^{14}N Quadrupole Interactions in Nitrogen-Containing Ceramics. Effects on ^{29}Si NMR Line Shapes and Structural Implications *

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Simulations of solid-state ^{29}Si NMR spectra in nitrogen-containing silicon ceramics and glasses are described. The range of SiN_xO_{4-x} tetrahedra is covered, with emphasis on the experimental conditions needed to observe the effect of the incompletely averaged ^{29}Si, ^{14}N dipolar coupling. A simple equation is discussed concerning its use in the interpretation of these ^{29}Si spectra, including the computation of ^{14}N quadrupole coupling constants with its absolute sign.

Key words: Residual ^{29}Si, ^{14}N dipolar coupling, ^{14}N Quadrupole coupling constants, ^{29}Si Solid-state NMR simulation.

Introduction

Structural details of ceramic materials have been probed through a variety of techniques, which have involved several NMR-active nuclei [1–3]. As static positional disorder is often found in advanced materials [4], local atomic probes such as dipolar and quadrupolar nuclei are highly appreciated in these instances. Since Si has no quadrupolar isotopes, information concerning electric field gradients (EFG) in silicon ceramics is restricted to other participating nuclei. In nitrogen-containing ceramics ^{14}N is a candidate, although difficulties may arise in measuring low quadrupole coupling constants (0.5–4 MHz) in a sample containing no suitable spin-$\frac{1}{2}$ nuclei. Information on quadrupole parameters for ^{14}N can nevertheless be extracted, albeit rather indirectly, from the effect communicated by this nucleus to the NMR lines of adjacent ^{29}Si nuclei [5, 6]. In the present work, a simple approach is presented concerning the calculation of solid-state ^{29}Si NMR line shapes in solid samples where tetrahedral SiN_xO_{4-x} sites occur, such as silicon nitride [5], silicon oxynitride [7], and Sialon glasses [8, 9]. It is shown that the multiplet pattern generated by the presence of ^{29}Si, ^{14}N pairs can be used to distinguish among different silicon sites. This information can be coupled with the known ^{29}Si chemical shift dependence on the electronic properties of its ligands, so that further insight on the microstructure of glassy or amorphous phases can be gained.

Results and Discussion

Quadrupole-Perturbed Dipolar Coupling

Solid-state NMR is a well establishing spectroscopic method used to probe the structure of important solid materials, whether they are crystalline, plastic or amorphous [10]. One of the most popular techniques, high-resolution solid-state NMR, involves rapid rotation (typically 3–6 kHz) of the sample about an axis inclined 54.7° with respect to the external magnetic field [11]. This magic-angle spinning (MAS) has the effect of averaging to their isotropic values those interactions transforming as second rank tensors provided the spinning frequency is higher than the width of the interaction. In NMR of spin-$\frac{1}{2}$ nuclei, spectra are usually perturbed by chemical shift and dipole-dipole interactions. The former is generally averaged to its isotropic value by attainable sample rotation speeds. For the latter, it depends on the participarting nuclei. Dipolar coupling to nuclei having high gyromagnetic ratios, such as ^{1}H, are removed by high-power irradiation at the ^{1}H Zeeman frequency [12, 13]. Coupling to low-γ nuclei, on the other hand, may be easily averaged out by MAS. Therefore, the combination of ^{1}H decoupling (performed in such a way that cross-polarization to dilute spins occurs,

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thereby increasing the sensitivity of the NMR experiment) [14] with MAS produces spectra which will normally consist of separate, single resonances for chemically non equivalent nuclei [15]. An exception arises when the dipole-dipole coupling occurs between the (observed) spin-$\frac{1}{2}$ nucleus and a quadrupolar neighbor. In this case, a perturbation appears in the angular dependence of the dipolar interaction so that it no longer takes the familiar form $(1-3\cos^2\Theta)$, and hence MAS is unable to suppress it [16–18]. The result is observed as a non-Lorentzian broadening, asymmetrically split resonances, or severely distorted J-coupled multiplets, all of which are field-dependent phenomena [19–25]. The effect has been reported many times in ^{13}C solid-state NMR of organic molecules [19–22]. Despite the extra complication it introduces in the spectral analysis, the phenomenon has been fruitful in a number of cases: ^{13}C signal assignment [25, 26], motion of aminoacids [27] conformation of macrocycles through non-bonded C, N interactions [28], distinction of potential energy profiles in proton-exchanging molecules [29], etc. Furthermore, the study of other accessibly nuclei by solid-state NMR techniques allowed the observation of similar effects in other spin pairs: ^{31}P, ^{14}N in phosphazenes [30], ^{31}P, ^{63,65}Cu in transition metal complexes [23, 31], ^{119}Sn, ^{35,37}Cl in organostannic compounds [23, 32, 33], ^{27}Al, ^{31}P in surface-immobilized substrates [34], and the subject of the present work, ^{29}Si, ^{14}N in ceramics [5, 6]. This growth of information opens up new possibilities for further studies derived from these effects, as some of the materials involved are highly significant from technological considerations.

Detailed theoretical analyses have been published on this phenomenon [16, 17], although it has been recently reported that a simple first-order perturbative approach is able to reproduce the experimental findings with striking accuracy [18, 35]. The most general form of the first-order equation, applicable to the signal of a spin-$\frac{1}{2}$ nucleus I, both dipolar and scalar coupled to quadrupolar nucleus S is:

$$\begin{aligned}\nu_m = & -mJ + (3\chi/20Z)\,[S(2S-1)]^{-1}\,[S(S+1)-3m^2] \\ & \cdot [(-\Delta J/3)(3\cos^2\beta^J - 1 + \eta\sin^2\beta^J\cos 2\alpha^J) \\ & + D(3\cos^2\beta^D - 1 + \eta\sin^2\beta^D\cos 2\alpha^D)], \qquad (1)\end{aligned}$$

where ν_m is the shift (relative to the unperturbed isotropic I resonance frequency) produced by $|m\rangle$ eigenstates of S ($m=S,\ S-1, \ldots, -S+1$), J is the isotropic I, S scalar coupling constant, χ the quadrupole coupling constant of S, η the asymmetry parameter of the EFG tensor at S, Z the Zeeman frequency of S, ΔJ the anisotropy in the J tensor, D the dipolar I, S coupling constant, β^J and α^J define the orientation of the z axis of the J tensor in the PAS of the EFG tensor, and β^D and α^D fix the location of the internuclear vector $r_{\mathrm{I,S}}$ in this latter frame. In (1) the J tensor has been considered as axially symmetric, an assumption that seems to be valid both from theory and experiment [36, 37]. The first term $(-mJ)$ gives a multiplet structure, while the second one acts as a perturbation on the former, causing a field-dependent distortion. The second effect is most noticeable at low fields, since the distortion is inversely proportional to the external magnetic field. This emphasizes the need of reaching a balance between the known advantages of using high-field equipments and the desire of seeing the fine structure described by (1). Further comments on this point are presented below. It should be noticed that (1) offers a link between structural data, such as distances and angles, and molecular parameters ($J, \chi, \Delta J$), allowing the measurement of χ with its appropriate sign when enough information is available [6, 18, 35, 38].

^{29}*Si NMR of ceramics and glasses*

^{29}Si solid-state NMR is rapidly evolving as a useful tool in the study of important materials such as zeolites, ceramics and glasses [7, 8, 39–42]. Silicon sites are typically tetrahedrally bound to four oxygen atoms. However, the range of Si environments has been recently expanded to the whole family of $\mathrm{SiN}_x\mathrm{O}_{4-x}$ tetrahedra [7, 8, 43]. In these cases, ^{29}Si is bonded to one or more quadrupolar ^{14}N nuclei and should therefore give rise to spectra governed by (1). The first hint that this was indeed the case was obtained by Hatfield et al. who ran excellent high-resolution ^{29}Si NMR spectra of the α and β forms of silicon nitride [5]. In the low field signal of the technologically important α phase a clear field dependent partition was observed [5]. Recently, simulations based on (1) were performed in order to extract information on $J(^{29}\mathrm{Si}, ^{14}\mathrm{N})$ and the ^{14}N quadrupole coupling constant [6]. In the present work, a discussion is presented as to how (1) can be implemented to produce further simulations so as to cover the entire range $\mathrm{SiN}_x\mathrm{O}_{4-x}$. The implications of the results concerning the structure of silicon ceramics are discussed, with the possibility of extending the range of ^{14}N quadrupole cou-

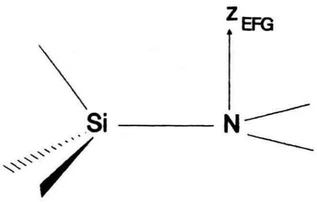

Fig. 1. Location of the z axis of the EFG tensor at the ^{14}N nucleus in silicon ceramics showing that $\beta^D = 90°$.

pling constant values to compounds containing NSi_3 units.

Equation (1) can be appreciably simplified through a series of plausible assumptions. Nitrogen environments are usually trigonal, so that an sp^2 planar configuration can be assumed, with the lone pair of electrons directed perpendicular to this plane and hence to the N–Si bond (Figure 1) [44]. This sets β^D at 90°. A further conclusion is that the EFG tensor is axially symmetric, so that $\eta = 0$ in (1). The value of D depends on the Si, N distance, which is usually found to be ca. 1.73 Å [45, 46], giving $D = 335$ Hz. The anisotropy ΔJ of the J tensor will have an appreciable effect provided its value is greater than $3D$ (ca. 1 kHz). Few reliable experimental values of ΔJ have been reported, and specifically there seem to be no experimental reports nor theoretical calculations on $\Delta J(^{29}\mathrm{Si}, ^{14}\mathrm{N})$ [47]. Both experimental data [36, 37] and calculations [48, 49] show that ΔJ is significant only when heavy nuclei are involved. Observed values of $J(^{29}\mathrm{Si}, ^{15}\mathrm{N})$ for Si, N containing compounds in solution lie in the range 5–40 Hz [50–53], and therefore one can anticipate that in the present case ΔJ effects are not likely to be higher than 1 kHz. If this were the case, (1) would give, once extended to the effect of x nitrogen atoms on the ^{29}Si line,

$$\nu = -J \sum m_i + (3D\chi/20Z) \sum (3m_i^2 - 2) \qquad (i = 1, \dots, x) \quad (2)$$

or

$$\nu = -J \sum m_i - S\left(\sum m_i^2 - 2x/3\right), \quad (i = 1, \dots, x) \quad (3)$$

where $S = -9D\chi/20Z$ is the familiar 2:1 splitting which corresponds to $x = 1$; $J = 0$. Table 1 shows the corresponding frequencies for nitrogen eigenstates, classified according to $\sum m_i$ and $\sum m_i^2$, and expressed as functions of J and S. Each line will have an intensity proportional to the number of contributing ^{14}N states (Table 1). For gaussian-convoluted spectra, individual lines are replaced by gaussian functions of area proportional to their intensities. Spectral simulations for $x = 1$, 2, 3, and 4 can be found in Fig. 2, 3, 4, and 5, respectively. In all cases the gaussian broadening is such that the width at half-maximum of individual lines equals $J/2$. An estimation of the relative values of S and J that can be expected in experimental spectra can be made as follows: for $Z = 14.4$ MHz (corresponding to a field in which ^{29}Si resonates at 40 MHz), $D = 335$ Hz, $\chi = -3$ MHz (a typical value for ^{14}N in N, Si compounds), ^{54}S is estimated as $+31$ Hz. Therefore, it is convenient to plot ^{29}Si lines for values of S ranging from 0 to $2J$, as found in Figures 2–5. Inspection of the simulations shown in these figures leads to several interesting conclusions. In the first place, the patterns arising for different values of x are seen to be uniquely determined by x. This fact could have significant implications concerning the characterization of local SiN_xO_{4-x} environments. It has been shown that a partial solution to this problem can be achieved by considering ^{29}Si chemical

Table 1. Line frequencies and intensities of ^{29}Si NMR lines affected by x ^{14}N nuclei as a function of J and $S = -9D\chi/20Z$.

	$\sum m_i$	$\sum m_i^2$	ν	I
$x = 1$	1	1	$-J-S/3$	1
	0	0	$2S/3$	1
	-1	1	$J-S/3$	1
$x = 2$	2	2	$-2J-2S/3$	1
	1	1	$-J+S/3$	2
	0	0	$4S/3$	1
	0	2	$-2S/3$	2
	-1	1	$J+S/3$	2
	-2	2	$2J-2S/3$	1
$x = 3$	3	3	$-3J-S$	1
	2	2	$-2J$	3
	1	1	$-J+S$	3
	1	3	$-J-S$	3
	0	0	$2S$	1
	0	2	0	6
	-1	1	$J+S$	3
	-1	3	$J-S$	3
	-2	2	$2J$	3
	-3	3	$3J-S$	1
$x = 4$	4	4	$-4J-4S/3$	1
	3	3	$-3J-S/3$	4
	2	2	$-2J+2S/3$	6
	2	4	$-2J-4S/3$	4
	1	1	$-J+5S/3$	4
	1	3	$-J-S/3$	12
	0	0	$8S/3$	1
	0	2	$2S/3$	12
	0	4	$-4S/3$	6
	-1	1	$J+5S/3$	4
	-1	3	$J-S/3$	12
	-2	2	$2J+2S/3$	6
	-2	4	$2J-4S/3$	4
	-3	3	$3J-S/3$	4
	-4	4	$4J-4S/3$	1

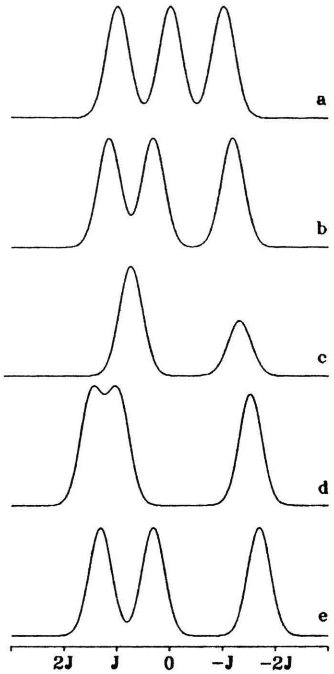

Fig. 2. Simulated spectra for ^{29}Si in a $SiNO_3$ tetrahedron arising from the combination of J and residual dipolar coupling effects, and including gaussian broadening. The following values of S/J are shown: a) 0; b) 1/2; c) 1; d) 3/2; e) 2.

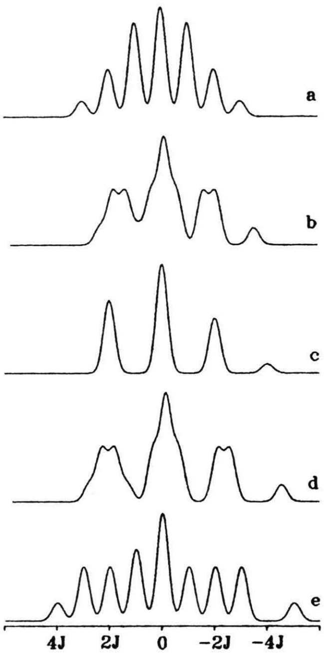

Fig. 4. Same simulated spectra as in Fig. 2, for a SiN_3O environment.

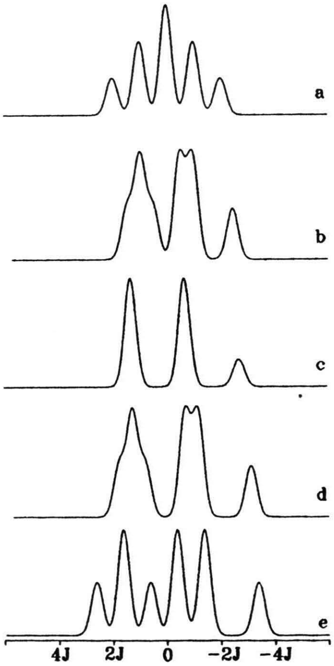

Fig. 3. Same simulated spectra as in Fig. 2, for a SiN_2O_2 environment.

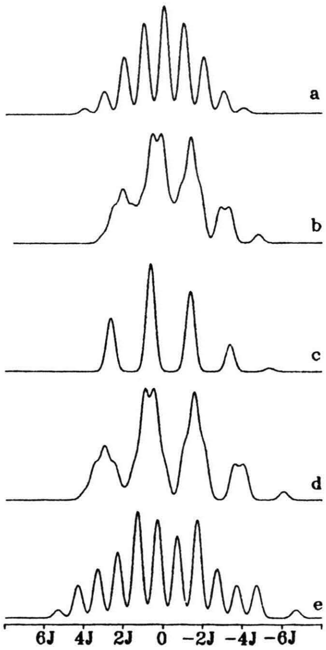

Fig. 5. Same simulated spectra as in Fig. 2, for a SiN_4 environment.

shifts which are dependent upon the electronegativity of Si ligands [8, 9]. However, spectral overlapping may preclude analyses of this type [8, 9]. If enough resolution is attained in these experiments, so that the fine structure implied in Figs. 2–5 is observed, then it would be possible to establish the value of x. This is relevant in the case of amorphous samples, where diffraction techniques do not give clear results. In the second place, once identified the correct value of x, the simulation should yield the values of J and χ, the latter with its corresponding sign. This stems from the fact that in (2) the direction (up or downfield) of the distortion of the J-coupled multiplet depends on the sign of χ. Since the magnitude of this distortion is field-dependent, it would be possible, in principle, to observe the evolution of spectral changes from *a* to *e* through the appropriate change in field strength. Furthermore, it can be seen that certain spectral patterns are repeated for different values of S/J, as occurs in Figs. 2–5 when one compares spectra *b* with *d*. These have the same appearance although on a different scale. It would not be possible to distinguish between them from a single measurement at one of these fields. Therefore, this emphasizes the need of conducting studies at varying fields, in order to characterize the proper value of S/J. An illustrative example, whose spectral data have been previously reported, and have only recently been interpreted in terms of the present analysis, is silicon nitride, where $x = 4$ [3, 4]. The downfield ^{29}Si signal of the α phase shows a pattern similar to that presented in Fig. 5c [5, 6] (see Figure 6). From variable field studies, a value of $\chi = -2.1$ MHz was obtained [6]. There are few reports on nuclear quadrupole coupling constants for ^{14}N in compounds containing N, Si bonds. When the nitrogen is bonded to one and two silicon atoms, the value of χ is consistently lowered compared to that found in NR_3 amines (R = H or alkyl group) [54]. Even more pronounced is this lowering when one takes into account the difference in hybridization that takes place on introducing silicon atoms (from sp^3 in NR_3 to sp^2 in $NSiR_2$ or NSi_2R), that is, after multiplying NR_3 values by (4/3). Specifically, experimental values are $-5.19\,x\,(4/3) = -6.92$ MHz for NMe_3; -4.86 MHz for $NSiR_2$ and -2.67 MHz for NSi_2R [54]. The value obtained for silicon nitride completes this series: NSi_3, -2.1 MHz [5, 6]. The implications are strong as regards the structure of Si, N containing compounds, since the interpretation of this lowering in χ is based on σ bond polarization due to the lower electronegativity of silicon as compared to carbon, and also to $(d-p)_\pi$ contribution to N, Si bonds, which depopulates the p_z ^{14}N lone pair.

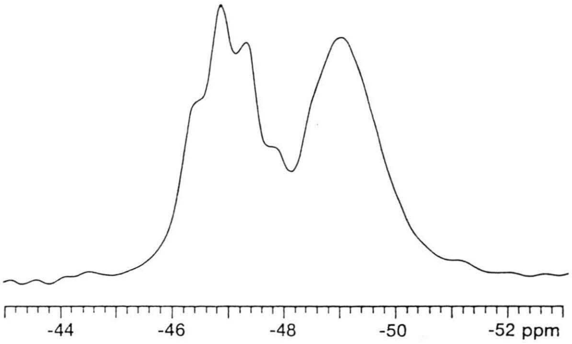

Fig. 6. High-resolution solid-state ^{29}Si NMR spectrum of α silicon nitride recorded at 60 MHz. For spectral details, see [5].

Related literature reports on ^{29}Si NMR of silicon glasses [7–9], however, do not seem to yield spectra having the expected multiplet patterns. The observed lines were broad at the external fields used (71.5 MHz for ^{29}Si) and this may indicate that further work at lower fields might be necessary.

In conclusion, this work shows how a simple, first order equation can be put in use to produce simulated spectra for ^{29}Si NMR data in solids having SiN_xO_{4-x} moieties, and what type of information may be gained from studies at variable magnetic fields.

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