

## Structure of Vitreous Germania

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A full partial structure factor analysis of vitreous germania has been obtained by a combination of neutron diffraction, x-ray diffraction, and anomalous x-ray scattering. The results are consistent with the identification of the first three peaks in the average neutron and x-ray structure factors with intermediate-range order, chemical short-range order, and topological short-range order, respectively. The values for the shortest distances for the three element pairs are in agreement with previous work and suggest that possible complications with this technique, which might arise for example from shifts of the centers of the electron distributions from the nuclei, are not serious in the case of oxide glasses. [S0031-9007(98)07248-2]

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Vitreous silica and germania are prototypic simple glasses which form the basis for large families of non-crystalline materials with considerable scientific interest as well as technological importance [1]. Although a sizable body of diffraction literature exists on the structure of silica, dating back to the pioneering work of Warren [2], and extensive computer simulations have been carried out with both classical [3] and *ab initio* [4] molecular dynamics, the low atomic numbers of its constituent elements and low contrast in the neutron scattering lengths of its isotopes preclude a complete determination of its structure at the partial level. For this reason recent interest has focused on vitreous germania, using a number of structural methods including neutron diffraction (ND) [5,6], high-energy x-ray diffraction (XRD) [7], and anomalous x-ray scattering (AXS) at the germanium edge [6,8,9].

In this Letter we report a measurement of the partial structure factors (psf's)  $S_{ij}(Q)$  for each element pair  $(i, j)$  of vitreous germania, obtained by a combination of ND, XRD, and AXS. This approach is now feasible since spallation neutron sources and synchrotron x-ray sources make it possible to obtain reliable diffraction data out to reasonably large values of the scattering vector  $Q$ . In appropriate conditions, it should be possible to obtain higher statistical accuracy than with either neutron diffraction with isotope substitution (NDIS) alone or AXS alone, since double difference measurements are required to obtain the partial structure factors with these methods. Furthermore, compared with isotope substitution this approach avoids the expense of separated isotopes and the need to prepare different samples (and ensure that they are structurally equivalent). However, it should be understood that (a) the use of two separate probes involves different sets of corrections and systematic errors which cannot be expected to cancel out, as they do in the case of difference measurements with a single probe, and

(b) the spatial distributions measured with the two probes are in principle not the same, since ND sees the nuclear coordinates, XRD the entire electron distributions, and AXS those of the core electrons. A recent comparison of ND and XRD on a molten salt, for example, has shown the sensitivity of the x-ray results to the degree of charge transfer [10]. The significance of these two factors with respect to the present measurements will be discussed.

The ND measurements were carried out on GLAD at IPNS and the x-ray experiments at the X-7A beam line at NLSL [9]. The results for the weighted average structure factors

$$S^{N,X}(Q, E) = \sum_{ij} W_i^{N,X}(Q, E) W_j^{N,X}(Q, E) S_{ij}(Q) \quad (1)$$

and for the Ge-difference structure factor [11]

$$S_{\text{Ge}}^X(Q, E) = \sum_j W_j^X(Q, E) S_{\text{Ge},j}(Q) \quad (2)$$

are given in Ref. [9]. The neutron and x-ray weighting factors in Eqs. (1) and (2) are

$$W_i^N(Q) = \frac{c_i \bar{b}_i}{\langle b \rangle} \quad \text{and} \quad W_i^X(Q, E) = \frac{c_i f_i(Q, E)}{\langle f(Q, E) \rangle}, \quad (3)$$

where  $c_i$ ,  $\bar{b}_i$ , and  $f_i(Q, E)$  are the concentration, coherent scattering length, and form factor for element  $i$ ,  $\langle \dots \rangle$  indicates the average over all atoms in the system, and the prime in Eq. (2) denotes the real part.

In the present work,  $S^N(Q)$  and  $S^X(Q, E)$  taken at energies 13 and 200 eV below the Ge  $K_\alpha$  absorption edge at  $E_\alpha = 11, 103$  eV were used as the experimental input. Writing these as a vector  $\mathbf{F}(Q) = [S^N(Q), S^X(Q, E_\alpha - 13), S^X(Q, E_\alpha - 200)]$  and the psf output as a vector  $\mathbf{S}(Q) = [S_{\text{GeGe}}(Q), S_{\text{Oo}}(Q), S_{\text{GeO}}(Q)]$ , Eqs. (1) and (2) can be written for the entire data set as

$$\mathbf{F} = \mathbf{A} \mathbf{S}, \quad (4)$$

where the elements of  $\mathbf{A}$  are linear combinations of the weighting factors in Eq. (3). Inserting the appropriate values for the nuclear and atomic parameters, it is found that degree of conditioning of  $\mathbf{A}^{-1}$  is comparable to that obtained in many ND experiments with isotope substitution, so that reliable structure factors should be derived, provided the systematic and statistical errors are small. With spallation neutron sources and synchrotron x-ray sources, the statistical errors can be made acceptably small with reasonable counting times. The main problem arises from systematic errors, especially at high  $Q$  where the measured x-ray Compton scattering increases (and is different at the two energies because of the different attenuation coefficients) and resonant Raman contributions near the absorption edge remain significant while the diffracted intensity decreases on account of the falling form factor. Fortunately this problem is compensated to some extent by the improved conditioning of  $\mathbf{A}^{-1}$  at high  $Q$ , because the anomalous (energy-dependent) term in  $f_{\text{Ge}}(Q)$  stays constant while the regular part is falling.

The results for the psf's are shown as points in Fig. 1. The principal features in the neutron and x-ray average structure factors for  $\text{GeO}_2$  are peaks occurring at  $Q = 1.54 \text{ \AA}^{-1}$  (the first sharp diffraction peak (FSDP) [12]),  $2.6 \text{ \AA}^{-1}$  (stronger in  $S^X(Q)$  and especially in  $S_{\text{Ge}}^X(Q)$  [9]), and  $\sim 4.5 \text{ \AA}^{-1}$ . From scaling considerations, these can be associated with intermediate-range order (IRO), chemical short-range order (CSRO), and topological short-range order (TSRO), respectively [13]. In the partials shown in Fig. 1, the FSDP shows up as a positive peak in  $S_{\text{GeGe}}$  and  $S_{\text{GeO}}$  and a shallow negative peak in  $S_{\text{OO}}$ , indicating that cation correlations dominate the IRO, as is generally the case in oxide and chalcogenide glasses [3,4,14,15]. The peak at  $2.6 \text{ \AA}^{-1}$  is strong and positive, with almost the same height, in  $S_{\text{GeGe}}$  and  $S_{\text{OO}}$ , and strong and negative, with almost the same magnitude, in  $S_{\text{GeO}}$ , confirming the CSRO nature of this peak. The TSRO peak occurs at  $4.4 \text{ \AA}^{-1}$ , predominantly in  $S_{\text{GeGe}}$ . A previous measurement of the partial structure factors of  $\text{GeO}_2$  by Waseda *et al.* [6] obtained generally similar results but with the FSDP appearing as a double peak at about  $1.5$  and  $2.0 \text{ \AA}^{-1}$  in all three partials, a behavior that does not appear very likely and is not found in the computer results for  $\text{SiO}_2$  discussed below.

The condition that the scattering intensity must be positive-definite leads to certain inequalities [16] that the partial structure factors must obey. In the present case these are  $S_{\text{GeGe}} > -2$ ,  $S_{\text{OO}} > -0.5$ , and  $(S_{\text{GeGe}} + 2)(2S_{\text{OO}} + 1) > 2(S_{\text{GeO}} - 1)^2$ . The first is clearly true everywhere, but the second and third break down between  $0.8$  and  $2.3 \text{ \AA}$ , indicating some systematic errors in the experimental procedure in this region whose origin is not yet understood.

We are not aware of any published molecular dynamics (MD) computer simulations of  $\text{GeO}_2$ , but  $\text{SiO}_2$  has been studied with classical MD by Vashishta *et al.* [3] and with

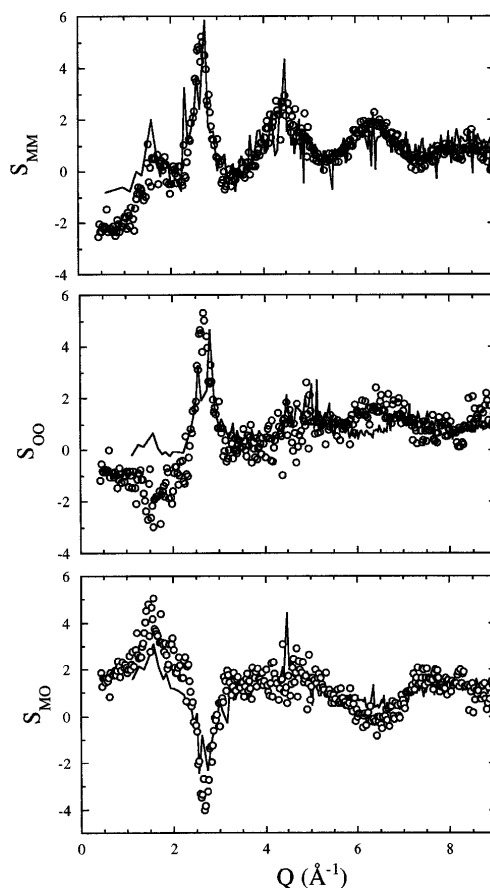


FIG. 1. Measured partial structure factors (Faber-Ziman definition) for the three atom pairs in vitreous germania at room temperature ( $M = \text{Ge}$ , points), together with corresponding results from *ab initio* MD computer simulation [4,17] of vitreous silica ( $M = \text{Si}$ , lines), with the  $Q$  scale reduced by a factor 1.075.

*ab initio* MD by Sarnthein *et al.* [4]. The *ab initio* MD results [17], with  $Q$  values scaled down by the ratio of the  $M$ -O distances in  $\text{GeO}_2$  and  $\text{SiO}_2 = 1.73/1.61 = 1.075$ , are plotted as solid lines in Fig. 1 for comparison. They are seen to be generally similar to the present results for  $\text{GeO}_2$ , the main qualitative difference being that the FSDP shows up as a weak positive feature in  $S_{\text{OO}}$ .

An alternative formulation of the partial structure factors was derived by Bhatia and Thornton [18] in terms of number density ( $N$ ) and concentration ( $C$ ) fluctuations, shown in Fig. 2 for the present data and the MD results for  $\text{SiO}_2$ , with  $Q$  scaled as in Fig. 1. A matter of some interest is the behavior of  $S_{\text{CC}}$  around the FSDP, since it shows up as a positive feature in the experimental results for molten  $\text{GeSe}_2$ ,  $\text{MgCl}_2$ , and  $\text{ZnCl}_2$ , perhaps reflecting the network character of these liquids [19]. In the present results for  $\text{GeO}_2$ ,  $S_{\text{CC}}$  is in fact slightly negative in this region, in contradiction to the inequalities discussed above. As expected, the CSRO peak shows up most strongly in  $S_{\text{CC}}$  and the TSRO peak in  $S_{\text{NN}}$ . The  $Q$ -scaled *ab initio* MD results for  $\text{SiO}_2$  are again

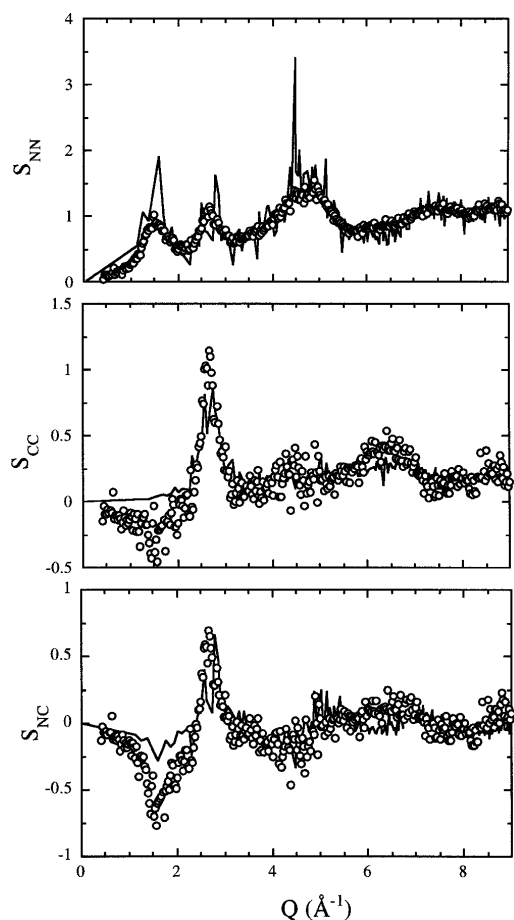


FIG. 2. Measured partial structure factors (Bhatia-Thornton definition [18]) in vitreous germania at room temperature (points), together with corresponding results from *ab initio* MD computer simulation [4,17] of vitreous silica ( $M = \text{Si}$ , lines), with the  $Q$  scale reduced by a factor 1.075.

qualitatively similar, except that  $S_{CC}$  is close to zero in the region of the FSDP. A similar behavior was found in the classical MD result for  $\text{SiO}_2$  [3] and the classical [14] and *ab initio* [15] MD results for  $\text{GeSe}_2$ .

We investigated the effect of changes in the input  $\mathbf{F}$  on the output  $\mathbf{S}$ . First, data from separate independent measurements, on the same instruments but at different times with new samples, were used as input. This had a relatively minor effect on the output. Second, a measurement of  $S^X(Q)$  at high energy (50 keV), using the setup described in Ref. [10], was used as an additional input and the partials extracted with an overconstrained least-squares procedure; this did not lead to any noticeable improvement in the results. Third, the effect of varying both the regular and anomalous terms in the Ge form factor was investigated; this had a significant effect in the case of large changes in the anomalous part but did not affect the general shape of the partials in Figs. 1 and 3. Thus, the results appear to be relatively robust, providing a reasonable degree of confidence in the conclusions reached.

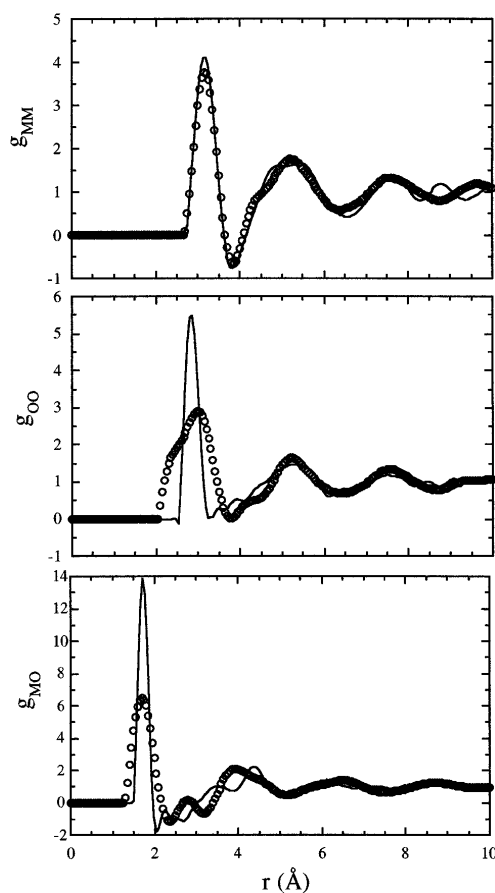


FIG. 3. Measured partial pair correlation functions for the three atom pairs in vitreous germania at room temperature ( $M = \text{Ge}$ , points), together with corresponding results from *ab initio* MD computer simulation [4,17] of vitreous silica ( $M = \text{Si}$ , lines), with the  $Q$  scale increased by a factor 1.075, both obtained by Fourier transformation of the results of Fig. 1.

Partial pair correlation functions  $g_{ij}(r)$ , obtained by Fourier transformations of the  $S_{ij}$ , are shown in Fig. 3. In the present data, the first peaks are well defined in each of the partials, although the peak in  $g_{OO}(r)$  has an unphysical structure reflecting a problem with the inversion of the data at high  $Q$ . Values for the positions of the first peaks in the three partials are given in Table I, together with corresponding values obtained in previous work. In previous work [5,9], it was pointed out that the value obtained for the Ge-Ge separation might be compromised by a possible contribution of Ge-O correlations to the peak in  $g^N(r)$  or  $G_{\text{Ge}}^X(r)$  identified with Ge-Ge; the present results show that any such effect is negligible. The values obtained here for the shortest Ge-O and Ge-Ge distances imply a bond angle of  $132^\circ \pm 5^\circ$ , consistent with the value of  $133^\circ$  obtained from recent high-energy XRD [7]. If the width of the first peak in  $g_{\text{GeO}}(r)$  is taken as a measure of the broadening due to the finite  $Q$  range in the Fourier transform, that of the first peak in  $g_{\text{GeGe}}(r)$  gives an estimated spread in bond angle of  $18^\circ \pm 2^\circ$ , again consistent with Ref. [7]. The peaks in the  $g_{ij}(r)$  at higher

TABLE I. Short-range structural parameters for GeO<sub>2</sub>.

Method	$r_{\text{GeO}}(\text{\AA})$	$r_{\text{OO}}(\text{\AA})$	$r_{\text{GeGe}}(\text{\AA})$	Ref.
ND + AXS	$1.73 \pm 0.03$	$2.83 \pm 0.05$	$3.16 \pm 0.03$	Present work
	1.75	2.82	3.18	[6]
ND	$1.739 \pm 0.005$	2.838	3.185	[5]
	$1.74 \pm 0.01$	$2.84 \pm 0.02$	$3.18 \pm 0.05$	[9]
XRD	1.73	2.83 <sup>a</sup>	3.17	[7]
AXS	$1.73 \pm 0.02$	...	$3.18 \pm 0.02$	[9]
	1.73	...	$3.17 \pm 0.04$	[8]

<sup>a</sup>Assumes perfect GeO<sub>4</sub> tetrahedron.

$r$  reflect the intermediate-range structure and appear to be significant. For comparison, crystalline GeO<sub>2</sub> in the  $\alpha$ -quartz structure [5], for example, has significant peaks in  $g_{\text{GeGe}}(r)$  at 4.5, 5.0, and 7.6  $\text{\AA}$ , in  $g_{\text{OO}}(r)$  at 5.1 and 7.5  $\text{\AA}$ , and in  $g_{\text{GeO}}(r)$  at 3.5 and 4.3  $\text{\AA}$ .

To provide a more meaningful comparison, the MD results for SiO<sub>2</sub> transformed in the same way as the present data are shown in Fig. 3, rather than the real-space results shown in Ref. [4], which are quite similar but show sharper first peaks without undershoot. The  $r$  values for the SiO<sub>2</sub> results are scaled up by 1.075. The agreement is generally good throughout the measured range of  $r$ . It should be noted, however, that the Si-Si distance is slightly underestimated in the MD result due to the large number of threefold rings [17], making the agreement for  $g_{\text{MM}}$  better than would be expected from the larger bond angle (148° as opposed to 133° in GeO<sub>2</sub> [7]).

In summary, this work provides results for the short- and intermediate-range order of vitreous germania in terms of the contributions of correlations involving the three element pairs. The results are consistent with the identification of the first three peaks in the average neutron and x-ray structure factors with IRO, CSRO, and TSRO, respectively. Results for the FSDP indicate that in this glass IRO is associated with cation correlations. The values for the shortest distances for the three element pairs are in agreement with previous work and suggest that possible complications with this technique, that might arise for example from shifts of the centers of the electron distributions from the nuclei, are not serious in the case of oxide glasses. We hope that these results will stimulate *ab initio* MD simulations of vitreous germania.

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