LETTER TO THE EDITOR

Direct measurement of the thermal expansion of the Si–O bond by neutron total scattering

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Abstract. The coefficient of thermal expansion of the Si–O bond has been obtained from neutron total scattering measurements of five different phases of silica, with value $(2.2 \pm 0.4) \times 10^{-6}$ K^{-1}. This value is smaller than values obtained by conventional x-ray diffraction measurements corrected for rigid-body thermal motion. Three of the datasets used in this study, tridymite and two zeolite structures, are completely new.

The Si–O bond is one of the most important chemical bonds in the physical sciences, playing an important role in many technologically important ceramics (silicate glasses, quartz), in chemistry (zeolites), and in geology (silicate rocks and minerals). In spite of this, there is little information about how the bond responds to changes in external variables such as temperature. This is not surprising given that the conventional technique for measuring structure, Bragg diffraction using x-ray or neutron radiation, does not measure bond lengths directly. The information that can be extracted from the Bragg peaks concerns the positions of atoms. The best that can be done is to associate interatomic distances with the distances between average positions, and this is only appropriate if there is no correlation between the instantaneous positions of atoms. The problem with trying to determine the Si–O distance using Bragg diffraction is that the fluctuations in the positions of the Si and O atoms are highly correlated. We will argue in this letter that total scattering is far better as a method for determining bond lengths. Recent measurements, augmented by new measurements reported in this letter, of the Si–O bond lengths at various temperatures in several different phases of silica has given us the unique opportunity to determine a general value for the coefficient of thermal expansion of the Si–O bond; this has not been attempted before.

In conventional x-ray or neutron diffraction analysis the distribution of atom positions is represented by a set of three-dimensional elliptical Gaussian functions. Conventionally, the centres of the ellipses are associated with the mean positions of the atoms, and the widths of the ellipses are associated with the amplitudes of the thermal motion. If the motions of the atoms give more complex shapes of the distributions of position, this analysis is not appropriate. This problem has been recognised for a long time. In the case of molecular solids, where molecules may be assumed to move as rigid objects, the distribution of the positions of the atoms is often represented by the TLS formalism. In this, the temperature factors are defined in a form that reflects the rigid body translations (T), librations (L) and coupled motion (S) of the molecule [1].

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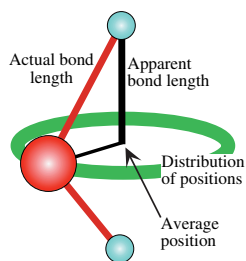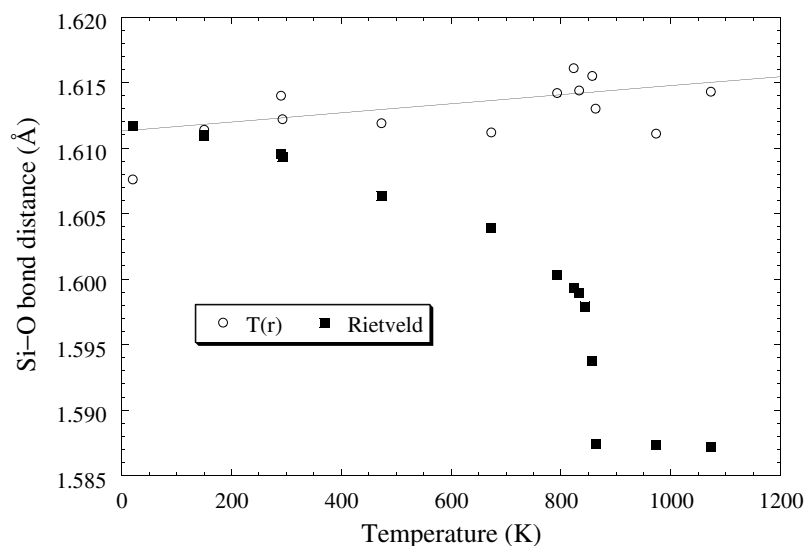
Figure 1. Temperature dependence of the distance between the positions of neighbouring Si and O atoms as determined by Rietveld refinement of the crystal structure of quartz (filled circles), compared with the true Si–O bond length (filled squares) determined by neutron total scattering measurements as discussed in this letter. The cartoon shows the origin of the shortening of the distance between the mean positions of the atoms compared to the true bond length.

Even allowing for the possibility of a centre of an atomic distribution to be accurately defined, if there are correlated motions of atoms, the distance between the mean positions of two atoms does not necessarily approximate to the mean distance between atoms. This is particularly problematic in a material containing Si–O bonds. Usually, at least at ambient pressures, silicon atoms are bonded to four oxygen atoms to form regular SiO_4 tetrahedra. Neighbouring tetrahedra are often linked at corners, with oxygen atoms bonded to two silicon atoms. This is the situation in pure silica, SiO_2, in the crystalline or amorphous phases. The Si–O bond is particularly strong, and thermal motions of the oxygen atoms are primarily determined by rigid body motions of the SiO_4 tetrahedra rather than by thermal vibrations of the Si–O bonds. The scale of the problem of determining the true bond length is shown in figure 1, where we show recent data for quartz [2]. The distance between the mean positions of bonded silicon and oxygen atoms, as determined by Rietveld refinement of neutron powder diffraction data, is seen to fall on heating, whereas the true value of the bond length, determined from neutron total scattering using methods discussed below, increases on heating. This point is illustrated by the cartoon in figure 1. The detailed temperature dependence of the distance between the mean positions is determined by the existence of the displacive phase transition at

846 K. Downs *et al* [3] have used a TLS approach to analyse the thermal motion in a range of crystalline silicates. Analysis of a wide range of data suggested that the coefficient of thermal expansion of the Si–O bond length varies between 0–12×10^{-6} K^{-1}.

However, there is also the problem of resolution. The real resolution of a diffraction experiment is set by the maximum value of the scattering vector, Q_{max} ($Q = 4\pi \sin\theta/\lambda$ in a diffraction experiment with radiation of wavelength λ and scattering angle 2θ). The resolution in real space is $\Delta r = 2\pi/Q_{max}$. For an experiment with a conventional Cu Kα source of x-rays, $\lambda = 1.54$ Å, if measurements can be performed to a maximum value of θ of $90°$, the real-space resolution is $\lambda/2 = 0.77$ Å. At this level of resolution, it is very hard to obtain unambiguous information about the complex shape of the distribution of atomic positions, but by the judicious use of constraints, it is possible to overcome the apparent limitations of this resolution to some extent. Moreover, the problems of resolution need not always be too severe, since if the distribution of positions or bond lengths is actually a symmetric function, it is possible to find the mid-point of the symmetric function to an accuracy that is much better than the resolution limit. However, if the distribution is not a symmetric function, the limited resolution will make it very hard to notice this, and the mid-point of the distribution determined by the analysis may not be the true mid-point. Herein lie the problems in determining the true thermal expansion of the Si–O bond!

In fact, the best way to determine true bond lengths is *not* by accurate measurements and sophisticated analysis of Bragg intensities, but by a measurement of the *total scattering*, Bragg + diffuse scattering (for pure silica incoherent scattering is negligibly weak). In the course of a study of the structure of disordered materials using neutron total scattering measurements from polycrystalline samples, we have obtained data on various crystalline silica phases over a range of temperatures. Our data include very recent measurements on quartz at 13 temperatures (20–1073 K) [2] and cristobalite at five temperatures (473–948 K) [4], and new data for tridymite at four temperatures (563–823 K) and silica in zeolite-Y and zeolite-ZSM5 structures at two temperatures (300 and 673 K) each. From this collection of data we have been able to determine the true temperature-dependence of the Si–O bond.

The intensity of the total scattering, whether using x-ray or neutron beams, contains information about the mean distances between atoms. This property has been exploited in the study of the structures of glasses and fluids. For isotropic materials, whether a fluid, glass or polycrystalline material, the intensity of the scattered beam at a given value of the scattering vector is given in terms of the individual pair distribution functions $g_{ij}(r)$:

$$\frac{1}{N}\frac{d\sigma}{d\Omega} = F(Q) + \sum_{i=1}^{n} c_i \overline{b_i^2}$$

$$F(Q) = \rho_0 \int_0^\infty 4\pi r^2 G(r) \frac{\sin Qr}{Qr} dr$$

$$G(r) = \sum_{i,j=1}^{n} c_i c_j \bar{b}_i \bar{b}_j [g_{ij}(r) - 1]$$

where the summations are over all atom types, ρ_0 is the average number density, c_j and b_j are the proportion and scattering length of atom type j respectively. $F(Q)$ is extracted from the measured scattering cross section by applying standard corrections (including the Placzek correction) as described by Wright [5,6]. We obtain $G(r)$ from $F(Q)$ using the inverse method developed by Pusztai and McGreevy [7]. We also define the function

$$T(r) = 4\pi r \rho_0 \left[G(r) + \left(\sum_{i=1}^{n} c_i \bar{b}_i \right)^2 \right]$$

which we use to determine the Si–O bond length because peaks in $T(r)$ correspond to the actual distribution of bond lengths [5,6]. These peaks are usually closely approximated by a Gaussian function, with widths that correspond to the mean squared amplitude of the vibrations of the bonds. Although the use of total neutron scattering within this formalism is not often applied to the study of crystalline materials, the methodology is equally applicable to crystals as to fluids and glasses, and because it is well-founded in studies of the latter materials its application to crystalline materials is robust.
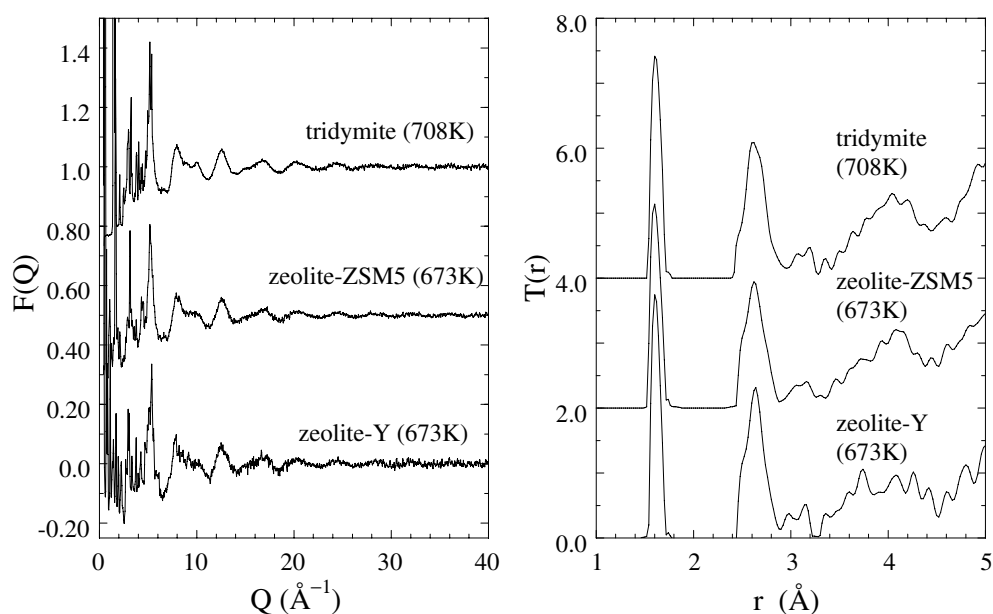
Figure 2. Some examples of $F(Q)$ and $T(r)$ data for tridymite and the two zeolite structures. The peaks in the $T(r)$ functions at around 1.6 Å correspond to the Si–O bonds. These peaks give the ripples in $F(Q)$ at high Q.

The experiments were performed on the LAD time-of-flight diffractometer at the ISIS pulsed neutron source [8]. Data were obtained to a value of $Q_{max} = 50$ Å^{-1}, which allow a real-space resolution of 0.13 Å. $F(Q)$ and $T(r)$ for quartz and cristobalite are given in earlier papers [2, 4, 9, 10]. Some of the new data for tridymite and the zeolites are shown figure 2.

The first peak in $T(r)$ corresponds to the Si–O bond, and its mid-point gives the mean value of the bond length. We extracted the mean value of the bond length from all measurements of $T(r)$ on the suite of silica phases. We then fitted the results for the temperature-dependence of the extracted Si–O bond lengths using an overall linear coefficient of thermal expansion, allowing the value of the bond length at 0 K to be different for each sample. The variation of the bond length with temperature was too small to allow non-linear expansion, particularly at low temperature, to be taken into account. The fitted coefficient of thermal expansion of the Si–O bond, ℓ, has the value $\alpha = \ell^{-1} \partial \ell / \partial T = (2.2 \pm 0.4) \times 10^{-6}$ K^{-1} (fitting $\chi^2 = 1.3$). The fitted 0 K values of the bond lengths were 1.611(2) Å for quartz, 1.610(1) Å for cristobalite, 1.614(1) Å for tridymite, 1.6113(6) Å for zeolite-Y, and 1.6079(2) Å for zeolite-ZSM5. These
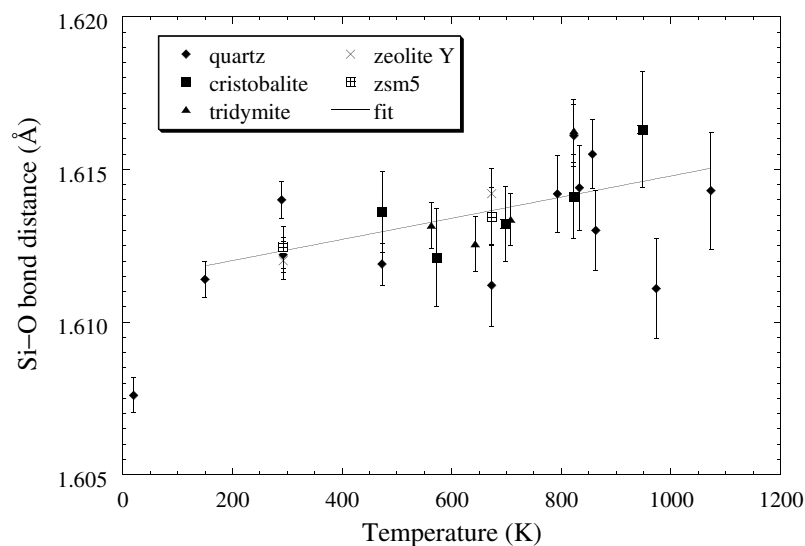
Figure 3. Temperature dependence of the Si–O bond length determined by neutron total scattering measurements for several different phases of silica. The straight line is a least-squares fit to the data.

results are close to the room temperature value of 1.608(4) Å obtained for amorphous silica by neutron total scattering measurements as reported by Wright [5,6]. We have subtracted an offset from the bond length values of the different data sets so that the 0 K values coincide with that of quartz (i.e. $1.610 - 1.611 = -0.001$ was subtracted from the cristobalite data, 0.003 was subtracted from the tridymite data and -0.0032 was subtracted from the zeolite-ZSM5 data, with no offset needed for the zeolite-Y data). This has been done in order to put all the data onto a common scale to show the variation with temperature in figure 3. The scatter of points in figure 3 appears to be relatively large, but the size of the scatter is well within the resolution calculated by Q_{max}. In fact the scatter only appears to be large because the thermal expansion is so small, and the range on the vertical scale is small. The errors on the individual data points are quite reasonable for this type of measurement. The largest discrepancy is for quartz at 20 K, and this data point was excluded from the fitting because of the bias it produced. We believe that this is appropriate because the Si–O distances obtained from the Rietveld refinements should become very close to the distances from $T(r)$ at low temperatures as the thermal motion is greatly reduced (this is validated by the data in figure 1), and the Si–O distance from the Rietveld refinement at 20 K actually lies very close to the fitted line in figure 3. Moreover, reverse Monte Carlo simulation based on the total scattering data from 20 K also gave a mean Si–O distance that lies close to the fitted line [2].

It is worth making one comment concerning the difference between the apparent distance between Si and O atoms from the Rietveld refinement and the actual bond length shown in figure 1. At high temperatures, this difference (almost 0.3 Å) is rather larger that the resolution given by Q_{max} (0.13 Å), and is therefore statistically significant.

The fitted value of the coefficient of thermal expansion can be compared with the results from the TLS rigid body analysis of Downs *et al* [3] applied to crystal structure refinements of various silicate phases using Bragg diffraction data. Our value of $\alpha = (2.2 \pm 0.4) \times 10^{-6}$ K^{-1} is at the low end of the range of values given by their analysis (up to 12×10^{-6} K^{-1}). Over a change in temperature of 1000 K, the length of the Si–O bond could increase by up to

0.02 Å from the latter results. Although this change is within the experimental resolution, a real change of this size would nevertheless have been seen in our data given in figure 3.

This is the first direct measurement of the temperature dependence of the Si–O bond in solid materials, and the consistency of the data from one structure to another suggests that the value of the coefficient of thermal expansion of the Si–O bond will differ little between different structures. The thermal expansion is very low, rather lower than previous estimates based on sophisticated corrections for thermal motion in crystal structure refinements. This knowledge of the true thermal expansion of the Si–O bond should now facilitate quantitative studies of the structures of disordered materials and of bulk thermal expansion of silicates [11, 12].

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