Simulations of void-filled vitreous silica to interpret the origin of the first sharp diffraction peak

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It has been proposed that the first sharp diffraction peak (FSDP) in the structure factor of covalent glasses is a prepeak in the concentration-concentration structure factor due to the chemical ordering of interstitial voids around cation-centered clusters in the structure. This void-based model predicts that if voids are occupied by extrinsic atoms the intensity of the FSDP will change. Dramatic changes in the FSDP have been observed by calculating the structure factor for a model of vitreous silica whose interstices were filled with He, Li, and Na. Moreover, a splitting of the FSDP has been observed in the case of the Na-filled model, similar to that observed experimentally for potassium silicate glasses. The origin of this splitting is found to arise from subtle cancellation effects among the partial structure factors.

I. INTRODUCTION

Medium-range order (MRO) in covalent glasses has been the subject of intense study.¹ In particular, the origin of the first sharp diffraction peak (FSDP) in the structure factor of covalent network glasses (e.g., SiO_2) remains controversial.^{2,3} The interest in the FSDP lies in its anomalous behavior and especially the negligible contribution to the real-space correlation function makes one believe that it contains rather subtle MRO information.

In consequence there have been many models²⁻⁴ suggested to explain the origin of the FSDP, e.g., quasicrystalline or cluster models. However, these models do not sufficiently explain a number of experimental observations and therefore another type of model based on voids has recently been proposed.^{2,3} The purpose of this work is to support this void-based model since it predicts many experimental results rather well.

II. VOID-BASED MODEL

The basis of this model is that an AX_2 type of glass (or liquid) can be regarded as comprising cation-centered quasispherical "clusters," AX_4 tetrahedra, which are separated by the average cation-cation distance, d = r(A - A), and surrounded by voids at an average distance D = r(A - V) from the cationic center. This structural representation enables us to apply to this type of glass Blétry's formulations⁵ for monatomic amorphous materials.

Blétry has shown that the structure of a tetravalent monatomic amorphous material (e.g., a-Si) can be represented approximately as a mixture of spherical atoms and holes, having the same diameter and concentration, arranged in a packing which maximizes the local chemical short-range order of holes and atoms. In accordance with this model, the overall neutron-scattering cross section in the Bhatia-Thornton formalism⁶ can be written as

$$\frac{d\sigma}{d\Omega} = N[\langle b \rangle^2 S_{\rm NN}(Q) + 2\langle b \rangle (b_a - b_v) S_{\rm NC}(Q) + (b_a - b_v)^2 S_{\rm CC}(Q)], \qquad (1)$$

where b_a and b_v are atomic and void scattering length, $S_{\rm NN}(Q)$, $S_{\rm NC}(Q)$, and $S_{\rm CC}(Q)$ are number-number, number-concentration, and concentration-concentration partial structure factors, respectively, and $\langle b \rangle$ is the compositionally weighted average scattering length,

$$\langle b \rangle = \sum_{i=1}^{n} x_i b_i = x_a b_a + x_v b_v , \qquad (2)$$

where x_i is the compositional fraction and b_i is the scattering length of component *i*. It has been shown⁵ that the first peak in the measured structure factor, S(Q), of this monatomic system, i.e., the FSDP, corresponds to a prepeak in $S_{CC}(Q)$.

Regarding AX_2 -type glasses as being constructed of quasispherical clusters, and applying to this model Blétry's conclusion, makes it possible to understand that the FSDP is a prepeak in the concentrationconcentration partial structure factor, $S_{\rm CC}(Q)$, due to the chemical short-range ordering of interstitial voids around cation-centered "clusters" in the structure of this model.^{2,3}

This model gives an interesting prediction. The intensity of the FSDP in this model is associated with the contrast in scattering length between the voids and the glassy matrix, according to the third term of Eq. (1), namely, $(b_a - b_v)^2 S_{CC}(Q)$, where b_v is supposed to be zero in the case of a pure AX_2 glass. Correspondingly the model predicts that, if the voids are filled with modifier atoms, say M, having positive neutron-scattering lengths, b_M , the contrast factor should be less and as a consequence the FSDP intensity should decrease. On the other hand, if b_M is negative, then it is predicted that the FSDP intensity should increase. Indeed, this behavior has been experimentally observed in some alkali-modified silicate⁷ and silver-modified germanium selenide glasses;⁸ the intensity of the FSDP in these glasses turned out, in general, to be much less compared with that in the modified



FIG. 1. Experimental structure factors, S(Q) of (a) $(Na_2O)(SiO_2)_2$, (b) $(Li_2O)(SiO_2)_2$, and (c) SiO_2 (Ref. 7).

network, viz., SiO_2 and $GeSe_2$.

Figure 1 shows the experimental structure factors of SiO₂ and some alkali disilicates.⁷ The changes in the intensity of the FSDP are obvious. Anomalously, the FSDP intensity increases in Li-modified silicate glasses; this behavior is understandable on the basis of the void model since Li has a negative scattering length⁹ $(b_{\text{Li}} = -0.203 \times 10^{-12} \text{ cm})$ and thus the contrast factor should increase with incorporation of Li. These experimental results are strongly supportive of the void-based model for the origin of the FSDP, although the mode of incorporation of modifier "ions" is known to be different from the case of simple stuffing of atoms into the interstitial sites. The introduction of modifier ions (e.g., Li⁺, Na^+ , and Ag^+ , etc.) depolymerizes the network (e.g., SiO₂ and GeSe₂, etc.) by forming negatively charged nonbridging anion centers at the expense of bridging anions.⁴ Therefore, structural changes of the network are also expected.

III. VITREOUS SILICA AS A REPRESENTATIVE MATERIAL

In order to obtain more evidence in support of the void-based model for the FSDP, some simulations have been performed by using vitreous silica, v-SiO₂, as a representative example of AX_2 -type glasses. This glass was selected because not only it but also alkali-modified silicates have been intensively studied by diffraction. The main aim of these simulations is that changes in S(Q), in particular the FSDP, may be demonstrated by comparing S(Q) for v-SiO₂ with and without M occupying a certain number of voids in the structure.

He, Li, and Na were used as atoms to be incorporated. Helium, with the smallest atomic radius, is known to dissolve into v-SiO₂ with a high solubility.^{10,11} It has been estimated that the saturated concentration of He in v-SiO₂ is 2.3×10^{21} atoms/cm³ under high pressure (several kbar).¹⁰ This means that about 10% of the interstices in v-SiO₂ are accessible to He.¹¹ Helium is suitable to test the void-based model since it is not supposed to interact with the v-SiO₂ network chemically and the only effect is expected to result from packing of the voids. Nonetheless, it is also very important to check if there are any changes in the FSDP when other atoms, e.g., Li or Na, are also accommodated into the voids.

IV. CALCULATION DETAILS

The model of vitreous silica used for these calculations was obtained from molecular-dynamics (MD) simulation.¹² This model was chosen because it gives the best agreement with experimental (diffraction) data for v-SiO₂.¹² Furthermore, in a previous void analysis of a number of different structural models of v-SiO₂,¹³ it was found that the void characteristics are practically independent of the model studied. The model contained 648 atoms (216 Si and 432 O) in a cube of side length 21.41 Å and the density of the model was 2.20 g cm⁻³ (0.066 atoms Å⁻³).

216 Li or Na atoms were inserted in the v-SiO₂ model in order to simulate approximately the alkali disilicate systems, namely, $(Li_2O)(SiO_2)_2$ and $(Na_2O)(SiO_2)_2$, respectively. However, no additional oxygen atoms were added to comply with these formulas. Thus, the compositions of these alkali-stuffed silica models are $(Li_2)(SiO_2)_2$ and $(Na_2)(SiO_2)_2$, rather than those of the real disilicates. This approximation neglects the complicated structural changes that are involved in real systems, such as the formation of nonbridging oxygen (NBO) configurations but enables us to concentrate on the changes in the FSDP when voids are filled with foreign atoms. In addition, the causes of subtle changes in the peaks in S(Q) can be clearly interpreted in this way by calculation of the partial structure factors. Li atoms were introduced into the same sites as Na so that any difference in calculated structure factors arises from scattering length effects alone and is not related to which voids are occupied by M atoms.

In order to accommodate M atoms, voids were identified in the structure. The basic void analysis was based on a previous work.¹³ In brief, all equidistant points from every set of four oxygen atoms in the sublattice of oxygen alone were calculated. In finding the voids, it was made sure that no oxygen atom was closer to the center of a void than the four oxygen atoms forming the void. It was also confirmed that no Si atom was closer to the center of a void than the radius of the sphere; thus, this procedure discarded the 216 sites occupied by Si atoms as well as voids which were nearer to silicon atoms than the four surrounding oxygen atoms. All voids left were certainly voids around SiO₄ tetrahedral quasiclusters so that they were suitable for consideration for the void-based model. These voids were sorted in order of their radius and M atoms were located at the centers of voids starting with the largest one, but only if the first O-M, as well as M-M, coordination shell simultaneously obeyed a Gaussian distribution,

$$F(x) = \frac{1}{\sqrt{2\pi\sigma}} \exp\left[\frac{-(x-\mu)^2}{2\sigma^2}\right],$$
(3)

where σ is the standard deviation and μ is the mean value of the position of the first peak in the radial distribution function (RDF).

In determining the value of σ and μ for the simulated stuffed glasses a model of glassy $(Na_2O)(SiO_2)_2$ was used.¹⁴ This system was used because of the ions under consideration, Na⁺ ions are the largest. It has been reported¹⁴ that the values of the first peak in the O-Na and Na-Na pair distribution functions of $(Na_2O)(SiO_2)_2$ glass are 2.40 and 3.33 Å, respectively, and therefore these values were used for μ . The values of the standard deviation, σ , were chosen to be 0.4 and 0.65 Å, respectively, for the O-Na and Na-Na distributions according to the approximate width of each distribution.¹⁴ The positions for M were searched one by one starting with the largest void. If the distances between this void and the nearest O and Na neighbors were greater than the average values, μ , it was unconditionally accepted; otherwise, it was accepted with a probability given by Eq. (3). If M atoms would be separated by a distance less than 2.0 Å, the void was also discarded. Choosing 2.0 Å for the minimum possible *M-M* separation is an arbitrary assumption, but this is physically meaningful for our purpose since the ionic radius of Na is about 1.0 Å.¹⁵ However, the possibility of percolation of M atoms accessing the voids from the surface of the model of v-SiO₂ was not considered. The aim of this algorithm was to construct models whose M atoms were separated by a reasonably large distance from each other and at the same time occupied large enough sites.

In the case of He, 22 atoms were chosen to be inserted since the saturated concentration of He in the cubic model of v-SiO₂ used corresponds to this value according to the experimental saturation concentration 2.3×10^{21} cm⁻³.¹⁰ Therefore, the composition of this model can be regarded as being (He)_{0.09}(SiO₂)_{0.91}. The He atoms were inserted in the largest voids found using the procedure outlined above. This model can be a plausible approximation of what the real structure of v-SiO₂ packed with He is like because, in the case of the real system, helium atoms will not change the network chemically but will occupy the available interstitial sites which already exist in the structure.

The length of the cube side of the model was maintained as 21.41 Å before and after the incorporation of Matoms, and number densities changed only in proportion to the numbers of atoms introduced. Table I shows the number densities of different models used in this study. Except for the case of silica these values are larger than the experimental number densities^{16,17} because, in this simulation, the size of cube was fixed to be 21.41 Å for the various models. It should be stressed again that models of $(M_2O)(SiO_2)_2$ (M = Li, Na) were not simulated in this study, but the values in the last column of Table I are the numbers to be expected if additional oxygens are included to comply with the formulas for the disilicates.

The total reduced RDF, G(r),

$$G(r) = 4\pi r \left[\sum_{ij} \frac{\dot{w}_{ij} \rho_{ij}(r)}{x_j} - \rho^0 \right]$$
(4)

was calculated from each model to obtain the structure factor S(Q), where x_j is the atomic fraction of element j, $\rho_{ij}(r)$ is the average number of j atoms per unit volume at a distance r from any i atom and the weighting factors w_{ij} are given by

$$w_{ij} = \frac{x_i x_j b_i b_j}{\langle b \rangle^2} , \qquad (5)$$

where b_i and b_j are the scattering lengths of atoms *i* and *j*, respectively.

The structure factor was calculated by Fourier transforming G(r),

$$S(Q) = 1 + \frac{1}{Q} \int_0^\infty G(r) \sin Qr \, dr \,. \tag{6}$$

Weighted partial radial distribution functions, $w_{ij}G_{ij}(r)$, and also structure factors, $w_{ij}S_{ij}(Q)$, were calculated to compare the individual contribution of each $G_{ij}(r)$ and $S_{ij}(Q)$ to the totals, since the total G(r) can be written as

$$G(\mathbf{r}) = \sum_{ij} w_{ij} G_{ij}(\mathbf{r}) \tag{7}$$

and accordingly the total S(Q) is written as

$$S(Q) = \sum_{ij} w_{ij} S_{ij}(Q) .$$
(8)

V. RESULTS AND DISCUSSION

The method of choosing *M* atomic positions from the voids, described above, resulted in Si-*M*, O-*M*, *M*-*M*

TABLE I. The number of atoms used for the simulations and the number densities of the models.

Number of atoms in a cube of side length =21.41 Å	SiO ₂	$(M)_{0.09}(SiO_2)_{0.91}, M = He$	$(M_2)(\mathrm{SiO}_2)_2,$ $M = \mathrm{Li}, \mathrm{Na}$	$(M_2 O)(SiO_2)_2,$ M = Li, Na
Si	21Ġ	216	216	216
Ο	432	432	432	540
М		22	216	216
Total	648	670	864	972
Number density				
$(\text{atoms } \check{A}^{-3})$	0.066	0.068	0.088	0.099ª

^aThe experimental number densities of $(Li_2O)_{0.33}(SiO_2)_{0.67}$ (Ref. 16) and $(Na_2O)_{0.33}(SiO_2)_{0.67}$ (Ref. 17) are 0.074 and 0.085 atoms Å ⁻³, respectively.

correlations whose first coordination shell was remarkably well defined. It is important to emphasize that the only criteria used in selecting the voids for accommodating M atoms was first size, and then the distance between voids, but voids were filled in random directions. As an example for the Na-stuffed silica model, Fig. 2 shows O-Na and Na-Na pair distribution functions whose values are multiplied by the corresponding weighting factors and are plotted on different scales. Both distribution functions have well-defined first coordination shells and rather well-defined peaks at larger distances. This is, in fact, a typical picture of partial correlation functions for glassy structures. The pairs O-Na and Na-Na can be renamed as O-void and void-void and therefore it is apparent that the interstices are indeed chemically ordered around SiO₄ clusters. It should be mentioned that a purely random selection of voids for decoration with Na or Li atoms, subject only to a minimum separation of 2.0 Å, gave very similar results to those shown in Fig. 2, with the exception of an unphysically sharp cutoff on the low-r side of the first peak in the Na-Na RDF. However, all partial structure factors calculated using this distribution were, nevertheless, very similar to those shown in Figs. 3-7. It is significant, also, that the first peak in the Na-Na partial RDF for the model curves at $r \approx 3.3$ Å (Fig. 2), is considerably smaller than the average Na-Na separation, $r \approx 4.4$ Å, calculated assuming a purely random (gaslike) distribution of Na ions [viz. r_{av} = $(4\pi\rho_{Na}/3)^{-1/3}$]. Thus, constraints imposed by the silica matrix prevent a truly random distribution of Na ions from being achieved.

The number of oxygen atoms around Na (or Li) in the first coordination shell (1.9-3.4 Å) was found from Fig. 2 to be 7.8. This value might be expected to be 4 since the Na positions were selected from the voids which were found from sets of four oxygen atoms. However, counting the number of oxygen atoms around a given Na atom within the range 1.9-3.4 Å should result in a value, generally, greater than 4 since this will include neighbouring oxygen atoms but which do not define a void in the strict sense used to define an interstitial void here. This value is rather larger than the experimental value of 5 for sodium disilicate glass obtained from extended x-ray absorption fine structure (EXAFS).¹⁸

The calculated total S(Q) for the model of v-SiO₂ is



FIG. 2. Calculated weighted partial radial distribution functions of O-Na and Na-Na correlations.



FIG. 3. Calculated total structure factors, S(Q). ----, SiO_2 ; ---, $(He)_{0.09}(SiO_2)_{0.91}$.

shown in Fig. 3 together with S(Q) calculated for $(\text{He})_{0.09}(\text{SiO}_2)_{0.91}$. For v-SiO₂, three major peaks can be noticed at about 1.6 Å⁻¹ (which is the FSDP), 2.9, and 5.2 Å⁻¹ and this curve reproduces the experimental neutron results of v-SiO₂ very well.¹⁹ A slight yet significant change of intensity is apparent in the FSDP between the unstuffed and stuffed models, while the other two peaks remain almost the same. This is in agreement with the prediction³ that if voids are replaced with other atoms (with positive scattering lengths), the intensity of the FSDP will be decreased. This is strong evidence for the void-based model.

Some other results from the simulations of alkalistuffed models also reinforce the void-based model. From Fig. 4, it can be seen that the intensity of the FSDP is enhanced by incorporating Li atoms into v-SiO₂, whereas inserting Na atoms resulted in a much less intense FSDP than in v-SiO₂. This behavior is consistent with the prediction of the void-based model.³ Figures 5 and 6 show that the changes in the FSDP result from the effect of incorporating alkali ions. In these figures, the $S_{ij}(Q)$'s are multiplied by their weighting factors w_{ij} , and also heteroatomic correlations which are involved in the total structure factor twice [Eq. (8)] are multiplied by 2 and



FIG. 4. Calculated total structure factors, S(Q). —, $SiO_2; --$, $(Li_2)(SiO_2)_2;$ —, $(Na_2)(SiO_2)_2$.



FIG. 5. Calculated weighted partial structure factors involving atom M. (a) $(\text{Li}_2)(\text{SiO}_2)_2$. \dots , $2w_{\text{SiLi}}S_{\text{SiLi}}(Q)-1$; --, $2w_{\text{OLi}}S_{\text{OLi}}(Q)-1$; \dots , $w_{\text{LiLi}}S_{\text{LiLi}}(Q)$. (b) $(\text{Na}_2)(\text{SiO}_2)_2$. \dots , $2w_{\text{SiNa}}S_{\text{SiNa}}(Q)-1$; --, $2w_{\text{ONa}}S_{\text{ONa}}(Q)-1$; \dots , $w_{\text{NaNa}}S_{\text{NaNa}}(Q)$.

subtracted by 1 to normalize to unity. This is in order to give the real relative magnitude of each partial structure factor contributing to the total S(Q). Partial structure factors for the model containing the modifying atoms are shown in Figs. 5(a) and 5(b) and partial structure factors of the silicaceous framework are presented in Fig. 6. In Fig. 6, the axes on the left and the right denote the values



FIG. 6. Calculated weighted partial structure factors not involving atom M. —, $w_{SiSi}S_{SiSi}(Q)$; ---, $2w_{Si}S_{Si}(Q)-1$; —, $w_{OO}S_{OO}(Q)$.



FIG. 7. Sums of calculated weighted partial structure factors of Si-Si, Si-O and O-O correlations and of Si-M, O-M and M-M correlations. (a) $(\text{Li}_2)(\text{SiO}_2)_2$. —, $w_{\text{SiSi}}S_{\text{SiSi}}(Q)$ $+2w_{\text{SiO}}S_{\text{SiO}}(Q)+w_{\text{OO}}S_{\text{OO}}(Q)-3$; --, $2w_{\text{SiLi}}S_{\text{SiLi}}(Q)$ $+2w_{\text{OLi}}S_{\text{OLi}}(Q)+w_{\text{LiLi}}S_{\text{LiLi}}(Q)-4$. (b) $(\text{Na}_2)(\text{SiO}_2)_2$. —, $w_{\text{SiSi}}S_{\text{SiSi}}(Q)+2w_{\text{SiO}}S_{\text{SiO}}(Q)+w_{\text{OO}}S_{\text{OO}}(Q)-3$; --, $2w_{\text{SiNa}}S_{\text{SiNa}}(Q)+2w_{\text{SiNa}}S_{\text{SiNa}}(Q)+w_{\text{ONA}}S_{\text{ONA}}(Q)+w_{\text{NaNa}}S_{\text{NaNa}}(Q)-4$.



FIG. 8. Experimental distinct scattering cross section, i(Q), for the potassium silicate, $(K_2O)(SiO_2)_{2.8}$ (Ref. 20).

TABLE II. The weighting factors w_{ij} for each atomic pair for different glasses.

Correlation	SiO ₂	Correlation	$(Li_2)(SiO_2)_2$	$(Li_2O)(SiO_2)_2$	Correlation	$(Na_2)(SiO_2)_2$	$(Na_2O)(SiO_2)_2$
Si-Si	0.069	Si-Si	0.091	0.062	Si-Si	0.045	0.034
Si-O	0.194	Si-O	0.255	0.217	Si-O	0.128	0.121
0-0	0.544	0-0	0.716	0.762	0-0	0.360	0.425
		Si-Li	-0.044	-0.030	Si-Na	0.040	0.030
		O-Li	-0.125	-0.106	O-Na	0.112	0.106
		Li-Li	0.022	0.015	Na-Na	0.035	0.026

for Li- and Na-stuffed v-SiO₂, respectively, since the weighting factors of the partial correlation functions of these two glasses are different. From these figures, it can be ascertained that the intensity of the FSDP is enhanced for Li or reduced for Na because of the Si-M and O-M partial contributions.

Figures 7(a) and 7(b) also clarify the role of the different incorporated ions. The solid and dotted lines depict, respectively, the sum of the partial structure factors of Si-Si, Si-O, and O-O pairs and of Si-M, O-M, and *M-M* pairs. These sums are appropriately multiplied and subtracted as described above. As a matter of fact, the sum of the partial structure factors of the silicaceous framework is more intense in the case of the Li-stuffed glass than for the Na-stuffed glass due to the differences in the values of the weighting factors (Table II). However, the principal change in the FSDP results from the extra addition of the partial structure factors including the M contributions. Because of the positive or negative contribution of the sum of the partial structure factors including M to the first peak at about 1.6 Å $^{-1}$, for Li and Na, respectively, this peak is significantly enhanced or reduced in each case.

There is another interesting aspect as well. The FSDP is observed to split into two peaks in the case of the $(Na_2)(SiO_2)_2$ model; a new peak appears at 2.1 Å⁻¹. A similar behavior has been observed experimentally in $(K_2O)(SiO_2)_{2.8}$ glass which exhibits a split peak at about 2.1 Å^{-1.20} The experimental distinct scattering cross section, i(Q), for the potassium silicate, $(K_2O)(SiO_2)_{2.8}$, is shown in Fig. 8. Because the neutron-scattering length of natural K is 0.371×10^{-12} cm⁻³,⁹ which is nearly the same as that of Na, 0.363×10^{-12} cm⁻³,⁹ these results can reasonably be compared with our simulated results.

The causes of this split peak can be rather easily explained by examining the partial structure factors $S_{ij}(Q)$ shown in Figs. 5–7. The peak at 2.1 Å⁻¹ in Na-stuffed silica is mainly due to the positive contribution of the peak at 2.2 Å⁻¹ in $S_{ONa}(Q)$ while the negative contribution of the peak at the same position in $S_{OLi}(Q)$ is mixed into the nearby minimum at 2.3 Å⁻¹. In Fig. 7(b), it is clearer that a rather subtle cancellation of the two types of sum results in the small split peak at 2.1 Å⁻¹.

However, this split peak was not observed experimentally for glassy $(Na_2O)(SiO_2)_2$ (Fig. 1). This may be because of the overestimated coordination number of oxygen atoms about Na and vice versa in this simulation. The value of 7.8 is closer to the coordination number of oxygen atoms around K, being between 5 and 6 in the case of $(K_2O)(SiO_2)_2$ glass.²¹ This affects the intensity of $G_{ONa}(r)$ and as well as $S_{ONa}(Q)$. A slight change in the intensity of the O-Na pair distribution function can greatly affect the small split peak.

In contrast to the experimental results in Fig. 1, the second peak in the structure factor at about 2.9 Å $^{-1}$ shows the reverse tendency of change of intensity with type of modifier; namely, in the simulated glasses, the intensity of the peak increases in Na-stuffed silica whereas it decreases in the Li-stuffed structure. This is another consequence of a delicate cancellation of partial structure factors. In the case of pure silica, the main contributions to the peak at 2.9 Å $^{-1}$ are a strong O-O correlation and a rather weak Si-Si correlation which is more or less cancelled out by a negative contribution of the Si-O correlation but nevertheless which still remains as a somewhat weak peak. In fact these three partial correlations are also the most important contributions to the second peak at about 2.9 Å ⁻¹ in the alkali-stuffed glasses. However, the negative contribution of the O-Li partial greatly reduces the intensity of this peak in the Li-stuffed glass, while the positive contribution of the O-Na partial increases the intensity in the Na-stuffed glass; accordingly the intensity of this peak in the total S(Q) has been changed by this effect.

This is the result of slight differences of weighting factors of the real disilicate glasses and our models of alkalimodified silica which do not involve as many oxygen atoms as those of the real materials. As Table II shows, the contribution of O-O correlations is smaller, and that of Si-O correlations is bigger, in the cases of $(Li_2)(SiO_2)_2$ and $(Na_2)(SiO_2)_2$ compared with the cases of $(Li_2O)(SiO_2)_2$ and $(Na_2O)(SiO_2)_2$; therefore the magnitude of these two contributions will be bigger in the case of the real glasses. This means that the intensity of the peak at about 2.9 Å $^{-1}$ contributed by the silicaceous framework alone must be more intense than that in our model. Moreover, since the absolute value of the weighting factor of O-M correlations (M = Li and Na) is actually smaller in the real glasses, these correlations do not contribute to the second peak at about 2.9 Å $^{-1}$ as much as in our models. These two opposing effects together change the peak significantly.

Since there is little extra contribution from the partial structure factors involving modifying ions, the trend of intensities with alkali type of the third peak at around 5.2 \AA^{-1} is the same as that in the experimental results shown in Fig. 1.

VI. CONCLUSION

A void-based model interprets the FSDP in structure factors of covalent glasses as being a prepeak in the concentration-concentration structure factor due to the chemical ordering of interstitial voids around cationcentered clusters in the structure. Therefore, it can be predicted that, if the voids are filled with foreign atoms, some changes in the FSDP will occur. In this study, calculations and comparisons of the structure factors of the representative material v-SiO₂ whose intersticies were filled with He, Li, and Na have been performed to simulate the void-based model. These simulations enabled us to observe remarkable changes in the FSDP in the structure factors of the three kinds of modified $v-SiO_2$. In the case of the structure stuffed with an element having a negative scattering length (Li), the neutron FSDP intensity increased, whereas for structures stuffed with positive scattering-length atoms, the FSDP intensity decreased

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relative to the pure material $(v-SiO_2)$. This is in qualitative agreement with the trends observed experimentally⁷ in lithium and sodium disilicate glasses. Because the only difference between these modified silica glasses and $v-SiO_2$ was the fact that some of the voids around the quasispherical SiO₄ tetrahedra were filled with foreign atoms, it is ensured that the results arise entirely from the void effects. Moreover, we have found a splitting of the FSDP for the Na-stuffed model, as found in the experimental neutron-scattering data for glassy potassium silicate. This splitting is traced to subtle cancellation effects in the addition of the partial structure factors.

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