

Solid-state Aluminium-27 Nuclear Magnetic Resonance Chemical Shift and Quadrupole Coupling Data for Condensed AlO_4 Tetrahedra

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Aluminium-27 n.m.r. isotropic chemical shifts and quadrupole coupling data for AlO_4 tetrahedra in polycrystalline aluminates and aluminate hydrates with various degrees of anion condensation and with different cations have been studied. It is shown that the various types of condensed AlO_4 tetrahedra differ in size and symmetry of the electric field gradient tensor at the Al site, but not in the ^{27}Al chemical shift. A slight variation in the chemical shift values of entirely connected AlO_4 tetrahedra around 80 p.p.m. indicates weak cation effects and other structural influences. A markedly increased Al shielding, however, was observed for tetrahedra with lengthened Al-O distances which occur in AlO_4 tetrahedra with neighbouring AlO_6 octahedra.

Aluminium-27 n.m.r. can provide structural information about the environment of the Al nuclei in polycrystalline and amorphous samples using either quadrupole coupling data or chemical shifts. In the first case the quadrupole moment of the Al nucleus (eQ) is used as a sensitive probe for the electric field gradient (e.f.g.) at the nuclear site. In the second case the magnetic shielding of the aluminium by its electronic environment is investigated. In a recent study¹ we have shown that by employing magic-angle spinning (m.a.s.) techniques at high magnetic fields the second method proved to be a powerful tool for the determination of the co-ordination state of aluminium-oxygen polyhedra. Subsequently this new method was applied to structural studies of numerous inorganic materials including zeolites (see ref. 2 and refs. therein), cements,³ clay minerals and layer silicates,⁴⁻⁶ and glasses.⁷⁻⁹

The striking extent of the range of chemical shifts for AlO_4 tetrahedra suggests, beyond the Al co-ordination with oxygen atoms, more subtle structural influences on the Al shielding. Corresponding ^{29}Si n.m.r. investigations on silicates and aluminosilicates¹⁰⁻¹³ have shown that such possible influences are: effects of neighbouring atoms in the second co-ordination sphere, cation effects, lattice geometry as bond distances and angles, and the degree of condensation of the tetrahedron under consideration.

Some of these structural influences have already been investigated in the case of ^{27}Al chemical shifts.^{1,14-16} The ^{27}Al chemical shift of tetrahedral Al with neighbouring TO_4 tetrahedra (T = Al, Si, or P) was found to decrease markedly with increasing electronegativity of T. Chemical shift increments of more than -10 p.p.m. are observed between these structural units. For one of these groups, AlPO_4 polymorphs, likewise influences of the lattice geometry were proved in the form of an empirical correlation between ^{27}Al chemical shift and mean Al-O-P angle.¹⁵ In the case of LiAlO_2 polymorphs,¹⁶ however, structural effects were reflected only in the e.f.g. tensors and not in the magnetic shielding of Al. In contrast to the well known dependence of the ^{29}Si and ^{31}P chemical shifts on the degree of condensation of the SiO_4 and PO_4 tetrahedra in silicates¹⁰⁻¹² and phosphates,¹⁷ respectively, knowledge about the behaviour of ^{27}Al chemical shifts of corresponding condensed aluminate anions is as yet lacking. In

part this has to be attributed to the fact that, probably due to the character of the Al-O bond, only comparatively few examples of aluminates with different anion constitutions are known. In aluminosilicates the number of possible AlO_4 environments is reduced by Loewenstein's rule¹⁸ which excludes Al-O-Al bonds. Moreover, a study of such condensation effects in aluminates is more complicated since in a three-dimensional network of AlO_2^- groups, contrary to SiO_2 groups, cations are necessary for a charge balance. These cations also build up a network of polyhedra with the lattice oxygen atoms. Therefore it is sometimes difficult to distinguish between aluminates and double oxides.

In addition to these chemical problems, aluminium as a quadrupolar nucleus gives rise to experimental difficulties. In evaluating m.a.s. n.m.r. spectra of quadrupolar nuclei of non-integral spin, quadrupole-induced shift effects have to be eliminated.¹⁹ This becomes even more critical for the investigation of condensation effects, since, particularly in the interesting cases of a partial condensation of the AlO_4 tetrahedra such as double tetrahedra, chains or rings, and layers, large e.f.g.s at the Al site are expected which should lead to strong line broadenings in the n.m.r. spectra.

In the present systematic investigation at different magnetic fields (up to the highest, commercially available magnetic field strength of 11.7 T) we tried to overcome these difficulties. However, the quadrupole coupling data derived in most cases from the static spectra do provide additional structural information about the Al sites.

Our investigation of condensation effects of AlO_4 tetrahedra is based upon the measurement of a series of selected aluminates and aluminate hydrates of known crystal structure. The ^{27}Al n.m.r. results on the system $\text{CaO-Al}_2\text{O}_3$ are discussed elsewhere²⁰ in detail. A series of alkali and alkaline-earth aluminates were reinvestigated with regard to cation effects on the Al shielding.

Experimental

Aluminium-27 n.m.r. spectra were recorded at 1.4, 6.4, 8.45, and 11.7 T. The measurements were carried out on a Bruker-Physik CXP-200 spectrometer equipped with a 8.45-T magnet (^{27}Al

Table 1. Aluminium-27 chemical shift and quadrupole coupling data of condensed AlO_4 tetrahedra in aluminates

Degree of condensation	Compound	e^2qQ/h (MHz)	η	Ref.	δ^a /p.p.m.
Q^0	$[\text{Al}(\text{OH})_4]^-$ in solution				80 ± 1
	$5\text{BaO} \cdot \text{Al}_2\text{O}_3$	2.3	0.8	<i>b</i>	80 ± 1
Q^1	$\text{KAlO}_2 \cdot 1.5\text{H}_2\text{O}$	5.0	0.25	<i>c</i>	81 ± 3
Q^2	$\text{KAlO}_2 \cdot \text{H}_2\text{O}$	6.5	0.6	<i>c</i>	83 ± 3
	$\alpha\text{-BaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}^d$	3.4	0.5	<i>c</i>	81 ± 1
		5.1	0.9	<i>c</i>	80 ± 3
	$3\text{CaO} \cdot \text{Al}_2\text{O}_3$	9.7	0.3	20	85 ± 3
Q^3	$\text{KAlO}_2 \cdot 0.5\text{H}_2\text{O}$	5.6	0.0	<i>c</i>	77 ± 2
	$12\text{CaO} \cdot 7\text{Al}_2\text{O}_3^e$	11	0.2	20	85 ± 8
Q^4	$\beta\text{-LiAlO}_2$	1.8	0.55	16	82.4 ± 0.5
	$\gamma\text{-LiAlO}_2$	3.2	0.7	16	81.3 ± 0.5
	$\beta\text{-NaAlO}_2$	1.4	0.5	<i>c</i>	80.1 ± 0.5
	KAlO_2	1.1	0.7	<i>c</i>	76.0 ± 0.3
	$\text{Ca}(\text{AlO}_2)_2$	2.7	0.85	<i>b</i>	80.5 ± 0.3^d
					83.3 ± 0.5^d
	$\text{Ba}(\text{AlO}_2)_2$	2.4	0.4	<i>b</i>	78.0 ± 0.5
	TlAlO_2	<i>f</i>	<i>f</i>		69 ± 1
	$4\text{CaO} \cdot 3\text{Al}_2\text{O}_3$	2.4	0.95	20	80.3 ± 1
	$4\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}^d$	1.8	0.5		78 ± 1
		5.4	0.45	<i>c</i>	79 ± 1
	$12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$	3.7	0.9	20	79 ± 1
	$\text{CaO} \cdot 2\text{Al}_2\text{O}_3^e$	6.7	0.8	20	78 ± 1
	13	0.1		60 ± 20^e	

^a Values for the calcium aluminates are taken from ref. 20. ^b D. Müller, W. Gessner, and A-R. Grimmer, *Z. Chem.*, 1977, 17, 453. ^c This work. ^d Values obtained from the simulation of the superimposed lines of the m.a.s. n.m.r. spectrum. ^e Values estimated from the simulation of the superimposed lines of the static spectrum. ^f Not measured.

frequency 93.8 MHz) and on a Bruker-Physik AM 500 (^{27}Al frequency 130.3 MHz) high-resolution n.m.r. spectrometer (Tallinn). The measurements at 6.4 T (^{27}Al frequency 70.4 MHz) were made on a FKS 176 solid-state high-resolution n.m.r. spectrometer (Jena). All high-field ^{27}Al n.m.r. spectra were recorded both with static samples and with rapid m.a.s. techniques (spinning rates 3–5 kHz). At 11.7 T between 100 and 1 000 free induction decays (f.i.d.s) were accumulated at a repetition time of 1 s. At 6.4 T usually up to 10 000 f.i.d.s were accumulated with a repetition time of 0.1 s. In addition, in some cases, conventional low-field ^{27}Al n.m.r. measurements were carried out on a wide-line n.m.r. spectrometer at 16 MHz, recording the first derivative of the spectra.

Chemical shifts (δ /p.p.m.) measured relative to an external standard of aqueous AlCl_3 solution are denoted by positive sign for low-field shifts. Quadrupole coupling constants e^2qQ/h and asymmetry parameters η of the e.f.g. at the Al sites were determined from computer simulation of the static spectra and/or the m.a.s. n.m.r. spectra using least-squares fitting procedures.

Special care was taken with regard to the precise determination of the ^{27}Al chemical shifts. The actual chemical shift values (considering quadrupole-induced shift effects¹⁹) were obtained by different methods: (i) directly from the fitted m.a.s. spectra; (ii) from the spinning sidebands of the satellite transitions;²¹ (iii) by adding a correction term which considers quadrupole-induced shifts to the experimental, field-dependent, apparent chemical shift value of the m.a.s. spectrum;^{15,16} (iv) from the fitted static spectrum; and (v) from the extrapolation of the field-dependent apparent chemical shift.

In most cases satisfactory agreement was achieved with the different methods. It is clear that for a determination of e^2qQ/h and η static low-field spectra are preferred, whereas most

accurate chemical shifts are obtained from the m.a.s. n.m.r. spectra at highest fields. The errors of the estimated quadrupole coupling constants are less than 10%; the asymmetry parameters were derived with an accuracy of ± 0.1 . The resulting errors of the derived chemical shift values are included in Tables 1 and 2.

The samples under investigation were prepared by standard procedures and checked by X-ray powder diffraction.

Results and Discussion

The actual isotropic ^{27}Al chemical shift values (considering quadrupole-induced shift effects) and quadrupole coupling data of tetrahedral Al are presented in Table 1 for the compounds investigated. The compounds in Table 1 are arranged in order of degree of condensation of their AlO_4 tetrahedra. For brevity the symbol Q^n is used for the AlO_4 tetrahedra, where the index n denotes the number of neighbouring AlO_4 tetrahedra sharing corner(s) with the tetrahedron under consideration.

In some cases the data for different tetrahedral Al sites are listed in Table 1. In the structure of $4\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$,²² for example, there are two types of differently distorted AlO_4 tetrahedra. The two sets of e^2qQ/h , η , and δ values for this compound were obtained from the computer simulation of the superimposed lines of the m.a.s. n.m.r. spectrum at 11.7 T (see Figure 1). In the same manner two data sets are obtained for $\alpha\text{-BaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$. The results are in agreement with the structure of this compound²³ which also contains two types of differently distorted AlO_4 tetrahedra (both Q^2 groups). In other cases, e.g., for $\text{Ba}(\text{AlO}_2)_2$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ the different Al sites could not be resolved in the n.m.r. spectra. The compound $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ contains both Q^3 and Q^4 units; the signals were assigned according to their e^2qQ/h and asymmetry parameter

Table 2. Aluminium-27 chemical shifts of AlO_4 tetrahedra with neighbouring AlO_6 octahedra

Compound	Al-O ^a /Å	Ref.	δ^b /p.p.m.	Ref.
Basic aluminium sulphate, $\text{Na}[\text{AlO}_4 \cdot \text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}][\text{SO}_4]_4 \cdot 13\text{H}_2\text{O}$	1.838	32	62.8 ± 0.3	c
Basic aluminium selenate, $\text{Na}[\text{AlO}_4 \cdot \text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}][\text{SeO}_4]_4 \cdot 13\text{H}_2\text{O}$			62.9 ± 0.3	c
Basic aluminium chloride, $[\text{AlO}_4 \cdot \text{Al}_{12}(\text{OH})_{25}(\text{H}_2\text{O})_{11}]\text{Cl}_6 \cdot 11\text{H}_2\text{O}$			62 ± 1	34
Zunyite, $[\text{AlO}_4 \cdot \text{Al}_{12}(\text{OH}, \text{F})_{16} \text{F}_2]\text{Si}_5\text{O}_{20}\text{Cl}$	1.798	31	72 ± 1	c
β -alumina	1.805	30	64 ± 1	1, d
γ -alumina			66 ± 1	e
η -alumina			62 ± 2	f
χ -alumina			64 ± 2	f
Synthetic spinel sample, ^g $\text{Mg}(\text{AlO}_2)_2$			70 ± 1	e
$\text{CaO} \cdot 6\text{Al}_2\text{O}_3$	1.815	29	64 ± 1	20
$\text{BaO} \cdot 6\text{Al}_2\text{O}_3$			70 ± 1	e

^a Mean Al-O distance in the AlO_4 tetrahedron. ^b Chemical shift of tetrahedral Al. Chemical shift values of octahedral Al are not included. ^c A. C. Kunwar, A. R. Thompson, H. S. Gutowsky, and E. Oldfield, *J. Magn. Reson.*, 1984, **60**, 467. ^d W. S. De Jong, C. M. Schramm, and V. E. Parziale, *Geochim. Cosmochim. Acta*, 1983, **47**, 1223. ^e This work. ^f V. M. Mastikhin, O. P. Krivoruchko, B. P. Zolotovskii, and R. A. Buyanov, *React. Kinet. Catal. Lett.*, 1981, **18**, 117. ^g Usually the Al occurs at the octahedral sites of $\text{Mg}(\text{AlO}_2)_2$ only.

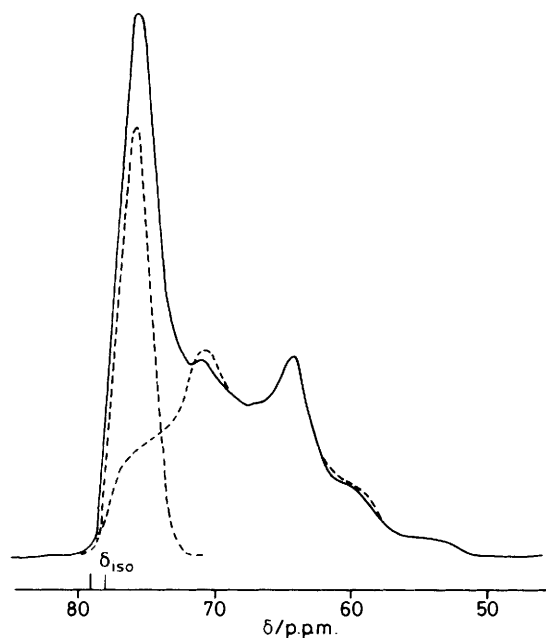


Figure 1. Aluminium-27 m.a.s. n.m.r. spectrum (—) at 11.7 T of $4\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$; (---) computed lineshape, values are given in Table 1. Resulting locations of δ_{iso} of the two superimposed signals are marked

values. A detailed structural discussion of the n.m.r. results on the aluminates in the $\text{CaO}-\text{Al}_2\text{O}_3$ system is given elsewhere.²⁰ It should only be noted here that the strikingly large values of e^2qQ/h for Q^4 units in $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ are due to the fact that the two types of AlO_4 tetrahedra in the structure share one or, respectively, two of the bridging oxygen atoms with two other tetrahedra forming so-called 'triclusters'.²⁴

In the $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ system only the crystal structure of $\text{KAlO}_2 \cdot 1.5\text{H}_2\text{O}$, consisting of pairs of Q^1 groups, is known.²⁵ From ^1H and ^{27}Al n.m.r. studies Q^2 groups for $\text{KAlO}_2 \cdot \text{H}_2\text{O}$ and Q^3 groups for $\text{KAlO}_2 \cdot 0.5\text{H}_2\text{O}$, respectively, were proposed.²⁶ In the present m.a.s. n.m.r. measurements of the potassium aluminate hydrates at 11.7 T the accuracy of the derived ^{27}Al chemical shift values could be improved considerably. Figure 2

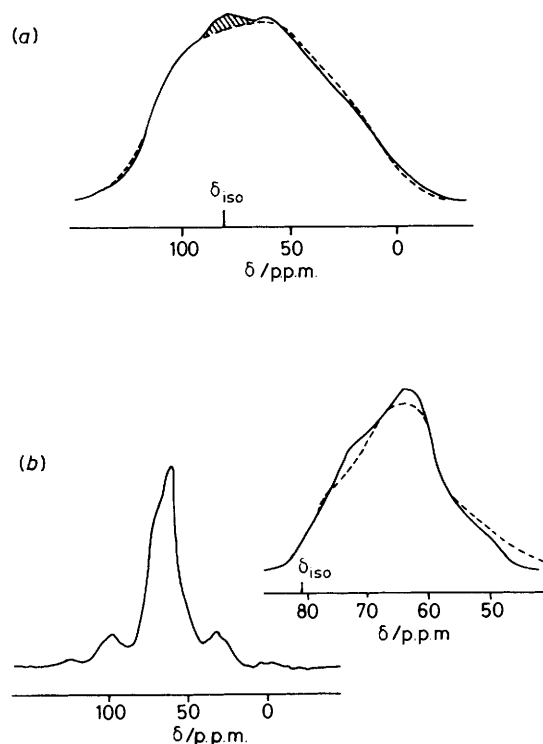


Figure 2. Aluminium-27 n.m.r. spectra at 11.7 T of $\text{KAlO}_2 \cdot \text{H}_2\text{O}$. (a) Experimental (—) and fitted (---) spectrum of the static sample. The shaded part of the signal at 80 p.p.m. indicates weak hydrolysis of the sample in air. (b) Experimental m.a.s. n.m.r. spectrum (left) and expanded spectrum (right) showing both experimental (—) and fitted (---) curves

shows, for example, the static and m.a.s. n.m.r. spectra of $\text{KAlO}_2 \cdot \text{H}_2\text{O}$ recorded at 11.7 T. Proton decoupling experiments were not performed. Therefore the static spectra of the aluminate hydrates at this high magnetic field are rather smeared by the increased contribution of the field-independent dipolar $^1\text{H}-^{27}\text{Al}$ interaction.

For all investigated compounds the static ^{27}Al n.m.r. spectra showed the theoretical behaviour for powder patterns of the

central transition in the case of second-order quadrupolar interaction as a dependence on the magnetic field strength (considering the field-independent dipolar broadening by a convolution with a Gaussian curve). This means that within the measuring accuracy, even at the highest field of 11.7 T, no effects of chemical shift anisotropy (c.s.a.) appear in the ^{27}Al n.m.r. spectra. This is, especially for the spectra of Q^1 , Q^2 , and Q^3 groups, a surprising result since such groups in corresponding silicates^{12,27} and phosphates^{17,28} give rise to considerable ^{29}Si and ^{31}P c.s.a. effects.

If there are c.s.a. effects in the case of aluminates, these effects must be small (less than 20 p.p.m.) and would be masked by huge e.f.g.s due to the anisotropic electric surroundings at the Al nucleus of such structural groups which broaden the static spectra. As yet no other evidence for ^{27}Al c.s.a. effects has been published.

As a possible reason for the small, negligible c.s.a. effects in aluminates the strong ionic character of the Al–O bond has to be considered. This is reflected in, among other things, smaller differences between the T–O_b (b = bridging) and T–O_{nb} (nb = non bridging) bond distances in aluminates compared with silicates and phosphates, and in smaller T–O_b–T angles. In the same way the more ionic Al–O bond has to be held responsible for the fact that, as can be seen from Table 1, in aluminates no distinct dependence of the isotropic ^{27}Al chemical shifts of the AlO₄ tetrahedra on the degree of condensation is observed. As seen from Table 1, the types of condensed AlO₄ tetrahedra differ in size and symmetry of the e.f.g. at the Al site but not in the isotropic ^{27}Al chemical shift. The actual chemical shift values of tetrahedral Al are close to 80 p.p.m. which is the value of isolated AlO₄ tetrahedra represented by $[\text{Al}(\text{OH})_4]^-$ anions in aqueous solutions.

As expected, for Q^1 and Q^3 structural groups asymmetry parameters near zero were found, reflecting axial symmetry of the e.f.g. Also as expected, compared to Q^0 and Q^4 units, relatively large quadrupole coupling constants are obtained for Q^1 , Q^2 , and Q^3 groups. The isotropic ^{27}Al chemical shifts of entirely connected AlO₄ tetrahedra (Q^4) show only slight variations with the type of structure and cation. Compared with previous results¹ at 6.4 T the chemical shift differences between alkali and alkaline-earth aluminates are now considerably reduced by considering the quadrupole-induced shifts. The influence of quadrupole-induced shifts is more pronounced in the alkaline-earth aluminates, which have more distorted AlO₄ tetrahedra, than in most of the alkali aluminates. The slight variation in the chemical shift values of Q^4 units in the two LiAlO₂ phases¹⁶ and within the series of calcium aluminates,²⁰ however, indicates additional structural influence.

If only alkali cations are considered, with decreasing Pauling electrostatic bond strength s ($s = z/v$, where z is the cation charge and v the co-ordination number)²⁹ and decreasing electronegativity of the cation, increased shielding of the Al nucleus is apparent from the values listed in Table 1. For example, for K^+ , with a low electronegativity and a low electrostatic cation bond strength, a ^{27}Al chemical shift value of 76 p.p.m. was found in KAlO_2 which is significantly lower than the values in the sodium and lithium aluminate phases.

In silicates the contrary and more reasonable behaviour of the ^{29}Si chemical shifts has been reported,^{11–13} which was discussed in terms of covalency of the M–O bonds. With the cations having low values of s (Li^+ , Na^+ , K^+ , Ca^{2+} , Ba^{2+}), however, in silicates also only slight variations of the ^{29}Si chemical shifts result. In addition, the cation effects are more pronounced in the less condensed SiO₄ tetrahedra (Q^0 , Q^1 , Q^2). Possibly in the series of aluminates studied here, structural effects predominate which may produce the reverse behaviour of ^{27}Al chemical shifts. Unfortunately, some of the structures are not known precisely enough for a systematic study of such effects.

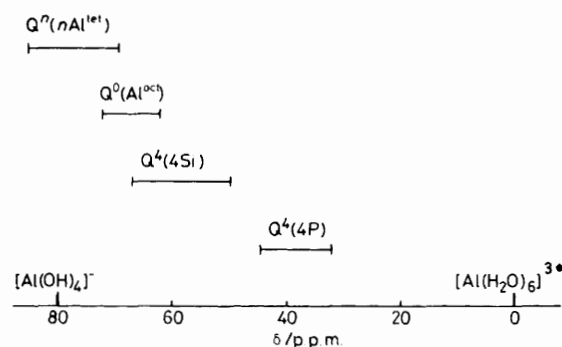


Figure 3. Schematic representation of isotropic ^{27}Al chemical shifts of AlO₄ tetrahedra. The number and the type of neighbouring TO₄ tetrahedra (T = Al, Si, or P) and AlO₆ octahedra, respectively, are denoted, in parentheses

Tetrahedral Al with neighbouring AlO₆ octahedra shows strikingly low chemical shift values (δ 62–72 p.p.m.) as presented in Table 2. According to the given definition for Q^n , such AlO₄ tetrahedra have to be denoted as Q^0 groups formally. On the other hand the oxygen atoms commonly shared by AlO₄ and AlO₆ groups can just as well be considered as bridging oxygens to some extent. This is reflected in the markedly increased Al–O distances of the AlO₄ tetrahedra which approach the values of Al–O distances in AlO₆ octahedra. For some AlO₄ tetrahedra, e.g., occurring in the spinel blocks of $\text{CaO}\cdot 6\text{Al}_2\text{O}_3$,³⁰ β -alumina,³¹ and other related compounds, or in the γ -alumina-like $\text{Al}_{13}\text{O}_{40}$ clusters of zunyite³² or the basic Al sulphate,³³ such increased Al–O distances of 1.80–1.84 Å are found (see Table 2). These values lie between those usually found in AlO₄ tetrahedra (1.76 Å) and in AlO₆ octahedra (1.85 Å). It must be noted that in all these cases the oxygen atoms at the corners of the AlO₄ tetrahedron are shared with three AlO₆ octahedra. The unusual, lengthened Al–O distances indicate a more ionic character of the Al–O bond and have already been discussed by Lampe *et al.*³⁴ as a possible reason for the increased Al shielding in zunyite and basic aluminium salts.

All the measured ^{27}Al chemical shifts of AlO₄ tetrahedra are summarized schematically in Figure 3. Distinct ranges of ^{27}Al chemical shifts are seen for AlO₄ groups dependent on the type of neighbouring TO₄ tetrahedra (T = Al, Si, or P) and AlO₆ octahedra, respectively. As shown the chemical shifts do not differ significantly for the various Q^n types of AlO₄ tetrahedra. Therefore no subdivision of the chemical shift range $Q^n(n\text{Al})$ results for different n . In aluminosilicate solutions¹⁴ and some ill-crystallized aluminosilicates,³⁵ however, individual ^{27}Al chemical shifts were found for different $Q^n(n\text{Si})$ groups in the range 64–74 p.p.m. ($n = 1, 2, \text{ or } 3$, where n also denotes the number of neighbouring SiO₄ tetrahedra).

Considering the results on aluminates, the variation of the ^{27}Al chemical shift for these groups seems mainly to be due to the varying number of neighbouring SiO₄ groups and less to the effect of condensation itself. For clarity, only the chemical shifts for $Q^4(4\text{Si})$ groups are included in Figure 3. The range of chemical shifts found for tetrahedral Al with neighbouring AlO₆ octahedra contrasts so clearly with the usual values of ca. 80 p.p.m. that it can be used in unknown structures empirically for the assignment to such structural units (provided that there are no neighbouring SiO₄ groups in the structure).

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