INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **15** (2003) S2387–S2395 PII: S0953-8984(03)62668-8

Dependence of bridging oxygen ^{17}O quadrupolar coupling parameters on Si–O distance and Si–O–Si angle

Ted M Clark and Philip J Grandinetti

Department of Chemistry, The Ohio State University, 120 W 18th Avenue, Columbus, OH 43210-1173, USA

E-mail: grandinetti.1@osu.edu

Received 25 April 2003
Published 23 July 2003
Online at stacks.iop.org/JPhysCM/15/S2387

Abstract

Ab initio quantum chemistry calculations and comparisons with experimental ^{17}O solid-state nuclear magnetic resonance (NMR) investigations were used to determine the dependence of the ^{17}O quadrupolar coupling constant and asymmetry parameter on the first-coordination-sphere structure around bridging oxygen. The quadrupolar asymmetry parameter was found to be dependent on the Si–O–Si angle, in agreement with previous studies, and independent of the Si–O distance. In contrast, the quadrupolar coupling constant was found to have a strong dependence on Si–O distance as well as Si–O–Si angle. Analytical expressions describing these dependences were proposed and used to develop an approach for relating measured ^{17}O quadrupolar coupling constant and asymmetry parameter values for bridging oxygen to their Si–O–Si angle and average Si–O distance. Examples of this approach were given using ^{17}O NMR results from the crystalline silica polymorphs, coesite, α-quartz, cristobalite, and ferrierite.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

As a probe of local structure in network-forming oxide glasses, ^{17}O nuclear magnetic resonance (NMR) spectroscopy has been an invaluable tool [1–10]. For bridging oxygen there are a number of structural features that play a role in determining the ^{17}O quadrupolar coupling parameters, with the most significant features occurring in the first coordination sphere of the bridging oxygen. In the mid-1980s Oldfield and co-workers [11–13] clearly established on the basis of their ^{17}O magic-angle spinning (MAS) NMR measurements that the electronegativity of the cations coordinated to a bridging oxygen atom is a primary factor influencing the magnitude of the C_q-parameter for the bridging oxygen. In a series of *ab initio* calculations

on model clusters focusing on the silicate bridging oxygen linkage Tossell and co-workers [14–16] predicted simple trends for the ^{17}O quadrupolar coupling parameters with Si–O–Si angle. These trends were later experimentally confirmed by Grandinetti *et al* [17] in ^{17}O dynamic-angle spinning (DAS) measurements on coesite.

In a more recent paper Clark and Grandinetti [18] used *ab initio* methods to study a number of clusters with the coordinating cations varied from group III to group VI and from periods 2 to 4 while simultaneously varying the network-forming cation–oxygen distance. A general trend was observed that the magnitude of C_q increases linearly with increasing network-forming cation–oxygen bond distance and cation group number, suggesting that group number and cation–bridging oxygen distance can serve as a better predictor of the bridging oxygen quadrupole coupling constant than electronegativity differences [12, 13].

Vermillion *et al* [19] further refined this understanding by examining the effect of additional coordination of the bridging oxygen by network-modifier alkali cations. They found that the previously established trend in ^{17}O C_q with Si–O–Si angle is systematically shifted to lower magnitudes with increasing number and field strength of coordinating alkali cations, and is relatively insensitive to variations in the alkali cation–bridging oxygen internuclear vector orientation. They also found that the previously established trend [14–16, 20] in ^{17}O quadrupolar coupling asymmetry parameter, η_q, with Si–O–Si angle is systematically shifted to higher values by the presence of one coordinating alkali cation, and only slightly shifted to higher values by the presence of two coordinating alkali cations. As with the quadrupolar coupling constant, the magnitude of the shift in asymmetry parameter increases with increasing field strength of the coordinating alkali cation(s).

Thus, the first-coordination-sphere structural features that appear to be most important in determining the ^{17}O quadrupolar coupling parameters of the bridging oxygen are the nature of the two coordinating network-forming cations, the T–O–T′ linkage angle, the T–O bond distances, and the nature and number of coordinating network-modifier cations. Contributions from beyond the first coordination sphere of the bridging oxygen appear to be secondary in importance. For example, Xue and Kanzaki [21] performed *ab initio* calculations employing clusters expanded out to four coordination spheres to model each of the silicate bridging oxygen linkages in coesite and obtained a slightly improved agreement with the experimental trends, with corrections of the order of a few per cent in the ^{17}O C_q- and η_q-values.

In a recent article by Bull *et al* [22] a series of multi-field double-rotation (DOR) NMR and multiple-quantum magic-angle spinning (MQ-MAS) ^{17}O NMR experiments were presented for a high-silica ferrierite sample and the isotropic chemical shift and the second-order isotropic quadrupolar shift for each of the ten crystallographically distinct bridging oxygen sites in ferrierite were extracted. To assist in the spectrum assignment a series of *ab initio* calculations of the ^{17}O chemical shift and quadrupolar coupling parameters using clusters modelling each of the ten bridging oxygen environments out to four coordination spheres were made. Unfortunately, the sensitivity of the experimental ^{17}O NMR data was insufficient for an unambiguous determination of the C_q- and η_q-values of the bridging oxygen sites in ferrierite and on the basis of chemical shift only a partial assignment of the resonances was possible. Nonetheless, on the basis of their *ab initio* calculations Bull *et al* [22] concluded that 'no simple correlation appears to exist between the zeolite structure, such as the Si–O–Si bond angles or lengths, and the ^{17}O NMR parameters'. On closer examination of their *ab initio* data, however, we find this is not quite the case. As can be seen in figure 1(A), there is a strong dependence on the calculated C_q-values in ferrierite on the Si–O–Si angle, although it is somewhat weaker than the dependence of the C_q-values in coesite on Si–O–Si angle. By fitting, separately, the experimental ^{17}O C_q-data from coesite and the *ab initio* calculated ^{17}O C_q from ferrierite to

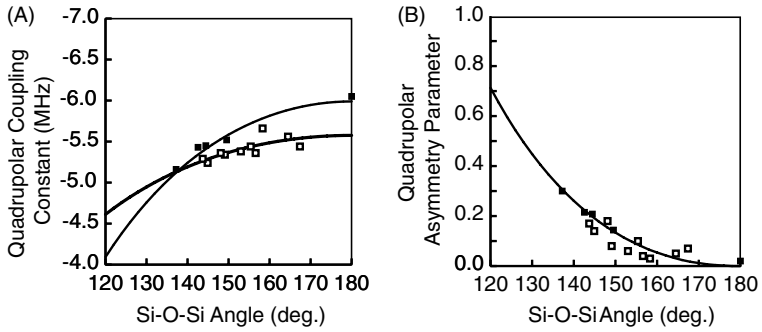

Figure 1. Plots of (A) ^{17}O quadrupolar coupling constants C_q versus Si–O–Si angle, and (B) ^{17}O quadrupolar coupling asymmetry parameters η_q versus Si–O–Si angle that were experimentally measured [17] for the oxygen sites in coesite (filled squares) and calculated with *ab initio* methods [22] for the ten oxygen sites in ferrierite (open squares).

the modified semiempirical correlations [17, 19] given below,

$$C_q(\Omega) = a\left(\frac{1}{2} + \frac{\cos\Omega}{\cos\Omega - 1}\right)^{\alpha}, \tag{1}$$

$$\eta_q(\Omega) = b\left(\frac{1}{2} - \frac{\cos\Omega}{\cos\Omega - 1}\right)^{\beta}, \tag{2}$$

we obtain the correlations shown as the solid curves in figure 1. In figure 1(B) is the plot of calculated η_q-values of Bull *et al* [22] in ferrierite as a function of Si–O–Si angle. In contrast to the case for C_q, there is good agreement for both the experimental η_q-values for coesite and *ab initio* predicted η_q-values for ferrierite with equation (2).

The obvious question here is why the ^{17}O quadrupolar coupling constant of the bridging oxygen in two pure silica compounds exhibit different trends as a function of ∠Si–O–Si. We show below that these differences arise from the strong dependence of the bridging oxygen C_q on the Si–O distance. As we have demonstrated elsewhere [18] the quadrupolar coupling constant has a strong linear dependence on the Si–O distance, of the order of 13 MHz Å^{-1}. This dependence is not explicitly indicated in equations (1) and (2), but rather is included implicitly by assuming that the Si–O distance is energetically constrained by the Si–O–Si angle. This did not seem to be an unreasonable assumption, as correlations between Si–O distance and ∠Si–O–Si were well established [23, 24] in the literature. In this paper, we present the results of a series of *ab initio* quantum chemistry calculations of ^{17}O quadrupolar coupling parameters for the Si–O–Si linkage where we eliminate this assumption and demonstrate how simultaneous measurements of the ^{17}O quadrupolar coupling constant and asymmetry parameter of a bridging oxygen can be used to determine both the Si–O–Si angle and average Si–O distance.

2. Methods

Ab initio calculations were performed using Gaussian 94 [25] at a restricted Hartree–Fock level with a 6−31+G(d) basis set used for all atoms. Gaussian 94 calculates the traceless electric field gradient (efg) tensor and outputs its Cartesian tensor elements. These calculated efg tensor elements are related to the quadrupolar coupling constant, C_q, and quadrupolar coupling asymmetry parameter, η_q, according to

$$C_q = e^2 Q\langle q_{zz}\rangle/h, \qquad \text{and} \qquad \eta_q = \frac{\langle q_{xx}\rangle - \langle q_{yy}\rangle}{\langle q_{zz}\rangle} \tag{3}$$

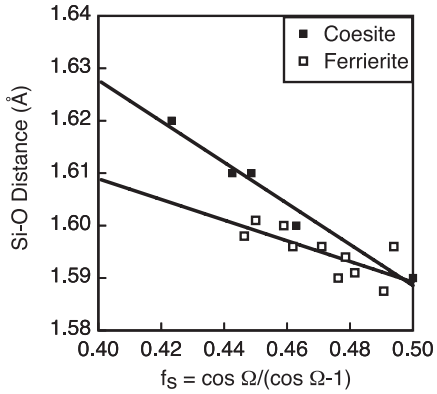

Figure 2. A plot of the average Si–O bond length for each bridging oxygen as a function of the fractional s character of the bridging oxygen, f_s. $d^{\text{coes}}_{\text{Si–O}} = -0.391\,4388\,f_s + 1.784\,295$ and $d^{\text{ferr}}_{\text{Si–O}} = -0.197\,0883\,f_s + 1.687\,759$.

where $e\langle q_{xx}\rangle$, $e\langle q_{yy}\rangle$, and $e\langle q_{zz}\rangle$ are the principal components of the efg tensor defined such that $|\langle q_{zz}\rangle| > |\langle q_{yy}\rangle| > |\langle q_{xx}\rangle|$, and Q is the nuclear electric quadrupole moment. For ^{17}O a value of $e^2Q/h = -6.11$ MHz au^3 was used to convert the q_{zz}-output from a Gaussian to the ^{17}O quadrupolar coupling constant. An additional scaling of 0.92 was employed to bring the coupling constant into agreement with experimental measurements [26].

3. Results and discussion

In a series of quantum chemistry calculations on the clusters modelling the bridging oxygen linkage Gibbs and co-workers [27, 28] showed that a two-dimensional energy surface as a function of Si–O distance and ∠Si–O–Si has minima that lead to a strong distance–angle correlation. They further showed that the silicon bridging oxygen distance in silicates follows a linear dependence on the s character of the bridging oxygen bonding orbital, f_s, which in turn varies as a function of the Si–O–Si angle according to

$$f_s(\Omega) = \frac{\cos\Omega}{\cos\Omega - 1}. \tag{4}$$

In figure 2 is a plot of the average Si–O bond length for each bridging oxygen as a function of the fractional s character of the bridging oxygen for each of the bridging oxygen sites in coesite and ferrierite. It is this difference in the distance–angle correlation of coesite and ferrierite coupled with the strong dependence of C_q on Si–O distance that is responsible for their different C_q-correlations shown in figure 1(A).

Generally, there are a number of factors to which the Si–O distances can be correlated [23, 24]. In the case of clathrasils, which form in the presence of inorganic and organic molecules directing the network towards less dense framework structures, one also needs to be aware of a strong correlation with static and/or dynamic disorder. Liebau [23, 24] found that the apparent Si–O bond lengths are significantly shorter (1.56 Å) and the Si–O–Si angles are significantly wider (175°), on average, in clathrasils than those observed (1.608 Å, 144°) for the silica polymorphs.

To investigate this matter, the Si–O distance dependence implicit in equation (2) has been removed by performing *ab initio* calculations for $[(OH)_3O–Si–O–(OH)_3]$ clusters with the Si–O distance held constant in a manner consistent with previous calculations [26]. In figure 3(A)

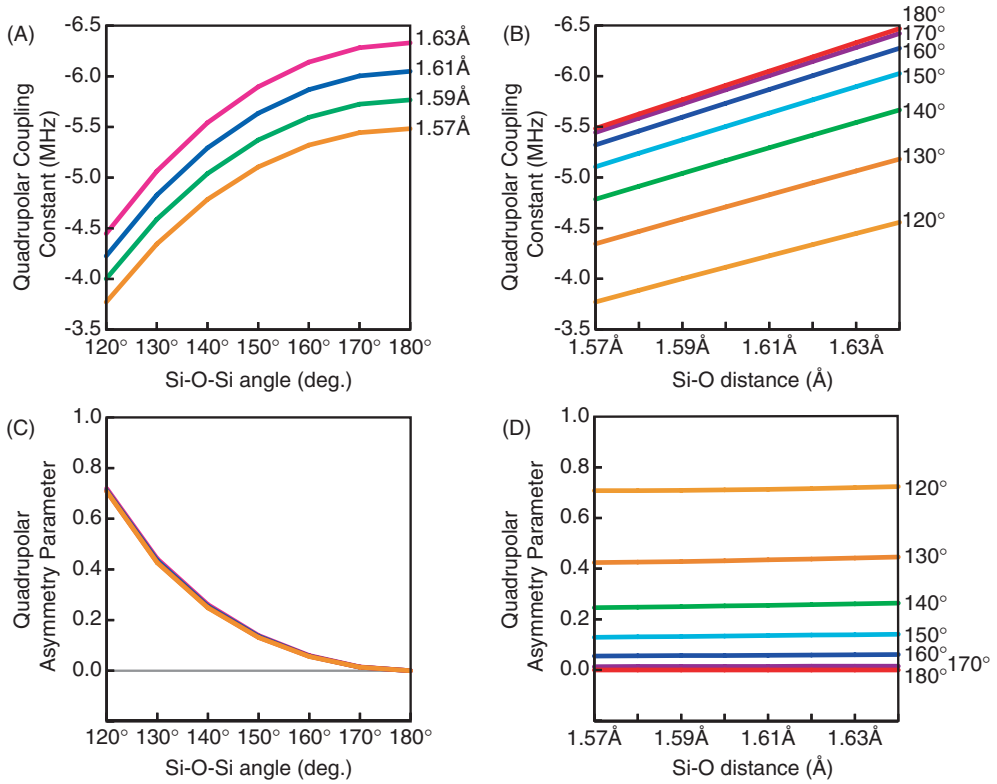

Figure 3. *Ab initio* predicted trends in (A) C_q as a function of Si–O–Si angle with Si–O distance held constant, (B) C_q as a function of Si–O distance with Si–O–Si angle held constant, (C) η_q as a function of Si–O–Si angle with Si–O distance held constant, (D) C_q as a function of Si–O distance with Si–O–Si angle held constant.

are the predicted trends in C_q as a function of Si–O–Si angle with the Si–O distance held constant at different values. The general trend as a function of Si–O–Si angle remains mostly unchanged other than an increase in the magnitude of C_q with increasing Si–O distance. The same C_q-data are presented in figure 3(B) as a function of Si–O distance with Si–O–Si angle held constant. Over the relevant range of Si–O distances the C_q-value follows a simple linear relationship [18]. The dependence of the quadrupolar asymmetry parameter on Si–O–Si angle and Si–O distance is shown in figures 3(C) and (D). Most importantly, the asymmetry parameter is independent of Si–O distance, and its behaviour is dominated by its dependence on Si–O–Si angle. This is also consistent with the findings of recent theoretical ^{17}O NMR calculations in silicates [29]. Thus, for the asymmetry parameter, η_q, the correlation of equation (2) can still be generally applied. Therefore, given the dependence of C_q on average Si–O distance, we propose the following relation between C_q and Si–O–Si angle and Si–O distance:

$$C_q(d_{TO}, \Omega) = a'\left(\frac{1}{2} + \frac{\cos\Omega}{\cos\Omega - 1}\right)^{\alpha'} + m_d(d_{TO} - d^{\circ}_{TO}), \tag{5}$$

where d_{TO} is the average silicon–oxygen bond distance. A least-squares fit of equations (2) and (5) to the experimental values for coesite [17], cristobalite [30], and α-quartz [31] as well as the *ab initio* predicted values for ferrierite [22] yields the parameter values $a' = -6.53$ MHz, $\alpha' = 1.80$, $m_d = -12.86$ MHz Å^{-1}, $d^{\circ}_{TO} = 1.654$ Å, $b = 4.73$, and $\beta = 1.12$.

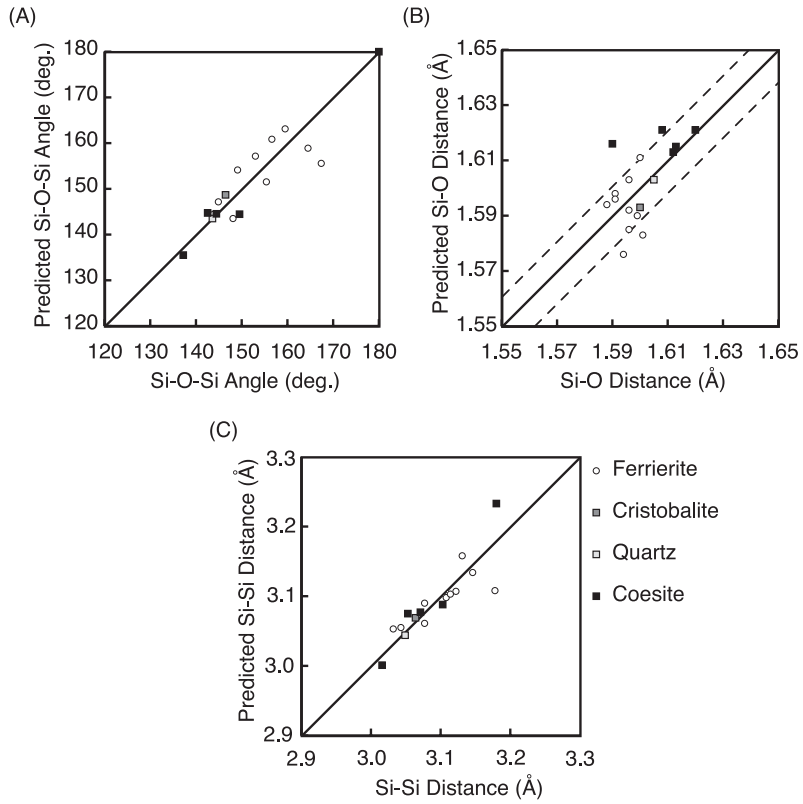

Figure 4. Comparison between the ^{17}O quadrupolar coupling predicted (A) Si–O–Si angle, (B) Si–O distance, and (C) Si–Si distance with corresponding quantities reported from x-ray crystallography [32–34]. Solid diagonal lines represent perfect agreement. The best-fit parameters for equations (2) and (5) are $a' = -6.53$ MHz, $\alpha' = 1.80$, $m_d = -12.86$ MHz Å^{-1}, $d^{\circ}_{TO} = 1.654$ Å, $b = 4.73$, $\beta = 1.12$.

A comparison of the Si–O–Si angles and Si–O distances predicted by these expressions with actual values is shown in figure 4. It is significant that these results demonstrate close agreement between predicted and reported values, even though only two structural variables are considered, i.e., average bond distance and bond angle. The Si–O–Si angles in figure 4(A) are predicted from η_q alone. The uncertainty in measuring the Si–O–Si angle from the quadrupolar asymmetry parameter will increase as η_q tends to zero, since the derivative of ∠Si–O–Si with respect to η_q diverges at 180° (see figure 3(C)). Over the range of values considered, however, η_q, appears to be an excellent probe of Si–O–Si angle, as expected. With the Si–O–Si angle determined by η_q, equation (5) is used to predict the Si–O distance from C_q, as shown in figure 4(B). The predicted Si–O distances are in good agreement with the actual distances, with the majority being within 0.01 Å of the predicted value. Having determined the Si–O distance for a given angle, it is also possible to determine the Si–Si distance. These values are shown in figure 4(C), and are in excellent agreement with reported Si–Si distances. Finally, we note that not only can the coupling constant and asymmetry parameter be used to measure the Si–O–Si angle and Si–O distance, but, as shown in figure 5, the simultaneous measurement of C_q and η_q for each bridging oxygen site can be used to obtain the correlation between Si–O–Si angle and Si–O distance. We note that the adoption of this approach for measuring Si–O–Si angle and Si–O distance requires a good measurement of the quadrupolar asymmetry

Note: This figure had an error in the original journal reprint. This figure has been corrected in this pdf file.

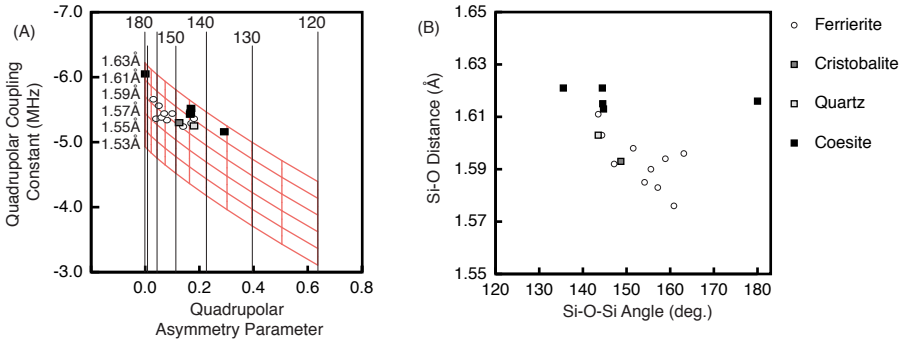

Figure 5. Simultaneous measurement of the ^{17}O quadrupolar coupling constant and asymmetry parameters can be used to measure the correlation between Si-O-Si angle and Si-O distance.

parameter, which has historically been more difficult to measure than the quadrupolar coupling constant. This situation has been improved, however, with the development of techniques such as rotor-assisted population transfer-enhanced [35-38] MAS-DAS [17, 39, 40] which allows overlapping anisotropic ^{17}O central transition lineshapes to be separated and measured with high sensitivity and minimal lineshape distortions.

4. Conclusions

Difficulties [22] in interpreting ^{17}O quadrupolar coupling constants for bridging oxygen in different crystalline silica polymorphs, such as coesite, α-quartz, cristobalite, and ferrierite, have been found to arise from (1) differences in structural correlations between Si-O-Si angle and Si-O distance, and (2) a strong linear dependence of the quadrupolar coupling constant on Si-O distance. Using *ab initio* quantum chemistry calculations the quadrupolar asymmetry parameter was found to be determined almost entirely by the Si-O-Si angle, while the quadrupolar coupling constant is nearly equally affected by Si-O-Si angle and Si-O distance. Since the bridging oxygen bond lengths in ferrierite do not increase as dramatically as a function of bridging oxygen angle as in coesite, the quadrupolar coupling constants in ferrierite exhibit a weaker dependence on Si-O-Si angle.

On the basis of these results, we have proposed analytical expressions for describing these dependences. Overall, we have found that ^{17}O is a richer probe of structure around the first coordinate sphere of bridging oxygen, and that the relationships described here can be generally used for relating measured ^{17}O quadrupolar coupling constant and asymmetry parameter values for bridging oxygen to their Si-O-Si angle and average Si-O distance. This approach could also be extended to other bridging oxygen environments, such as the Ge-O-Ge linkage [41]. Such an approach will be valuable for obtaining structural details in materials not easily treated with scattering methods of measurement, such as microcrystalline and amorphous network-forming oxides.

Acknowledgments

We thank Subramanian Prasad for helpful discussions. This material is based upon work supported by the National Science Foundation under Grant No CHE 0111109. Any opinions,

findings and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation (NSF).

References

[1] Jellison G E, Panek L W, Bray P J and Rouse G B 1977 Determinations of structure and bonding in vitreous B_2O_3 by means of ^{10}B, ^{11}B, and ^{17}O, NMR *J. Chem. Phys.* **66** 802

[2] Geissberger A E and Bray P J 1983 Determinations of structure and bonding in amorphous SiO_2 using ^{17}O NMR *J. Non-Cryst. Solids* **54** 121

[3] Youngman R E, Haubrich S T, Zwanziger J W, Janicke M T and Chmelka B 1995 Short- and intermediate-range structural ordering in glassy boron oxide *Science* **269** 1416

[4] Farnan I, Grandinetti P J, Baltisberger J H, Stebbins J F, Werner U, Eastman M A and Pines A 1992 Quantification of the disorder in network-modified silicate glasses *Nature* **358** 31

[5] Wang S and Stebbins J F 1998 On the structure of borosilicate glasses: a triple-quantum magic-angle spinning ^{17}O nuclear magnetic resonance study *J. Non-Cryst. Solids* **231** 286

[6] Zhao P, Kroeker S and Stebbins J F 2000 Non-bridging oxygen sites in barium borosilicate glasses: results from ^{11}B and ^{17}O NMR *J. Non-Cryst. Solids* **276** 122

[7] Florian P, Vermillion K E, Grandinetti P J, Farnan I and Stebbins J F 1996 Cation distribution in mixed alkali disilicate glasses *J. Am. Chem. Soc.* **118** 3493

[8] Stebbins J F, Oglesby J V and Xu Z 1997 Disorder among network-modifier cations in silicate glasses: new constraints from triple-quantum ^{17}O NMR *Am. Mineral.* **82** 1116

[9] Stebbins J F, Lee S K and Oglesby J V 1999 Al–O–Al oxygen sites in crystalline aluminates and aluminosilicate glasses: high-resolution oxygen-17 NMR results *Am. Mineral.* **84** 983

[10] Lee S K, Musgrave C B, Zhao P and Stebbins J F 2001 Topological disorder and reactivity of borosilicate glasses: quantum chemical calculations and ^{17}O and ^{11}B NMR study *J. Phys. Chem.* B **105** 12583

[11] Schramm S and Oldfield E 1984 High-resolution oxygen-17 NMR of solids *J. Am. Chem. Soc.* **106** 2502

[12] Timken H K C, Janes N, Turner G L, Lambert S L, Welsh L B and Oldfield E 1986 Solid-state oxygen-17 nuclear magnetic resonance spectroscopic studies of zeolites and related systems *J. Am. Chem. Soc.* **108** 7236

[13] Timken H K C, Schramm S E, Kirkpatrick R J and Oldfield E 1987 Solid-state oxygen-17 nuclear magnetic resonance spectroscopic studies of alkaline earth metasilicates *J. Phys. Chem.* **91** 1054

[14] Tossell J A and Lazzeretti P 1987 *Ab initio* calculations of oxygen nuclear quadrupolar coupling constants and oxygen and silicon NMR shielding constants in molecules containing Si–O bonds *Chem. Phys. Lett.* **112** 205

[15] Tossell J A and Lazzeretti P 1988 Calculation of NMR parameters for bridging oxygens in $H_3T–O–T'H_3$ linkages (T, T′ = Al, Si, P), for oxygen in SiH_3O^-, SiH_3OH and SiH_3OMg^+ and for bridging fluorine in $H_3SiFSiH_3^+$ *Phys. Chem. Minerals* **15** 564

[16] Lindsay C G and Tossell J A 1991 *Ab initio* calculations of ^{17}O and ^{n}T NMR parameters ($^{n}T = {}^{31}P$, ^{29}Si) in H_3TOTH_3 dimers and T_3O_9 trimeric rings *Phys. Chem. Minerals* **18** 191

[17] Grandinetti P J, Baltisberger J H, Werner U, Pines A, Farnan I and Stebbins J F 1995 Solid-state ^{17}O magic-angle and dynamic-angle spinning NMR study of coesite *J. Phys. Chem.* **99** 12341

[18] Clark T M and Grandinetti P J 2000 Factors influencing the ^{17}O quadrupole coupling constant in bridging oxygen environments *Solid State Nucl. Magn. Reson.* **16** 55

[19] Vermillion K E, Florian P and Grandinetti P J 1998 Relationships between bridging oxygen ^{17}O quadrupolar coupling parameters and structure in alkali silicates *J. Chem. Phys.* **108** 7274

[20] Sternberg U 1993 The bond-angle dependence of the asymmetry parameter of the oxygen-17 electric field gradient tensor *Solid State Nucl. Magn. Reson.* **2** 181

[21] Xue X and Kanzaki M 2000 An *ab initio* calculation of ^{17}O and ^{29}Si NMR parameters for SiO_2 polymorphs *Solid State Nucl. Magn. Reson.* **16** 245

[22] Bull L M, Bussemer B, Anupold T, Reinhold A, Samoson A, Sauer J, Cheetham A K and Dupree R 2000 A high-resolution ^{17}O and ^{29}Si NMR study of zeolite siliceous ferrierite and *ab initio* calculations of NMR parameters *J. Am. Chem. Soc.* **122** 4948

[23] Boisen M B, Gibbs G V, Downs R T and D'Arco P 1990 The dependence of the SiO bond length on structural parameters in coesite, the silica polymorphs, and the clathrasils *Am. Mineral.* **75** 748

[24] Liebau F 1985 *Structural Chemistry of Silicates* 1st edn (Berlin: Springer)

[25] Frisch M J, Trucks G W, Schlegel H B, Gill P M W, Johnson B G, Robb M A, Cheeseman J R, Keith T, Petersson G A, Montgomery J A, Raghavachari K, Al-Laham M A, Zakrzewski V G, Ortiz J V, Foresman J B, Peng C Y, Ayala P Y, Chen W, Wong M W, Andres J L, Replogle E S, Comperts R, Martin R L, Fox D J, Binkley J S, Defrees D J, Baker J, Stewart J P, Head-Gordon M, Gonzalez C and Pople J A 1995 *Gaussian 94, revision b.3* (Pittsburgh, PA: Gaussian)

[26] Clark T M, Grandinetti P J, Florian P and Stebbins J F 2001 An ^{17}O NMR investigation of crystalline sodium metasilicate: implications for the determinations of local structure in alkali silicates *J. Phys. Chem.* B **105** 12257

[27] Newton M D and Gibbs G V 1980 *Ab initio* calculated geometries and charge distributions for H_4SiO_4 and $H_6Si_2O_7$ compared with experimental values for silicates and siloxanes *Phys. Chem. Minerals* **6** 221

[28] Gibbs G V 1982 Molecules as models for bonding in silicates *Am. Mineral.* **67** 421

[29] Profeta M, Mauri F and Pickard C J 2003 Accurate first principles prediction of ^{17}O NMR parameters in SiO_2: assignment of the zeolite ferrierite spectrum *J. Am. Chem. Soc.* **125** 541

[30] Spearing D R, Farnan I and Stebbins J F 1992 Dynamics of the alpha–beta phase transitions in quartz and cristobalite as observed by *in situ* high temperature Si-29 NMR and O-17 NMR *Phys. Chem. Minerals* **19** 307

[31] Dupree R 2000 Nuclear magnetic resonance as a structural probe of SiO_2 *Structure and Imperfections in Amorphous and Crystalline Si O*$_2$ ed R Devine, J P Durand and E Dooryhee (New York: Wiley) pp 107–20

[32] Geisinger K L, Spackman M A and Gibbs G V 1987 Exploration of structure, electron density distribution, and bonding in coesite with Fourier and pseudo atom refinement methods using single-crystal x-ray diffraction data *J. Phys. Chem.* **91** 3237

[33] Downs R T and Palmer D C 1994 The pressure behavior of alpha-cristobalite *Am. Mineral.* **79** 9

[34] Kihara K 1990 An x-ray study of the temperature dependence of the quartz structure *Eur. J. Mineral.* **2** 63

[35] Yao Z, Kwak H-T, Sakellariou D, Emsley L and Grandinetti P J 2000 Sensitivity enhancement of the central transition NMR signal of quadrupolar nuclei under magic-angle spinning *Chem. Phys. Lett.* **327** 85

[36] Kwak H-T, Prasad S, Yao Z, Grandinetti P J, Sachleben J R and Emsley L 2001 Enhanced sensitivity in RIACT/MQ-MAS NMR experiments using rotor assisted population transfer *J. Magn. Reson.* **150** 71

[37] Prasad S, Kwak H T, Clark T and Grandinetti P J 2002 A simple technique for determining nuclear quadrupole coupling constants using RAPT solid-state NMR spectroscopy *J. Am. Chem. Soc.* **124** 4964

[38] Kwak H-T, Prasad S, Clark T M and Grandinetti P J 2003 Selective suppression and excitation of solid-state NMR resonances based on quadrupole coupling constants *J. Magn. Reson.* **160** 107

[39] Chmelka B F, Mueller K T, Pines A, Stebbins J, Wu Y and Zwanziger J W 1989 Oxygen-17 NMR in solids by dynamic-angle spinning and double rotation *Nature* **339** 42

[40] Mueller K T, Wooten E W and Pines A 1990 Pure-absorption-phase dynamic-angle spinning *J. Magn. Reson.* **92** 620

[41] Clark T M and Grandinetti P J 2000 Relationships between bridging oxygen ^{17}O quadrupolar coupling parameters and structure in germanates *J. Non-Cryst. Solids* **265** 75