type of thermal or "mechanicochemical" treatment. Because of the quality of the ^{27}Al NMR spectra and the poorly defined solids discussed, we do not believe that these reports constitute a documented observation of 5-coordinate aluminum by ^{27}Al MAS NMR spectra.

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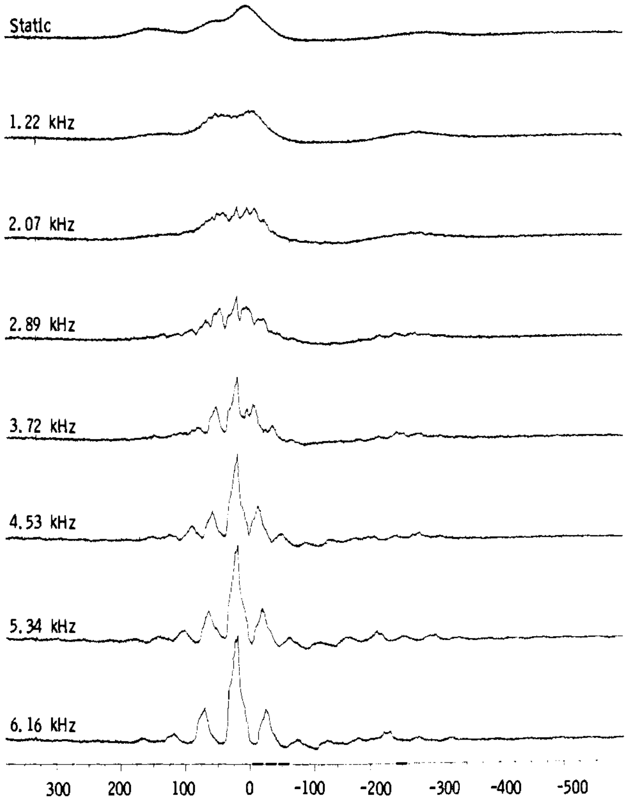

Figure 5. Scaled, 130.3-MHz ^{27}Al NMR spectra of static andalusite and at various spinning rates less than 1° away from the magic angle.

delay (RD) = 40 ms, number of acquisitions (NS) = 10 000, and line broadening factor (LB) = 0 Hz. Proton decoupling had virtually no effect.

A JEOL FX-200 NMR spectrometer was used to obtain an ^{27}Al NMR spectrum of barium aluminum glycolate at ν_L = 51.94 MHz (Figure 3). The solution 90° pulse was 5.9 μs. Other parameters were as follows: 657 mg, ν_r = 5.5 kHz, t_p = 2.0 μs, TD = 384 points, SI = 4K, SW = FW = 40 kHz, DE = 25 μs, AQ = 4.8 ms, RD = 350 ms, NS = 1024, and LB = 50 Hz. Proton decoupling had virtually no effect.

Gem quality andalusite (confirmed by X-ray powder diffraction) from Minas Gerais, Brazil, was ground by hand in an agate mortar. The very wide, 130.3-MHz ^{27}Al NMR spectra of andalusite (Figures 4 and 5) required that the largest possible spectral width (125 kHz) be used. Other parameters were as follows: t_p = 1.5 μs, TD = SI = 8K, FW = 250 kHz, DE = 7.5 μs, AQ = 33 ms, RD = 3 ms, NS = 10000, and LB = 10 Hz. For each set of spectra (Figures 4 and 5), the spectrum obtained with the fastest rotation was subjected only to zero-order phasing, and the same phasing was applied to the other spectra.

Results and Discussion

1. Barium Aluminum Glycolate. Cruickshank and Glasser recently reported the synthesis of a new barium aluminum glycolate containing 5-coordinate aluminum (a highly distorted AlO_5 trigonal bipyramid).[13] The AlO_5 groups share edges that give rise to isolated dimers. A complete description of the structure, including bond angles and distances, has been reported.[13b] Our synthesis yielded a solid whose X-ray data exactly match the simulated X-ray powder diffraction pattern for the 5-coordinate aluminum species (Figure 1). Consequently, the relatively strong ^{27}Al NMR signal near δ 37 (Figure 2) can only result from 5-coordinate aluminum. [There also are weak signals for octahedral (δ 8) and tetrahedral (≃δ65) aluminum, presumably due to a small amount of amorphous alumina not detected by X-ray.] The two signal maxima near δ 37 result from two different types of 5-coordinate aluminum because the 51.9-MHz (Figure 3) and 130.3-MHz (Figure 2) ^{27}Al NMR spectra cannot be simulated with just one quadrupole coupling constant and one asymmetry parameter. Since the two aluminum atoms in the aluminate dimer[13] are symmetrically equivalent, the two signal maxima near δ 37 may be due to a slight perturbation of the chemical environment around aluminum, possibly as a result of hydration.

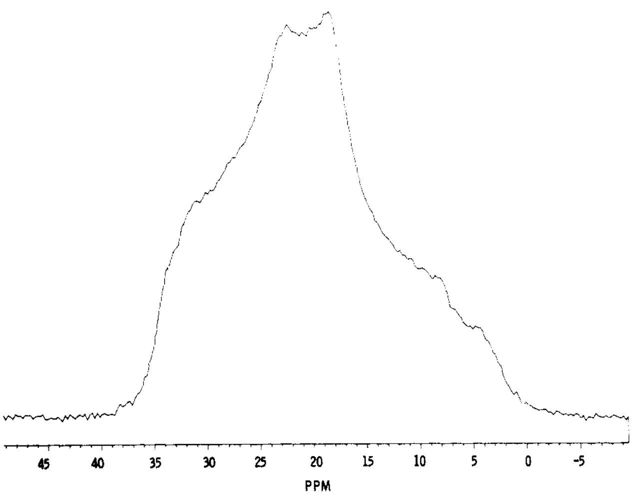

Figure 6. The centerband for the 5-coordinate aluminum in andalusite: 6.16 kHz spinning less than 1° away from the magic angle.

2. Andalusite (Al_2SiO_5). Andalusite is a naturally occurring aluminum silicate mineral named after one of the locations where it is found (Andalusia, Spain). It is one of three Al_2SiO_5 polymorphs, the others being sillimanite and kyanite, which are of great importance to the metamorphic petrologist in defining metamorphic zones. These minerals have been the subject of extensive chemical, structural, and petrographic study.[36a] The structure of andalusite consists of AlO_6 octahedra linked in chains parallel to *c* that are cross-linked by SiO_4 tetrahedra and AlO_5 distorted trigonal bipyramids. The complete X-ray crystal structure has been reported.[36b,c]

Andalusite gives extremely complex ^{27}Al NMR spectra (Figures 4 and 5). The trigonal bipyramidal aluminum[4] in andalusite has a quadrupole coupling constant e^2qQ/h = 5.9 MHz and an asymmetry parameter η = 0.70, while the octahedral aluminum has e^2qQ/h = 15.6 MHz and η = 0.08.[37] (Henceforth, qcc will usually be used instead of e^2qQ/h.) Such large values for qcc relative to ν_L (130.3 MHz) result in a very substantial broadening and upfield shift, $\delta_{obsd} - \delta_{iso}$, of the signal for the two types of aluminum, especially for the octahedral aluminum[35,38-40]

$$\delta_{obsd} - \delta_{iso} = \frac{-3(10^6)(e^2qQ/h)^2[I(I + 1) - 3/4][1 + (\eta^2/3)]}{40(\nu_L^2)[I(2I - 1)]^2}$$

where I = the nuclear spin ($^5/_2$ for ^{27}Al). Furthermore, since neither qcc is negligible compared to ν_L, highly complex line shapes are to be expected. The MAS spectra (Figure 4) clearly show this. With such a large qcc for the octahedral aluminum, the center of gravity of its signal has to be shifted far upfield ($\delta_{obsd} - \delta_{iso}$ = −86 ppm), while the center of gravity of the signal for the 5-coordinate aluminum, which has a much smaller qcc, is shifted much less upfield ($\delta_{obsd} - \delta_{iso}$ = −14.3 ppm). The MAS spectra reveal a signal with a maximum at δ 18. Such a chemical shift is too far downfield to result from AlO_6 units, even in a perfectly symmetrical environment (i.e., qcc = 0). Consequently, this signal must be the centerband for the 5-coordinate aluminum. An expanded plot of the centerband is shown in Figure 6 with the sample spinning at 6.16 kHz less than 1° away from the magic angle in order to suppress the signals for the noncentral transitions (see below). Signal maxima are evident at δ 18.4 and δ 22.3. Because the 5-coordinate aluminum has a much smaller qcc, its signal is inherently narrower and can be further narrowed by MAS at the relatively modest spinning rates possible on our spectrometer. Therefore, faster spinning reduces the percentage of 5-coordinate

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aluminum signal intensity in the spinning sidebands. This can be clearly seen from the increase of the centerband intensity at δ 18 as the spinning rate increases.

One-half of the integrated area of the centerband for the 5-coordinate aluminum signal is upfield of δ 20.9 (Figure 6). This chemical shift ($\delta_{A/2}$) does not coincide with the chemical shift for the center of gravity of the centerband (δ_{obsd} for the 5-coordinate aluminum signal because δ_{obsd} can rigorously be calculated only from a mathematical analysis of the line shape. However, for $\nu_L = 130.3$ MHz, qcc = 5.9 MHz, and $\eta = 0.70$, δ_{obsd} and $\delta_{A/2}$ would be almost the same. Consequently, the center of gravity in the absence of a quadrupole-induced upfield shift (i.e., at infinite magnetic field) would be $\simeq\delta$ (20.9 + 14.3) = δ 35. The line shape for the centerband is, as expected, similar to that obtained from simulations using reported values[37] for qcc and η, although the quality of the fit is at least as good with values for qcc and η that are about 5% larger.

The spectra of andalusite exhibit interesting features in addition to the signal for 5-coordinate aluminum. Very broad signals near δ −250 and δ +150 become more evident as ν_r decreases (Figures 4 and 5). Such signals result from the octahedral aluminum, whose quadrupole coupling constant (15.6 MHz[37]) is so large that spinning at 6 kHz is totally inadequate for line narrowing. For the octahedral aluminum, $\eta = 0.08$.[37] A static or slowly spinning solid with $\eta \simeq 0$ will give a complex line shape with two well-separated peak maxima of comparable intensity.[35,39,41,42] The line shape becomes even more complex when $\nu_L < 10$ qcc,[43] as is the case for the octahedral aluminum in andalusite. If the sample could be spun rapidly enough to enable most of the signal intensity for the octahedral aluminum to be in a well-defined centerband, its center of gravity would be at about δ −85 because of the quadrupole-induced upfield shift.

The 130.3-MHz ^{27}Al MAS NMR spectrum of basic aluminum sulfate[35] supports the interpretation of the andalusite spectra. The tetrahedral aluminum (qcc = 0.8 ± 0.2 MHz) of basic aluminum sulfate gives a sharp signal at δ 63, while the octahedral aluminum (qcc = 10.2 ± 0.5 MHz) gives a broad, complex signal from δ 110 to δ −160.[35] Because line width is approximately proportional to the square of the quadrupole coupling constant, increasing qcc by a factor of 1.5 (i.e., qcc for octahedral aluminum in andalusite) more than doubles the line width.

The 130.3-MHz ^{27}Al MAS NMR spectrum of sillimanite,[44] another Al_2SiO_5 polymorph, also supports the interpretation of the andalusite spectra. Sillimanite has tetrahedral aluminum with qcc = 6.77 MHz and $\eta = 0.53$ and octahedral aluminum with qcc = 8.93 MHz and $\eta = 0.46$.[37] As Samoson et al.[44] show, the signal for the tetrahedral aluminum is much narrower than the signal for the octahedral aluminum because the tetrahedral aluminum has a smaller quadrupole coupling constant. (The difference of 2.2 MHz apparently is significant because line width is approximately proportional to the square of the quadrupole coupling constant.) Qualitatively similar signals are shown by the 5- and 6-coordinate aluminum in andalusite, where the difference in quadrupole coupling constants is much greater and only the 5-coordinate aluminum gives a well-defined signal. It is reasonable that for the nonoctahedral aluminum in sillimanite and andalusite, the larger quadrupole coupling constant and smaller asymmetry parameter in sillimanite result in a line shape for which second-order quadrupolar effects are more apparent, i.e., two signal maxima and shoulders.[44]

The disappearance of the wavy base line (Figure 4) upon spinning andalusite at a fixed angle setting less than 1° away from the magic angle (Figure 5) indicates that signals for the noncentral transitions were seen with MAS[33-35] (rather than paramagnetic species causing large magnetic susceptibility broadening of the signal for the central transition[45,46]). The signals are undoubtedly for the $(^3/_2,^1/_2)$ and $(-^1/_2,-^3/_2)$ transitions, as recent work by Samoson[47] indicates that for any spin-$^5/_2$ nucleus, the numerous signals separated by the spinning frequency for the $(^3/_2,^1/_2)$ and $(-^1/_2,-^3/_2)$ transitions are much narrower and taller than the signals for the $(^5/_2,^3/_2)$ and $(-^3/_2,-^5/_2)$ transitions. The complexity of the MAS spectra also precludes detecting the quadrupole-induced *downfield* shift for any of the noncentral transitions[47] (cf. the quadrupole-induced upfield shift for the central transition).

As noted earlier, the signal intensity for the octahedral aluminum clearly decreases as ν_r increases. (This can be better seen in Figure 5, where the signals for the noncentral transitions are so broad as to be virtually undetectable.) There may be destructive interference at about 5 kHz between the mechanical spinning of the rotor and some other interaction (e.g., natural molecular motion or dipole–dipole interactions).[48] The complexity of the spectra makes more detailed analysis difficult.

It is known that spinning a sample at certain angles other than the magic angle (depending on η) sometimes narrows the signals of noninteger spin quadrupolar nuclei for which the second-order quadrupolar interaction is much greater than the chemical shift anisotropy or dipole–dipole interactions.[35,41,46,49-51] Andalusite is clearly worth a high field, variable angle study.

Finally, we note that in marked contrast to these complex ^{27}Al NMR spectra, the SiO_4 groups in andalusite give a single, sharp ^{29}Si MAS NMR signal at δ −80 (as previously reported[52]). Clearly, our sample has no readily detectable silicon-containing impurities. A signal at δ −80 is even downfield of the region in which ^{29}Si signals for $Si(OAl)_4$ units of zeolites appear.[1-3]

Conclusions

We have observed the presence of 5-coordinate aluminum in solids by ^{27}Al NMR spectra. To our knowledge, this is the first such documented observation with spinning at or near the magic angle. Having the strongest, persistent superconducting magnet greatly aided detecting the signal for 5-coordinate aluminum in andalusite. However, as the ^{27}Al NMR spectra of andalusite, sillimanite,[44] and other solids[35] with very large quadrupole coupling constants show, even stronger, persistent superconducting magnetic fields and probes capable of much faster sample rotation, neither of which yet exists, will be helpful.

Acknowledgment. We thank John L. Schlenker for obtaining the atomic coordinates of barium aluminum glycolate and calculating the simulated X-ray powder diffraction pattern. We thank Shel E. Sommer of our Dallas laboratory for the sample of andalusite. We thank Kirk D. Schmitt and Suzanne E. Schramm of our Princeton laboratory for the low-field spectrum and the simulations, Donald E. Woessner (Dallas), Joseph G. Bendoraitis, Michael E. Landis, and Jeffrey C. Trewella for helpful discussions, David T. Geston for his excellent technical assistance with the synthesis of the glycolate, and the Technical Information Services staff for their assistance in finding and obtaining several of the articles on ^{27}Al NMR of 5-coordinate aluminum.

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Note Added in Proof. Three relevant papers appeared after this manuscript was submitted.

Cruickshank et al.[53] reported the 104.1-MHz ^{27}Al MAS NMR spectra of barium aluminum glycolate and andalusite. The spectrum of the glycolate exhibits a signal maximum at δ 35.3 (and, as in our sample, a signal for octahedral aluminum from an impurity). The results for the two samples of barium aluminum glycolate at the three field strengths suggest that the 5-coordinate aluminum has a qcc $\simeq$ 4 MHz. The stongest signal in the 104.1-MHz spectrum of andalusite is at about δ 15. The quadrupole-induced upfield shift of the center of gravity for the 5-coordinate aluminum signal is about 8 ppm greater at 104.1 MHz than at 130.3 MHz [i.e., $(130.3/104.1)^2(-14.3 \text{ ppm}) = -22.4$ ppm], which in light of our Figure 6 leaves no doubt that the signal reported by Cruickshank et al.[53] near δ 15 results from 5-coordinate aluminum, not from octahedral aluminum as is indicated in their figure. (The octahedral aluminum gives an undetectably broad, far upfield signal at lower field strengths.[54] A much shorter pulse than the 10-μs pulse used[53] would appear desirable for recording ^{27}Al NMR spectra of solids, particularly when the quadrupole interactions are so large.[55,56]) The signal in their spectrum near δ 50 clearly results from a spinning sideband—the spinning rate of 3.7 kHz results in sidebands at 35-ppm intervals—not from the 5-coordinate aluminum centerband as is indicated in their[53] figure.

Our interpretation of the spectrum of andalusite is consistent with those recently reported by two other groups.[54,57] Lippmaa et al.[54] reported that the 130.4-MHz ^{27}Al MAS NMR spectrum of andalusite gives a value of δ 36.0 for the chemical shift of the 5-coordinate aluminum after correcting for the quadrupole-induced upfield shift. (We estimated δ 35.) Dupree et al.[57] reported the 104-MHz ^{27}Al MAS NMR spectra of two amorphous alumina films. In addition to signals for tetrahedral and octahedral aluminum, each film gives a signal near δ 28 that does not result from spinning sidebands. This signal is attributed to AlO_5 species because andalusite is reported[57] to give a signal for 5-coordinate aluminum at about δ 35.

Registry No. Barium aluminum glycolate, 97867-12-4; andalusite, 12183-80-1.

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Simplification of Two-Dimensional ^{1}H NMR Spectra Using an X-Filter[1]

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Abstract: X-Filtering is a new method for simplifying two-dimensional (2D) homonuclear ^{1}H NMR spectra, which is based on spin-spin couplings between protons and a NMR-active X-nucleus. The X-filtered 2D NMR spectra contain exclusively cross peaks and diagonal peaks from protons coupled to X. The procedure is applied to ^{1}H 2D correlated spectroscopy (COSY) and ^{1}H 2D nuclear Overhauser and exchange spectroscopy (NOESY). Potential applications include studies of small molecules as well as biological macromolecules which contain NMR-active X-nuclei. For example, with the use of X-filtering the coordination sites of NMR-active metal ions may be identified, which could otherwise often only be achieved with laborious chemical isotope labeling procedures.

The advent of two-dimensional NMR spectroscopy has revolutionized the analysis of homonuclear and heteronuclear spin systems in solution, both for small molecules as well as macromolecules such as proteins and nucleic acids.[2,3] Work with macromolecules benefits in particular from techniques capable of simplifying 2D NMR spectra and thus enhances the accessible information content. Examples are multiple quantum spin filters,[4] X-relayed magnetization transfer,[5] and editing techniques based on gated heteronuclear decoupling.[6] The present paper introduces a novel filtering procedure, which utilizes heteronuclear spin-spin couplings to simplify homonuclear ^{1}H 2D NMR spectra. This technique also modifies in characteristic ways the multiplet structure of cross peaks connecting protons which are coupled to a particular X-nucleus. The 2D NMR measurements needed for this method ensure that both the complete *and* the X-filtered spectrum are obtained from one experimental setup, without an increase in measuring time relative to the corresponding conventional ^{1}H 2D NMR experiment. As an illustration, ^{113}Cd-

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(1) Abbreviations used: NMR, nuclear magnetic resonance; rf, radio frequency; FID, free induction decay; 1D, one-dimensional; 2D, two-dimensional; ppm, parts per million; *J*, spin-spin coupling constant; COSY, two-dimensional correlated spectroscopy; MQF, multiple quantum filter; 2QF-COSY, two quantum filtered COSY; NOE, nuclear Overhauser enhancement; NOESY, two-dimensional nuclear Overhauser and exchange spectroscopy; MQC, multiple quantum coherence; EDTA, ethylenediaminetetraacetic acid; Tris, 2-amino-2-hydroxymethyl-1,3-propanediol; TSP, trimethylsilylpropionic acid sodium salt.

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