The Chemical Shift of the ^{29}Si Nuclear Magnetic Resonance in a Synthetic Single Crystal of Mg_2SiO_4

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Dedicated to Professor Dr. Alarich Weiss on the occasion of his 60th birthday

The angular dependence of the chemical shift of the ^{29}Si nuclear magnetic resonance has been measured in a synthetic single crystal of Mg_2SiO_4 (space group Pbnm, $Z = 4$). The measurements were performed at room temperature at a frequency of 39.758 MHz using the FT-NMR technique. The eigenvalues of the shift tensor with respect to ^{29}Si in TMS are $\delta_x = -38.8$ ppm, $\delta_y = -55.3$ ppm and $\delta_z = -95.4$ ppm, with the eigenvector $\boldsymbol{y}$ parallel to $\boldsymbol{c}$ and the eigenvector $\boldsymbol{z}$ forming an angle of 7.5° with $\boldsymbol{a}$. The results show clearly the influence of the individual Si–O bonds on the chemical shift tensor. The chemical shift along the Si–O bond depends in good approximation exponentially on the Si–O bond distance.

Introduction

Experimental investigations of electronic and structural properties of silicate anions in minerals can, in principal, be performed by using the chemical shift effect of the ^{29}Si nuclear magnetic resonance (NMR). Lippmaa et al. [1] have shown that with magic angle sample spinning signals from various silicon environments in polycrystalline solids can be resolved. These authors measured the isotropic shifts of the ^{29}Si NMR transitions in silicates and aluminosilicates. The results are discussed with respect to the degree of condensation of the SiO_4 anion present in the particular sample. Grimmer et al. [2] measured the ^{29}Si NMR in polycrystalline silicates using the cross polarization double resonance technique. They found that the shortest Si–O bond corresponds with the largest shift of the ^{29}Si NMR transition.

Smith et al. [3] found a correlation between the isotropic chemical shift of polycrystalline silicates and the averaged Si–O bond strength. We present the first investigation of the angular dependence of the ^{29}Si NMR in a silicate single crystal.

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The measurements were undertaken to investigate the correlation between the individual Si–O bonds in the SiO_4 anion and the chemical shift along these bonds. The olivine end member, Mg_2SiO_4 (forsterite), seems to be well suited for such an investigation because its orthorhombic structure (space group Pbnm) is built by isolated SiO_4 tetrahedra [4]. Furthermore, the Si–O bonds are of the same type [5] and as may be seen from Table 2 they are sufficiently different to provide the opportunity for testing the above mentioned correlation.

Experimental Procedure and Results

In practice, the chemical shift δ of the NMR transition of a particular spin in a certain sample is expressed with respect to the shift of that spin in a reference compound. Experimentally, δ is found as the normalized difference

$$(\nu - \nu_{ref})/\nu_{ref} = \delta,$$

where ν and ν_{ref} denote the frequencies at which the NMR transition of the spin under consideration occurs in the sample and reference compounds, respectively. A negative sign of δ corresponds to a shift of the NMR transition to lower frequencies ν at constant external field.

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The experiments were performed at room temperature on a commercial Bruker pulse Fourier transform spectrometer at 39.75800 MHz. The signals of the ^{29}Si are rather weak due to the low ^{29}Si abundance of 4.7% and the low gyromagnetic ratio of 8.458 MHz/T. The difficulty of long spin lattice relaxation times was avoided by using a synthetic single crystal doped with 0.027 weight % Cr. The crystal cube has dimensions of $15 \times 15 \times 15\ mm^3$. The linewidth of the ^{29}Si NMR transitions was about 6 ppm and the chemical shift δ was measured with respect to ^{29}Si in tetramethylsilan (TMS) with an accuracy of $\pm$ 1 ppm. The measurements have been carried out with external standard and with no correction for the demagnetising field of the sample. The crystal was rotated in the external magnetic field $\boldsymbol{B}_0$ around the crystallographic axes ***a***, ***b***, and ***c*** using a one circle goniometer. The accuracy for the rotation angle α was $\pm$ 1°. For the ***a***, ***b***, and ***c*** axis rotation α was varied from 0° to 180°. The results are shown in Figs. 1 a, b, c where the points denote the experimental values and the solid curves were obtained by a least squares fit using the function

$$\delta_i(\alpha) = \delta_{0,i} + \delta_{1,i} \cos 2\alpha + \delta_{2,i} \sin 2\alpha \quad (i = a, b, c). \tag{1}$$

The extremum shift values from Fig. 1 and (1) follow as $\delta_I = -38.8$ ppm with an angle of $\pm$ 7.5° to ***b***, $\delta_{II} = -55.3$ ppm exactly along ***c***, and $\delta_{III} = -95.4$ ppm with an angle of $\pm$ 7.5 to ***a***. For the analysis of these data, it has to be considered that with the orientations $\boldsymbol{B}_0 \parallel \boldsymbol{a}$, $\boldsymbol{B}_0 \parallel \boldsymbol{b}$, $\boldsymbol{B}_0 \parallel \boldsymbol{c}$, $\boldsymbol{B}_0 \perp \boldsymbol{a}$, and $\boldsymbol{B}_0 \perp \boldsymbol{b}$ all Si atoms per unit cell are magnetically equivalent resulting in a single ^{29}Si NMR signal (Figures 1 a, b). In contrast, with the orientation $\boldsymbol{B}_0 \perp \boldsymbol{c}$ two of the four crystallographically equivalent Si positions become magnetically inequivalent. Thus, the ^{29}Si NMR signal must split into two components except when $\boldsymbol{B}_0$ is parallel to ***a*** or ***b***. This is in agreement with the experimental result (Figure 1 c). Because Si is placed on the mirror plane m which is perpendicular to ***c*** one eigenvector of the shift tensor is parallel ***c***. The other two eigenvectors lie in the (*a b*) plane and, hence, can directly be determined from the extremum shift values in this plane. Applying the definitions [6]

$$|\delta_z - \delta_{iso}| \geqq |\delta_x - \delta_{iso}| \geqq |\delta_y - \delta_{iso}|,$$

where

$$\delta_{iso} = \tfrac{1}{3}(\delta_I + \delta_{II} + \delta_{III}) = -63.2 \text{ ppm}$$

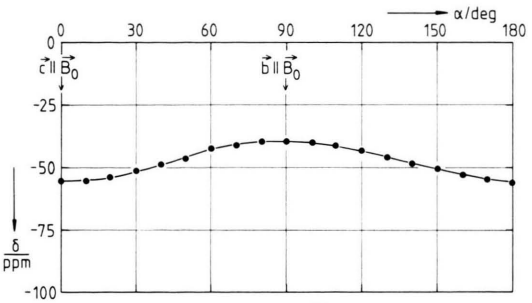


Fig. 1 a. Chemical shift δ of the ^{29}Si NMR in Mg_2SiO_4. ***B*** was rotated in the ((*b c*) plane from $\boldsymbol{c} \parallel \boldsymbol{B}$ to $-\boldsymbol{c} \parallel \boldsymbol{B}$. The points denote the experimental values to which the solid curve was fitted using (1).

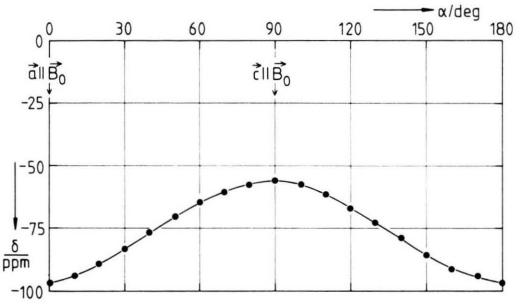


Fig. 1 b. Chemical shift δ of the ^{29}Si NMR in Mg_2SiO_4. ***B*** was rotated in the (*ac*) plane from $\boldsymbol{a} \parallel \boldsymbol{B}$ to $-\boldsymbol{a} \parallel \boldsymbol{B}$. The points denote the experimental values to which the solid curve was fitted using (1).

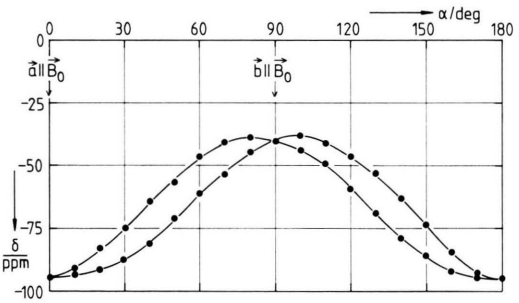


Fig. 1 c. Chemical shift δ of the ^{29}Si NMR in Mg_2SiO_4. ***B*** was rotated in the (*ab*) plane from $\boldsymbol{a} \parallel \boldsymbol{B}$ to $-\boldsymbol{a} \parallel \boldsymbol{B}$. The points denote the experimental values to which the solid curve was fitted using (1).

Table 1. Direction cosines of the eigenvectors ***x***, ***y***, ***z*** of the shift tensor 1 (upper signs) and 2 (lower signs) with respect to the crystallographic axes ***a, b, c***.

	x	*y*	*z*
a	± 0.13053	0	0.99144
b	0.99144	0	∓ 0.13053
c	0	1	0

two chemical shift tensors with the same eigenvalues

$\delta_x = -38.8$ ppm, $\delta_y = -55.3$ ppm, $\delta_z = -95.4$ ppm

but different orientations of the eigenvectors are obtained. Table 1 shows the direction cosines of the eigenvectors x, y, z of the two tensors with respect to the crystallographic axes. The upper signs belong to a tensor called tensor 1 and the lower signs belong to tensor 2. Tensor 1 is related to tensor 2 by the space group symmetry operation n.

The isotropic shift of -63.2 ppm is in good agreement with the one reported by Smith et al. [3]. However, the eigenvalues obtained by these authors are in error. This is very likely due to the indirect determination of the eigenvalues from spectra of polycrystalline samples.

Discussion

In solids several interactions may cause a shift of the NMR transition [7]. The most important interactions are the Knight shift [8], the paramagnetic shift [9, 10], and the chemical shift [7, 11, 12]. Nuclear quadrupole [13] and dipole-dipole [14] interactions may further occur yielding beside a shift a broadening and/or a splitting of the NMR lines. In the case of ^{29}Si with nuclear spin $I = 1/2$ there are no quadrupole interactions. Magnetic (Knight and paramagnetic) shift effects do not arise since Mg_2SiO_4 is an insolator and the concentration of the paramagnetic Cr centers is too small. Dipole-dipole interactions are also negligible because the natural abundance of ^{25}Mg, ^{29}Si, and ^{17}O is only 10%, 4,7% and 0.04%, respectively. Thus, the observed shift of the ^{29}Si NMR transition results mainly from the Si–O bonds in the SiO_4 anion.

In the discussion of the angular dependence the problem arises to assign tensor 1 and 2 to the two magnetically inequivalent SiO_4 tetrahedra. This can be solved by taking into account the bond overlap population n(Si–O) which was calculated by Louisnathan and Gibbs [15] for the olivine silicate anion and the experimental electron density distribution in Mg_2SiO_4 which was determined at room temperature e.g. by Fujino et al. [16] using the x-ray technique. All authors found that the electron density between Si and O increases with decreasing Si–O bond length. A larger electron density between Si and O, however, should produce a larger magnetic screening of the Si nuclei by interaction with the external magnetic field, and, hence, shift the ^{29}Si NMR transitions to lower frequencies resulting in a larger δ value.

Therefore, the tensors 1 and 2 are assigned to the two magnetically inequivalent SiO_4 anions in that way that the angle between the Si–O1 bond which is the shortest in the olivine anion SiO_4 and the corresponding eigenvector of δ_z is smallest (Figure 2). On the basis of this assignment the chemical shift along the individual Si–O bonds can be calculated and the results are listed in Table 2. Additionally, so called individual δ values for the SiO_4 units in $Ca_6(Si_2O_7/(OH)_6)$ and $((CH_3)_4N)_8Si_8O_{20} \cdot 69H_2O$ [2] are given which can be calculated for axial symmetric shift tensors assuming the largest shift to be parallel to the shortest Si–O bond.

Yosida and Moriya [17] have shown, that the degree of covalence λ of an A–B bonding may be estimated from chemical shift data of either the A or the B ions. They deduced a relation $\lambda \sim \delta$. Since λ is proportional to the square of the overlap integral, it is approximately proportional to the repulsive potential between Si and O. This potential can be expressed in the form $\exp(-r/\varrho)$ according to Born and Mayers well known theory [18], r being the

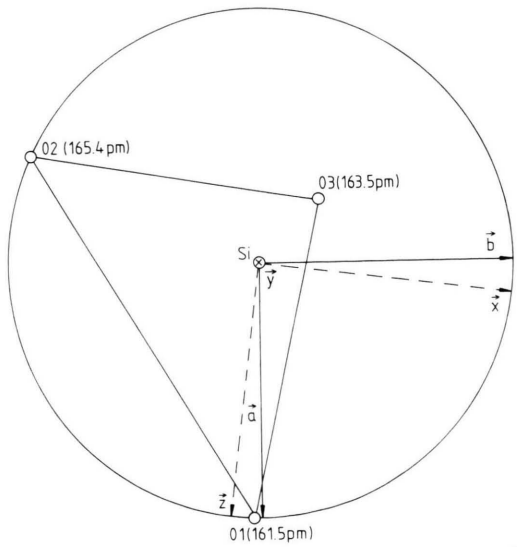
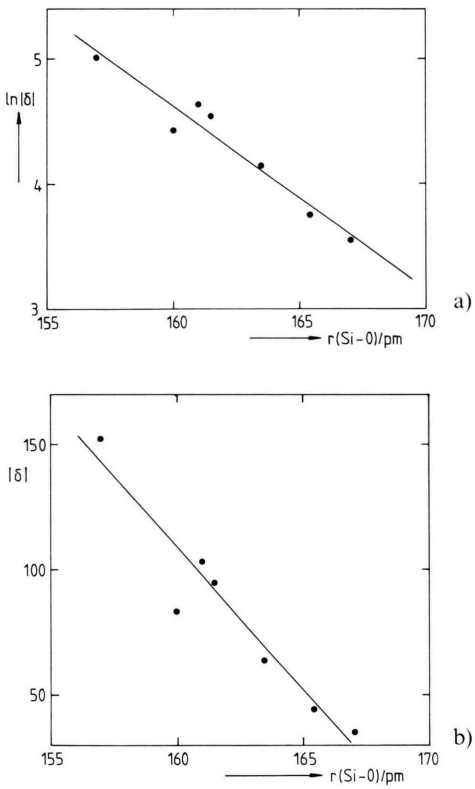


Fig. 2. Stereographic projection of one of the magnetically inequivalent SiO_4 anions and of the corresponding tensor eigenvectors on the mirror plane m. The Si–O distances are given in brackets.

Table 2. Chemical shift data of the ^{29}Si NMR and bond strength values for several Si–O bond distances. The type of the silicon oxygen tetrahedron according to Lippmaa's notation is given too.

r(Si–O) / pm	$\delta(^{29}Si)$ / ppm	ln $\lvert\delta\rvert$	s/valence units: $s_0 = 1$, $r_0 = 160.5$ pm, $N = 4$	s/valence units: $s_0 = 1$, $r_0 = 162.5$ pm, $N = 4.5$	Type of silicon oxygen tetrahedron [1]	References
167.0	− 35.0	3.56	0.8532	0.8843	Q^1	[2]
165.4	− 43.7	3.78	0.8867	0.9235	Q^0	this work
163.5	− 63.6	4.15	0.9286	0.9728	Q^0	this work
161.5	− 94.5	4.55	0.9755	1.0282	Q^0	this work
161.0	− 104.7	4.65	0.9876	1.0426	Q^1	[2]
160.0	− 83.1	4.42	1.0126	1.0723	Q^3	[2]
157.0	− 152.0	5.02	1.0922	1.1676	Q^3	[2]



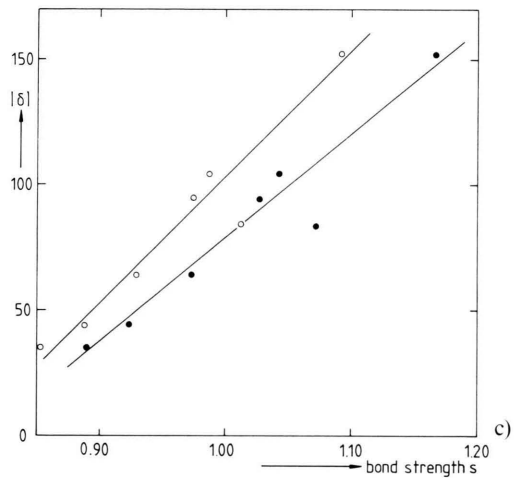


Fig. 3. Plot of a) ln $\lvert\delta\rvert$ versus r(Si–O), b) $\lvert\delta\rvert$ versus r(Si–O), and c) $\lvert\delta\rvert$ versus bond strength s (○: $s_0 = 1$, $r_0 = 160.5$ pm, $N = 4$; ●: $s_0 = 1$, $r_0 = 162.5$ pm, $N = 4.5$).

interionic distance and ϱ a constant parameter for the Si–O bonds. With $\lambda \sim \delta$ in a first approximation $\delta \sim \exp(-r/\varrho)$ follows.

There are other concepts to correlate δ with structure data as mentioned earlier. Using the "individual" data of Table 2 which enlarge the chemical shift range by a factor of 2 and the distance range considerably these concepts can be checked over a wide range. We, therefore, plotted the chemical shift data i) semilogarithmically against the bond length r (Fig. 3a), ii) against r following the proposal of Higgins and Woessner [19] (Figure 3b), and iii) against the bond strength s as proposed by Smith et al. [3] (Figure 3c). $s = s_0(r/r_0)^{-N}$ is defined according to Paulings concept of the bond strength where s_0 is the ideal strength of the bond length r_0 and N is a constant which is different for each cation/anion pair. s was calculated using two differ-

ent sets of s_0, r_0, and N (see Tables 1 and 3 in the paper of Brown and Shannon [20]).

The Figs. 3a, 3b, and 3c show that the simple plots $|\delta|$ versus r and, especially, $\ln|\delta|$ versus r fit the data at least as well as the plot of $|\delta|$ versus the bond strength s. The correlation of isotropic chemical shift values with mean values for the bond strength of the four Si−O bonds in the SiO_4 anion has been found to be better than the correlation with mean values for the bond distances by Smith et al. [3]. It may be that the bond strength concept partly compensates effects due to the use of mean values and isotropic chemical shift data. This is not necessary by regarding the Si−O bonds within the SiO_4 tetrahedron separately. Of couse, more single crystal ^{29}Si NMR data have to be collected to prove this in greater detail. Finally it should be noted that the concept of Lippmaa [1] does not hold for individual chemical shift values along the Si−O bonds (see Table 2).

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