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Direct observation of highly distorted hexa-coordinated aluminium in andalusite by very fast ^{27}Al MAS NMR

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Highly distorted hexa-coordinated Al in andalusite can be detected by very fast (> 30 kHz) ^{27}Al magic-angle spinning (MAS) and triple-quantum MAS NMR spectroscopy.

Andalusite is a naturally occurring aluminium silicate named after Andalusia (Spain) where it has been found, and it is one of the three known Al_2SiO_5 polymorphs, the other being sillimanite and kyanite. The crystal structure of andalusite consists of $[AlO_6]$ octahedra forming chains parallel to *c* which are cross-linked by $[SiO_4]$ tetrahedra and $[AlO_5]$ trigonal bipyramids.[1,2] Several studies reporting ^{27}Al magic angle (and variable angle) spinning NMR spectra of andalusite are available.[3,4] ^{27}Al is a half-integer quadrupole ($I = 5/2$) nucleus and obtaining a good MAS NMR spectrum of andalusite presents a great challenge because all the aluminium nuclei are in highly distorted environments (characterised by large quadrupole coupling constants) and, hence, give very broad peaks.[4] In particular, the $[AlO_6]$ octahedron is so distorted that its ^{27}Al MAS NMR resonance has not previously been observed, even when the sample was spun at 15 kHz.[4] Recently, NMR probes capable of achieving spinning rates of 30–35 kHz became commercially available. Here, we wish to report that the use of such a probe and very fast (> 30 kHz) MAS allows the detection of the broad hexa-coordinated ^{27}Al NMR andalusite resonance. In addition, we also show that by combining very fast MAS and very powerful (> 250 kHz) radiofrequency (rf) fields a ^{27}Al triple-quantum (3Q) MAS NMR spectrum[5] of andalusite can be recorded.

Andalusite from Minas Gerais, Brazil, was characterised by powder X-ray diffraction and ^{29}Si MAS NMR (single peak at $\delta\,-79.6$). 'Conventional' (single-quantum) ^{27}Al MAS NMR spectra of andalusite recorded at different spinning rates are shown in Fig. 1. In order to obtain meaningful relative signal intensities we have used short (0.6 μs, equivalent to 10^0) and strong rf pulses. The 32.5 kHz MAS spectrum clearly contains two broad resonances centred at δ *ca.* 13 and -110 (with peak singularities at $\delta\ -46$ and -184), displaying characteristic second-order quadrupole lineshapes. The former has been previously assigned to penta-coordinated aluminium.[3,4] In our 9.4 T magnetic field, the presence of the very broad peak centred at δ *ca.* -110 becomes apparent at MAS rates in excess of 20 kHz, but its lineshape is only well defined at *ca.* 30 kHz. The second-order quadrupole patterns can be simulated to yield the isotropic chemical shifts, δ_{iso}, the quadrupole coupling constants, C_Q, and the asymmetry parameters, η (Fig. 2). The following values are obtained for the penta- and hexa-coordinated Al species, respectively: δ_{iso} 35.5 and 13.0; C_Q = 5.8 and 15.3 MHz; η = 0.69 and 0.08. These quadrupole parameters are in good agreement with previously reported data (C_Q = 5.9 and 15.6 MHz; η = 0.70 and 0.08 for penta- and hexa-coordinated Al, respectively).[3,4,6] The relative intensities of these two Al peaks (the spinning sidebands arising from the $m = +1/2 \leftrightarrow m = -1/2$, central transition hexa-coordinated Al line are included) measured directly from the spectrum are in a 1 : 0.85 ratio, respectively. According to the published crystal structure, this ratio should be 1 : 1 and, thus, NMR slightly underestimates the hexa-coordinated Al population. A more precise estimation of the two Al populations requires the simulation not only of the central transition ^{27}Al MAS NMR spectrum but also of the ($\pm 3/2 \leftrightarrow \pm 1/2$ and $\pm 5/2 \leftrightarrow \pm 3/2$) satellite-transitions spectra. This work is in progress in our laboratory.

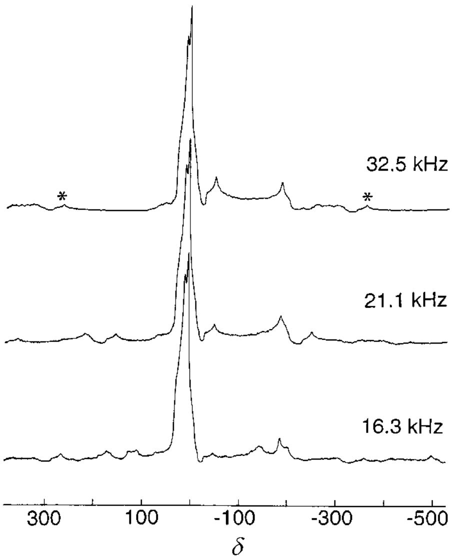

Fig. 1 ^{27}Al MAS NMR spectra of andalusite recorded at 104.3 MHz on a Bruker MSL 400P spectrometer using a Bruker 2.5 mm double-bearing probe, 0.3 s recycle delays, and the spinning rates indicated. Chemical shift reference $[Al(H_2O)_6]^{3+}$. The asterisks denote spinning sidebands arising from the central transition hexa-coordinated Al line.

The large C_Q values of the andalusite Al species make the excitation of ^{27}Al NMR multiple-quantum coherences a very difficult task. We were particularly interested in finding out whether the hexa-coordinated ^{27}Al NMR resonance (with C_Q = 15.3 MHz) could be observed in a triple-quantum experiment. Fig. 3 shows the ^{27}Al 3Q MAS NMR spectrum of andalusite recorded with a very fast sample spinning. The penta-coordinated Al peak is clearly seen and it exhibits an almost undistorted lineshape (inset in Fig. 3). Although very weak, the hexa-coordinated Al resonance is observable. Both peaks (in

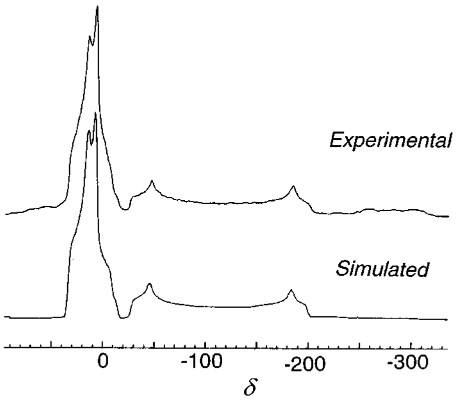

Fig. 2 Experimental and simulated ^{27}Al MAS NMR spectra of andalusite (spinning rate 32.5 kHz).

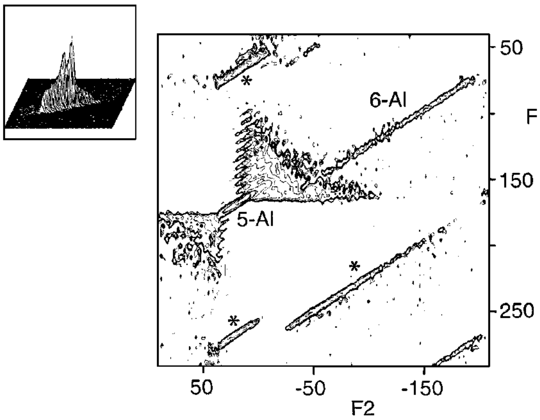

Fig. 3 Unsheared ^{27}Al triple-quantum MAS NMR spectra of andalusite recorded with a rf field amplitude of *ca.* 265 kHz and a spinning rate of 30.2 kHz. 512 data points (864 transients per point) were acquired in the t_1 dimension in increments of 1 μs (or 4.1 μs for the inset spectrum). To produce pure-absorption lineshapes a simple two-pulse sequence was used.[7] The ppm scale was referenced to ν_0 frequency in the ν_2 domain and to $3\nu_0$ in the ν_1 domain (reference [Al(H$_2$O)$_6$]$^{3+}$). The inset depicts the penta-coordinated Al resonance. Asterisks denote spinning sidebands along F1.

particular the latter) display strong spinning sidebands along F1.

In the recent past, the use of relatively slow ($<$ 15 kHz) MAS did not allow the detection of Al in highly distorted environments and, thus, the correct quantification of aluminium by NMR was sometimes impossible. ^{27}Al NMR resonances with quadrupole coupling constants in excess of 15 MHz can now be studied with commercially available MAS probes at sample spinning rates of *ca.* 30 kHz. In addition, combining fast MAS and very strong rf fields ($>$ 250 kHz) allows the excitation of ^{27}Al 3Q NMR coherences of highly distorted (C_Q up to *ca.* 15 MHz) Al species.

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