A computational investigation of $^{17}$O quadrupolar coupling parameters and structure in $\alpha$-quartz phase GeO$_2$

Travis H. Sefzik, Ted M. Clark, Philip J. Grandinetti*

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

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Abstract

$Ab$ initio band-structure calculations based on density functional theory have been completed for $\alpha$-quartz phase GeO$_2$ to obtain electric-field gradients (efg) for oxygen atoms, including those for GeO$_2$ at elevated pressure and temperature. To interpret the resulting efg values and examine correlations between structure and $^{17}$O quadrupolar coupling parameters, additional $ab$ initio self-consistent Hartree-Fock molecular orbital calculations were completed. The quadrupolar coupling constant was found to have a strong dependence on Ge–O distance and $f_{\text{Ge}_2\text{O}_2\text{Ge}}$, with the quadrupolar asymmetry parameter being primarily dependent on $f_{\text{Ge}_2\text{O}_2\text{Ge}}$. Analytical expressions describing these dependencies consistent with earlier investigations of analogous silicate compounds are also reported. © 2007 Elsevier Inc. All rights reserved.

1. Introduction

Germanate compounds, including $\alpha$-quartz phase GeO$_2$, are of interest to a wide range of researchers in several disciplines because they serve as an experimental proxy for silicate systems of fundamental importance. The compression behavior of GeO$_2$ largely parallels that of SiO$_2$, but at pressures much more easily attained experimentally [1,2]. Crystalline germanates have been investigated by a variety of methods [1,3–5], including a more recent determination of the crystal structure of $\alpha$-quartz phase GeO$_2$ as a function of pressure [6]. Amorphous germanates have also been investigated by a variety of methods [2,4,7–13]. Recent neutron and X-ray diffraction studies of ambient and permanently densified germania glass concluded that a decrease in Ge–O and O–O distances occurs upon densification, caused by a rotation about the Ge–O–Ge bonds and a distortion of the GeO$_4$ tetrahedra [14].

In spite of these recent successes, improved methods are still needed to resolve a number of outstanding questions about structural variations in tetrahedral oxides glasses. An experimental approach that has great potential for describing bridging oxygen environments in both crystalline and amorphous materials is $^{17}$O solid-state nuclear magnetic resonance (NMR) spectroscopy. Advances in solid-state NMR have led to a significant increase in the number of bridging oxygen environments with experimentally determined NMR parameters [15–20]. The relationships between structure and the $^{17}$O NMR parameters in tetrahedral oxides have been an area of focus for some time [21–26]. First coordination sphere features of the bridging oxygen site, such as the $\angle\text{T–O–T}$ and T–O bond distance, have been studied and analytical expressions proposed to predict the nuclear electric quadrupolar coupling constant ($C_Q$) and asymmetry parameter ($\eta_Q$). Such relationships have been indispensable for interpreting $^{17}$O NMR data obtained for amorphous silicates [15,27,28].

Unfortunately, unlike the situation for crystalline silicates [29–34], there is only one experimental measurement of $^{17}$O nuclear electric quadrupolar coupling parameters in a crystalline germanate with a Ge–O–Ge linkage [20]. Therefore, in this work we have focused on predicting the quadrupolar coupling parameters of germanate bridging oxygen by combining $ab$ initio computational approaches that incorporate crystal periodicity [35,36] with those that utilize model clusters to represent the salient features in the local environment [16,36–42]. As we have shown earlier [23], there are advantages for employing both approaches when determining trends in quadrupolar
couplings for oxygen sites. In this investigation we concentrate on calculations of the $^{17}$O quadrupolar coupling parameters for crystal structures determined for quartz-type GeO$_2$ at elevated pressures and temperatures. Previously reported trends$^{[22]}$ between structural parameters, such as $\angle T\text{–}O\text{–}T$ or T–O distance, are also considered and are discussed with respect to trends reported for similar silicate environments.

2. Calculations

The efg tensor components are related to the quadrupolar coupling constant ($C_q$) and quadrupolar asymmetry parameter ($\eta_q$) according to

$$C_q = \frac{eQ}{\hbar}\langle eq_{zz}\rangle,$$  \hspace{1cm} (1)

and

$$\eta_q = \frac{\langle eq_{xx}\rangle - \langle eq_{yy}\rangle}{\langle eq_{zz}\rangle},$$  \hspace{1cm} (2)

where $Q$ is the nuclear electric quadrupole moment and $\langle eq_{xx}\rangle$, $\langle eq_{yy}\rangle$, and $\langle eq_{zz}\rangle$ are the principal components of the traceless efg tensor defined such that $|\langle eq_{zz}\rangle| > |\langle eq_{yy}\rangle| > |\langle eq_{xx}\rangle|$.

2.1. Periodic structure calculations

The full-potential, linearized, augmented plane-wave (LAPW) package WIEN2k$^{[35]}$ was used to perform density functional theory (DFT) using the generalized gradient approximations (GGA) for the exchange and correlation potentials$^{[43,44]}$. In the LAPW method the unit cell is divided into spheres centered at the atomic positions and an interstitial region. For the interstitial region, the basis set consists of plane waves which are augmented by atomic-like solutions inside the spheres. Sphere radii of 1.4550 and 1.1640 a.u. were used for Ge and O, respectively. The cutoff for the plane wave basis set was chosen as $R_{\text{mt}}K_{\text{max}} = 7.00$, where $R_{\text{mt}}$ corresponds to the smallest atomic sphere radii and $K_{\text{max}}$ is the plane wave cutoff. These parameters typically resulted in more than 6000 LAPWs being used in the basis sets. Additional calculations confirmed that these results were well converged for these cut-off values. The number of $k$-points in the irreducible Brillouin zone (IBZ) for the calculations was consistently 12 throughout the study. Nonspin-polarized calculations were studied in all cases. The procedure for obtaining the electric field gradient tensor with WIEN2k is given in Ref.$^{[36]}$.

2.2. Structure fragment calculations

$Ab$ $initio$ molecular orbital calculations were performed using the Gaussian 03$^{[45]}$ software package at a restricted Hartree-Fock level with a 6-311 + $G(d)$ basis set used for all atoms. A value of $e^2Q/\hbar = -6.11$ MHz$^{-1}$ was used for $^{17}$O to convert the largest magnitude principle component of the efg tensor in atomic units to the $^{17}$O quadrupolar coupling constant in megaHertz.

Bridging oxygen centered fragments, as shown in Fig. 1A, consisting of one tetrahedral shell (1T), (OH$_3$)Ge–O–Ge(OH$_3$), were employed for calculation of the electric-field gradient. A select number of two GeH$_3$ terminated tetrahedral shells (2T), (H$_3$GeO)$_2$Ge–O–Ge(OGeH$_3$)$_3$, as shown in Fig. 1B, were also examined. The geometries of the fragments are consistent with the crystal structure determined by neutron diffraction investigations$^{[6,46]}$. Fragments were terminated either at germanium or oxygen atoms by hydrogen atoms placed along the direction of the Ge–O or O–Ge bond in the actual crystal structure. The O–H and Ge–H bond distances were fixed at 0.96 and 1.52 Å, respectively.

Model 1T clusters were also used to examine trends between structure and quadrupolar coupling parameters GeO$_2$ systems. For these calculations the $\angle \text{Ge–O–Ge}$ angle was varied between 125° and 160° in steps of 5°. The

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**Fig. 1.** Oxygen centered crystal fragments for quartz-type GeO$_2$. The one tetrahedral shell (1T), and two tetrahedral shell (2T) fragments, depicted in (A) and (B), respectively, are based on the crystal structure for ambient GeO$_2$. 

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central Ge–O distances were varied between 1.70 and 1.75 Å in 0.01 Å increments for each of these angles. Both symmetric and asymmetric distance pairs were examined.

3. Results and discussion

3.1. Structures

Crystal structures have been reported for quartz-type GeO2 under different conditions. High pressure GeO2 crystal structures, based on a neutron diffraction study, have been reported by Glinnemann [6]. A series of crystal structures has also been reported by Haines [46] for GeO2 as a function of temperature, again based on neutron diffraction data. Structure refinements for GeO2 under ambient pressure and temperature conditions have been reported by Smith [49] and Sowa [50]. All of these studies are in good agreement with respect to the ambient GeO2 structure with a \( \angle \text{Ge}–\text{O}–\text{Ge} \) value of 130.1°, asymmetric Ge–O distances of 1.737 and 1.741 Å, and tetrahedral O–Ge–O angles of ranging from 106.3° to 113.1°.

The structural changes that occur in quartz-type GeO2 with temperature or pressure changes are shown in Fig. 2. The response of crystalline \( \alpha \)-quartz phase SiO2 to changes in these two variables is also included for comparison [47,48]. As shown in Fig. 2A, the trend in \( \angle \text{T}–\text{O}–\text{T} \) (where T = Ge or Si) is similar for both GeO2 and SiO2, with the angle contracting as the unit cell volume decreases. It should be noted, however, that considerably higher pressures are required to compress the unit cell for SiO2 in comparison to GeO2. For example, the unit cell volume of SiO2 is decreased from approximately 113 to 100 Å\(^3\) with a pressure change of 61.4 kbar. In comparison, the unit cell volume of GeO2 is decreased from approximately 121 to 108 Å\(^3\) with a much smaller pressure change of 5.57 GPa. In terms of unit cell expansion as a function of temperature the response of each system are similar; the unit cell volumes increase by approximately 5 Å\(^3\) for SiO2 or GeO2 with a temperature increase of 1000 K.

Similar trends are also apparent for T–O distance as a function of unit cell volume shown in Fig. 2B. The unit cell expands as the temperature is increased and the T–O distances decrease by approximately 0.01–0.02 Å when the temperature is increased to approximately 1300 K in comparison to the ambient structure. With unit cell contraction the T–O distances are largely unchanged with respect to the ambient structure. Finally, the relationship between angle and distance is present as the unit cell volume increases with rising temperature, i.e., the bridging oxygen angle decreases and the T–O distance increases. In contrast, a clear negative correlation is not apparent for the compressed unit cell structures for either GeO2 or SiO2.

3.2. Calculation of quadrupolar coupling parameters

Using the reported \( \alpha \)-quartz GeO2 crystal structures of Glinnemann [6] as a function of pressure and Haines [46] as a function of temperature, the quadrupolar coupling parameters in Table 1 were calculated for the bridging oxygen. One set of calculations were performed on the full crystal lattice structures using the periodic DFT methods in WIEN2k, and another on the 1T fragments using Gaussian 03. The \( C_q \) and \( \eta_q \) values obtained are shown in Table 1. The WIEN2k values for the ambient crystal structure are in reasonable agreement with the experimental values reported by Dupree and co-workers [19] of \( C_q = 7.3 \pm 0.1 \) MHz and \( \eta_q = 0.48 \pm 0.05 \) as determined by NMR. This agreement is not surprising given the effectiveness of LAPW calculations for similar systems [23,36,51]. The \( C_q \) values calculated for 1T fragments, also shown in Table 1,
The first-coordination sphere geometry of 1T fragments were taken from the crystal structure. The last column is the ratio of the calculated value or the experimentally determined value with WIEN2k and experiment. This suggests that the efg is partially dependent on the fragment size employed in a given calculation. The \( q \) value obtained using the 2T fragment is slightly smaller than that obtained for the 1T fragment and also in better agreement with experiment. These findings are consistent with previous investigations of analogous silicate environments which demonstrated that IT-fragment are sufficient for determining the quadrupolar coupling parameters of a bridging oxygen atom \[52\], and a prudent choice given the significantly longer time required to complete 2T fragment calculations.

Having demonstrated that \textit{ab initio} molecular orbital calculations employing oxygen centered 1T fragments are suitable for determining the quadrupolar coupling parameters in these germanate systems, it is now possible to examine which structural features in the first coordination sphere most affect the efg. Earlier investigations have identified several factors that may influence the efg at bridging oxygen sites in germanate, silicate, or other related compounds \[23,25,26\]. This prior work strongly suggests that \( C_q \) will be affected by changes in both \( \angle \text{Ge}–\text{O}–\text{Ge} \) and Ge–O distance, with variations in \( \angle \text{O}–\text{Ge}–\text{O} \) being a secondary factor. It is also expected that \( q \) will be affected by changes in \( \angle \text{Ge}–\text{O}–\text{Ge} \), with other contributions in the first coordination sphere being of minor importance.

To examine these hypotheses, IT models were constructed and the efg-components calculated. By systematically varying the \( \angle \text{Ge}–\text{O}–\text{Ge} \) and Ge–O distances it is possible to compute quadrupolar coupling parameters for structures with far greater first-coordination sphere variability than that present in reported crystal structures. In Fig. 3 are the predicted trends in \( C_q \) and \( q \) as both \( \angle \text{Ge}–\text{O}–\text{Ge} \) and Ge–O distance are independently varied.

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<th>Temp. (K)</th>
<th>( \angle \text{Ge}–\text{O}–\text{Ge} ) ((^\circ))</th>
<th>( d(\text{Ge}–\text{O}) ) (( \AA ))</th>
<th>( \angle \text{O}–\text{Ge}–\text{O} ) ((^\circ))</th>
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<th>( q )</th>
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Table 1

Reported structural parameters and calculated quadrupolar coupling constants and asymmetry parameters (this study) at oxygen sites in quartz-type GeO\(_2\) at various pressure \([6]\) and temperature \([46]\) conditions.

The first-coordination sphere geometry of 1T fragments were taken from the crystal structure. The last column is the ratio of the \( C_q \) values for LAPW calculation over the 1T fragment calculation.
Other than the magnitude of $C_q$, these trends are virtually identical to those described earlier by Clark and Grandinetti for the Si–O–Si linkage [22]. Over the relevant range of Ge–O distances the $C_q$ value follows a simple linear relationship [26]. Most importantly, the asymmetry parameter is nearly independent of Ge–O distance, and its behavior is dominated by its dependence on $\angle$Ge–O–Ge. These trends can be described using the same expressions used for the Si–O–Si linkage [26]:

$$C_q(d_{TO}, \Omega) = a \left( \frac{1}{2} + \frac{\cos \Omega}{\cos \Omega - 1} \right)^\alpha + m_d(d_{TO} - d_{TO}^0),$$

and

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

where $\Omega$ is $\angle$Ge–O–Ge and $d_{TO}$ is the average germanium-oxygen bond distance. The parameters obtained from fitting the theoretical data to Eqs. (3) and (4) are $a = -6.1$ MHz, $m_d = -10.60$ MHz/Å, $d_{TO}^0 = 1.449$ Å, $\alpha = 4.58$, $b = 3.22$, and $\beta = 0.992$.

As a check we used the quadrupolar coupling parameters predicted in our periodic structure calculations for $\alpha$-GeO$_2$, LAPW in Table 1, and Eqs. (3) and (4) to back predict the Ge–O–Ge angles and Ge–O distances. This comparison is shown in Fig. 4. The nearly perfect correlation in Fig. 4A shows, as was the case for the Si–O–Si linkage, that the $\eta_q$ value serves as a highly reliable probe of the $\angle$T–O–T. With $\angle$Ge–O–Ge determined by $\eta_q$, Eq. (3) is used to predict the Ge–O distance from $C_q$, as shown in Fig. 4B. The predicted Ge–O distances are also in good agreement, with the majority being within 0.005 Å from the predicted value. Having determined the Ge–O distance for a given angle, it is also possible to determine the Ge–Ge distance. These values are shown Fig. 4C. Finally, we note that the simultaneous measurement of $C_q$ and $\eta_q$ for each bridging oxygen site can be exploited to obtain the correlation between Ge–O–Ge angle and Ge–O distance [2,22].

Previous investigations of the relationship between structure and quadrupolar coupling parameters, e.g., in silicate systems, have focused primarily on symmetric T–O bond distances at bridging oxygen sites. Although this assumption is justified since Si–O bonds are typically quite symmetric for a given oxygen site in most crystalline SiO$_2$ polymorphs, with germanates such an assumption is less valid. As seen in Table 1, it is not unusual to have Ge–O distances differ by 0.01 Å at an oxygen site. To examine the effect such structural asymmetries may have on $C_q$ and $\eta_q$, additional calculations have been completed on 1T model clusters with asymmetric Ge–O bond lengths. These calculations, in which asymmetries of up to 0.05 Å were...
considered, strongly suggest that the average T–O distance, as included in Eq. (3), remains very useful for describing even asymmetric bridging oxygen environments. For example, 1T-clusters with $\angle$Ge–O–Ge = 135° and Ge–O distances pairs of 1.73–1.73, 1.74–1.72, and 1.75–1.71 Å (average $d$(Ge–O) = 1.73 Å) have calculated $C_q$ values of 7.51, 7.51, and 7.52 MHz, respectively. The calculated $\eta_q$ are even less varied, with a value of 0.40 determined for each cluster. Although it remains possible that other asymmetric features further removed from a bridging oxygen atom, such as varied $\angle$O–Ge–O, may complicate the relationships between structure and quadrupolar coupling parameters in germanates, vis-à-vis silicates, Eqs. (3) and (4) should remain valid for a wide range of germanate structures.

4. Conclusion

General trends in the $^{17}$O quadrupolar coupling parameters for bridging oxygen atoms in germanates have been described based on ab initio self-consistent field Hartree-Fock molecular orbital calculations on germanate clusters. These results were calibrated by performing band-structure calculations based on the density functional theory for a range of α-quartz phase GeO$_2$ structures obtained as a function of pressure [6] and temperature [46]. As suggested by earlier investigations, the quadrupolar asymmetry parameter was found to be primarily dependent on the $\angle$Ge–O–Ge (and largely independent of Ge–O distance). The quadrupolar coupling constant was found to have a strong dependence on Ge–O distance, as well as $\angle$Ge–O–Ge. Having established the manner in which local structural parameters influence the $^{17}$O quadrupolar coupling parameters, it is now possible to gain significant insights into the structure of germanate glasses. Since the relationships between structure and the $^{17}$O quadrupolar coupling parameters appear similar for both germanate and silicate systems, future work describing correlated structural distributions in GeO$_2$ glasses should be possible, as has been recently reported for silica glass [15].

Acknowledgments

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