RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 62, NUMBER 8 15 AUGUST 2000-II

Si-O-Si bond-angle distribution in vitreous silica from first-principles ^{29}Si NMR analysis

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(Received 12 June 2000)

The correlation between ^{29}Si chemical shifts and Si-O-Si bond angles in SiO_2 is determined within density-functional theory for the full range of angles present in vitreous silica. This relation closely reproduces measured shifts of crystalline polymorphs. The knowledge of the correlation allows us to reliably extract from the experimental NMR spectrum the mean (151°) and the standard deviation (11°) of the Si-O-Si angular distribution of vitreous silica. In particular, we show that the Mozzi-Warren Si-O-Si angular distribution is not consistent with the NMR data. This analysis illustrates the potential of our approach for structural determinations of silicate glasses.

The interest in disordered SiO_2 systems is shared by several disciplines, including condensed-matter physics, materials science, and geophysics. In particular, vitreous silica occupies a prime position, not only as a prototype of strong network-forming glasses, but also as a key material in several industrial sectors, such as in glass, fiber, and electronic-device manufacturing.

Vitreous silica is generally pictured as a chemically ordered continuous random network consisting of corner-sharing tetrahedra.[1] Because the structural parameters defining the tetrahedra show sharp and narrow distributions,[2] the characterization of the disorder primarily rests on the determination of the broad Si-O-Si bond-angle distribution. The parameters defining this distribution are often used for interpreting a variety of physical properties of SiO_2 networks, such as, for instance, the vibrational properties[3,4] and the photoemission binding energies.[5,6] Moreover, this distribution is used as a reference for the construction of empirical potentials used in classical molecular dynamics simulations.[7,8]

Despite the importance of vitreous silica a general consensus on the Si-O-Si bond-angle distribution has not yet been reached. By analyzing x-ray diffraction spectra, Mozzi and Warren obtained a distribution,[9] which has only seldomly been disputed.[10] However, in a recent diffraction study in which neutron and x-ray data were combined, Neuefeind and Liss yielded a distribution of a considerably different shape,[11] causing a resurgence of this problem. Alternatively, NMR has emerged as a viable tool for structural determinations through the use of an empirical correlation between ^{29}Si chemical shifts and Si-O-Si bond angles,[12–21] which has been derived from measurements on well characterized crystalline SiO_2 polymorphs. However, this approach suffers from the necessity of extrapolating the correlation beyond the range of angles for which it was established,[12,13,18,22,23,21] and has so far prevented the extraction of a definite angular distribution for vitreous silica.[14,17,24] Indeed, in vitreous silica, Si-O-Si angles up to 180° occur, whereas the largest average Si-O-Si angle found in crystalline polymorphs is about 157°. Overall, the above considerations strongly suggest that a substantial degree of indetermination still persists in currently available bond angle distributions for vitreous silica, were they derived by diffraction or by NMR.

In this paper, we extract the Si-O-Si bond-angle distribution for vitreous silica from the NMR spectrum using a recently developed density-functional[25] approach for the calculation of NMR chemical shifts in solids.[26,27] We establish the correlation between ^{29}Si chemical shifts and Si-O-Si bond angles for the *full* range of angles present in vitreous silica by *ab initio* calculations on SiO_2 polymorphs under compressive and tensile pressures. This allows us to overcome the experimental constraints which limit the range of Si-O-Si bond angles available in crystalline compounds. By adopting a refined extraction procedure, we then determine definite values for the first and second moment of the Si-O-Si bond-angle distribution in vitreous silica.

Following the experimental convention, we quote NMR Si chemical shifts (δ_{TMS}) in part per million (ppm) relative to the Si shift of a liquid sample of tetramethylsilane (TMS) with spherical shape at 300 K. Instead of fixing the absolute shift of liquid TMS by a direct calculation, we take the calculated value for the average shift of meteoritic tridymite to coincide with the experimental one.[28] In the calculations, the core-valence interactions are described by pseudopotentials[29] and the wave functions are expanded in plane waves with a cutoff of 600 Ry. The Si $2s$, $2p$, $3s$, and $3p$ electrons are explicitly described with pseudopotential core radii of 0.44 bohr.

As reference material, we consider α-cristobalite, which contains just one inequivalent Si site with four equal Si-O-Si bond angles. By relaxing the internal coordinates under compressive or tensile pressures, the Si-O-Si angle ranges between 130° and 180°, while the tetrahedral units are preserved. This property is reflected in the low bulk modulus of α-cristobalite compared to, e.g, that of quartz. Calculated NMR shifts vs Si-O-Si bond angles show a linear depen-

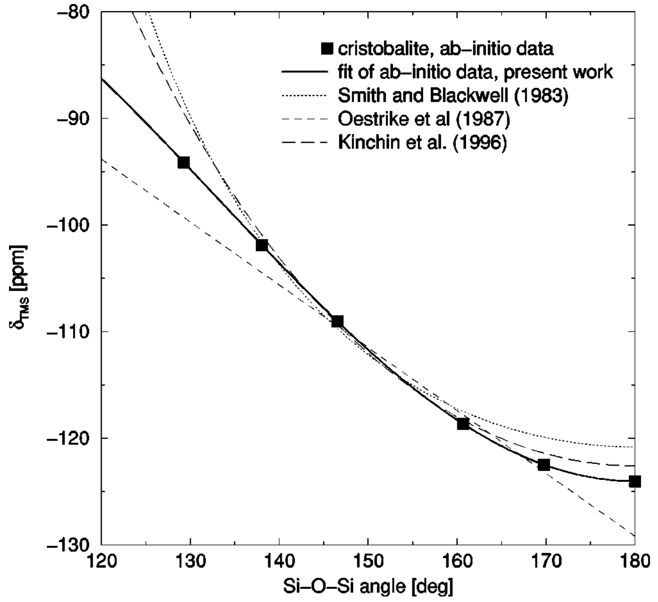

FIG. 1. Calculated dependence of the ^{29}Si NMR shift on Si-O-Si bond angles for α-cristobalite at various pressures. The squares are the *ab initio* results, and the solid line is the analytical interpolation, Eq. (1). For comparison we also report some of the empirical correlations derived in the literature as a dotted (Ref. 12), dashed (Ref. 18) and long-dashed line (Ref. 21).

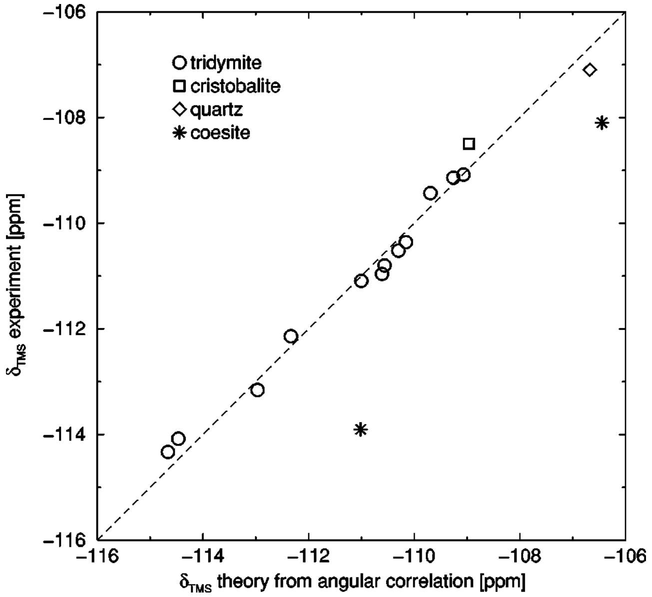

FIG. 2. Comparison between calculated and measured ^{29}Si NMR shifts for cristobalite (Ref. 12), quartz (Ref. 12), meteoritic tridymite (Ref. 28), and coesite (Ref. 12). In the calculations, we used the angular correlation given by Eq. (2) and structures defined by experimental values for the angles (Refs. 12, 33 and 34).

dence up to 160° and a saturation at larger angles (Fig. 1), which can well be described by

$$F_{\alpha c}(\theta)=-93.12+8.66\cos\theta-22.27\cos 2\theta, \tag{1}$$

where θ is the Si-O-Si bond angle. For comparison we also report in Fig. 1 some of the empirical NMR shift bond-angle correlations derived in the literature.[12,18,21]

When the four nearest neighbor Si-O-Si bond angles are inequivalent, we use the relation obtained for α-cristobalite to predict the NMR shift, assuming that the contributions of each angle are independent, i.e.,

$$\delta_{\mathrm{TMS}}=\frac{1}{4}\sum_{n=1}^{4} F_{\alpha c}(\theta_n). \tag{2}$$

Shifts obtained using Eq. (2) for several crystalline polymorphs show excellent agreement with the corresponding measured values (Fig. 2). The agreement is particularly significant for meteoritic tridymite,[28] because it contains 12 inequivalent $\mathrm{SiO_4}$ tetrahedra covering a large range of NMR shifts. Moreover the mean NMR shift of meteoritic tridymite is very close to that of amorphous silica. The agreement is worse for coesite, most likely because of the large differences between Si-O-Si angles ($\sim 43°$) centered on a given Si site.[24,21,22]

The most recent measurements of the ^{29}NMR line of vitreous silica[16,18,20] all agree on the position of the peak, but a slight disagreement still persists for the linewidth. The width can be significantly affected by contaminants and has steadily been decreasing as samples of higher purity became available.[17,16,18,20] In our analysis, we therefore adopt as the experimental reference the most recently measured spectrum,[20] which can well be described by a Weibull function with the maximum at -111.8 ppm, and a full width at half maximum of 9.5 ppm.

In order to extract the bond-angle distribution, we carry out a fitting procedure. At first, we assume a parametrized expression for the bond-angle distribution, for instance,

$$\rho(\theta)=k\{1-\mathrm{erf}[(\cos\theta-p_1)/p_2]\}\sin\theta, \tag{3}$$

or

$$\rho(\theta)=k\exp[-(\theta-p_1)^2/p_2]\sin\theta, \tag{4}$$

where p_1 and p_2 are free parameters to be determined and k is a normalization constant. Using Eq. (2), we obtain the theoretical spectrum $G(\delta_{\mathrm{TMS}})$ by numerical integration:

$$G(\delta_{\mathrm{TMS}})=\int d\theta_1 d\theta_2 d\theta_3 d\theta_4 \rho(\theta_1)\rho(\theta_2)\rho(\theta_3)\rho(\theta_4) \times\delta\left(\delta_{\mathrm{TMS}}-\frac{1}{4}\sum_{n=1}^{4}F_{\alpha c}(\theta_n)\right), \tag{5}$$

where $\delta(x)$ is the Dirac δ function and we assume that the individual bond angles at each corner of the tetrahedral unit are statistically independent.[14] Comparison of $G(\delta_{\mathrm{TMS}})$ to the experimental NMR spectrum[20] and a χ^2 minimization yields the optimal parameters.

Using Eq. (3), a very good description of the experimental NMR spectrum is achieved (Fig. 3). However, because of the multiple convolutions in Eq. (5), the determination of the *full* bond-angle distribution from NMR remains unrealistic. In fact, by assuming an angular distribution as that in Eq. (4), we also obtain an acceptable theoretical spectrum (Fig. 3). Nevertheless, both distributions show virtually the same first

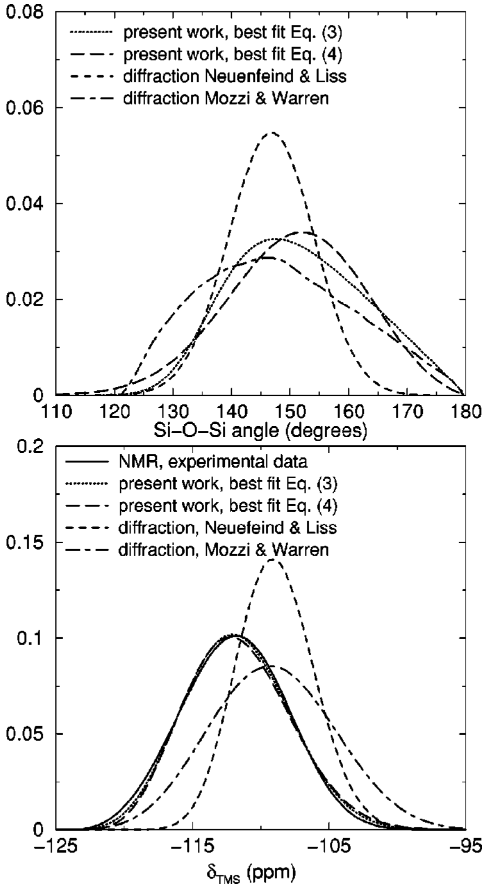

FIG. 3. In the lower panel, we compare the experimental ^{29}Si NMR spectrum of vitreous silica (full line) with the optimal theoretical spectra obtained with angular distributions as in Eq. (3) (dotted line) and Eq. (4) (long-dashed line). We also include the spectra obtained using the angular distributions deduced by Mozzi and Warren (Ref. 9) (dot-dashed line) and by Neuefeind and Liss (Ref. 11) (dashed line) from diffraction data. The upper panel shows the corresponding Si-O-Si angular distributions.

and second moment (Table I), indicating that an analysis of the NMR data is sufficiently accurate for an unequivocal determination of these properties. This is further confirmed by the great sensitivity of the NMR spectrum to first and second moments. Indeed, distributions derived from diffraction data,[9,11] which are characterized by different first and second moments (see Table I), exibit large deviations from the experimental NMR spectrum.

TABLE I. Mean (θ_{ave}), and standard deviation (σ_θ) for Si-O-Si bond-angle distributions derived from diffraction data and obtained in this work.

Distribution	Reference	θ_{ave}	σ_θ
Mozzi & Warren	9	147.9°	12.7°
Neuefeind & Liss	11	146.7°	7.3°
Using Eq. (3)	present	151.4°	11.3°
Using Eq. (4)	present	150.6°	11.5°

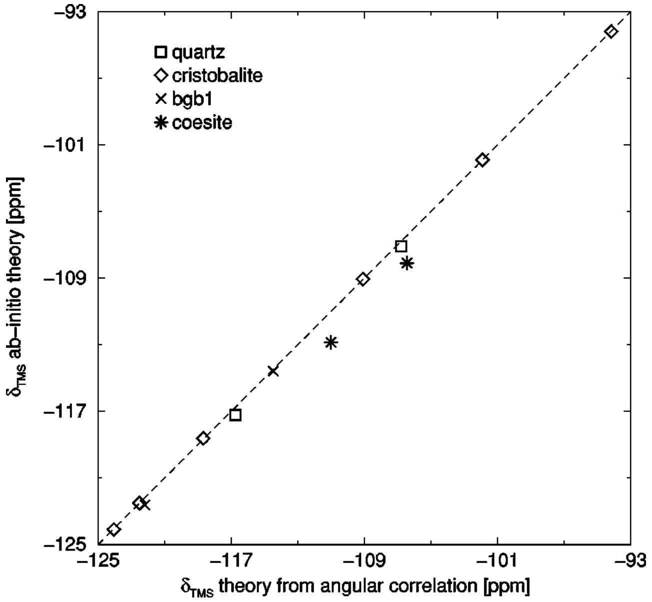

FIG. 4. Comparison between NMR shifts obtained using relation (2) and those resulting from an explicit first-principles calculation, for a set of polymorphs. Here, the *ab initio* results have been rescaled by a constant factor to correct for a systematic error (see text).

We now verify for the whole range of ^{29}Si shifts found in vitreous silica that the angular correlation Eq. (2) is universal, i.e., independent of the ring topology. To this purpose, we consider a set of silica polymorphs, namely α-quartz, α-cristobalite, coesite, and BGB1.[30] For each polymorph, we additionally generated several structures with different Si-O-Si angles by relaxing the internal coordinates under compressive or tensile pressures. For all the structures in this set, we obtain the NMR ^{29}Si chemical shifts by an explicit first-principles calculation.[26,27] To afford the large unit cells of some of the polymorphs, we here use less stringent conditions than in the calculations of Fig. 1. We chose an *s* and *p* Si core radius of 0.60 bohr, such that a calculation at 200 Ry is sufficient to yield converged results. This introduces a systematic error on the NMR shift which can easily be corrected for by a constant rescaling factor. The overall small deviations (Fig. 4) between the *ab initio* shifts and those predicted by Eq. (2) strongly support the universal validity of Eq. (2).

To investigate the effect of sources of broadening other than deriving from the bond-angle distribution, we modified our fitting procedure by introducing a convolution of $G(\delta_{TMS})$ with a Gaussian of standard deviation η. For η as large as 1 ppm, the values of θ_{ave} and σ_θ in Table I vary negligibly, by less than 0.1° and 0.5°, respectively. Assuming that the effect of contaminants has been suppressed,[20] the major remaining source of broadening is the static disorder in the Si-O bond lengths.[33] The dependence of ^{29}Si NMR shifts on the bond length can be calculated by considering α-cristobalite structures with scaled Si-O bond lengths. For a standard deviation of 0.015 Å in Si-O bond lengths,[31] we then derive a value for η smaller than 0.9 ppm. Such small spreads do not affect the moments extracted in this work.

In conclusion, by combining first-principles methods and experimental NMR data, we determined the lowest moments of the Si-O-Si distribution in vitreous silica, which had hitherto remained elusive. This result establishes this approach as a highly accurate tool for structural determinations, and offers new prospects in the study of silicate glasses.

We wish to thank W. Kob, D.M. Teter, and K. Vollmayr for providing structural coordinates from previous studies.[32,30] We acknowledge support from the PROFIL program of the Swiss NSF (A.P.), and from the U.S. NSF and D.O.E. (B.G.P., Y.G.Y., and S.G.L.). The calculations have been performed at the EPFL and at the IDRIS-CNRS computer centers.

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