# Formation of channels for fast-ion diffusion in alkali silicate melts: A quasielastic neutron scattering study

F. Kargl,[1,*] A. Meyer,[1,†] M. M. Koza,[2] and H. Schober[2]

[1]*Physik Department E13, Technische Universität München, 85747 Garching, Germany*
[2]*Institut Laue-Langevin, 38042 Grenoble, France*

The mechanism of alkali ion diffusion in sodium, lithium, and potassium disilicate melts is studied by means of quasielastic neutron scattering. Although scattering on alkali atoms comprises coherent and incoherent contributions, only incoherent scattering contributes to the quasielastic signal of the diffusing alkali atoms on time scales up to about 60 ps. Such a decoupling of incoherent from coherent correlations is a signature of an alkali ion diffusion along channels that are embedded in the relatively immobile Si-O network.

In alkali silicates the diffusion of the alkali atoms is even in the melt orders of magnitude faster than the diffusion of the network forming constituents Si and O.[1,2] It was found that besides this behavior the extraordinary nonlinear dependence of viscosity on the alkali oxide concentration[3,4] cannot be explained by a homogeneous distribution of the alkali atoms. Lacking an explanation for these properties, preferential pathways for the alkali ion diffusion have been proposed and searched for in the last years.[5,6] Preferential pathways for ion conduction are one means to potentially explain the decoupling of the SiO-network dynamics of the alkali ion diffusion.

Recently, molecular dynamics (MD) simulations on sodium silicate models showed that the sodium atoms diffuse in a relatively immobile Si-O network via sodium rich channels.[7,8] A pronounced feature of this network of channels is a prepeak in the static structure factor around $0.9$ Å$^{-1}$. A neutron scattering study on a sodium disilicate melt indeed revealed an emerging prepeak at $0.9$ Å$^{-1}$ that becomes more pronounced with increasing temperature.[9] A qualitative agreement was observed between the temperature and concentration dependence of the elastic structure factors measured by inelastic neutron scattering and those derived from the MD simulation.[10] The existence of preferential pathways is not only reflected by the correlation peak but also by the dynamics of the Na ions and the network. The MD simulation reveals a decoupling of the time scales for the decay of the Na-Na pair as well as the network self- and pair correlators from the decay of the Na self-correlator.[7] Moreover, the relaxation time scales show a distinct dependence on the momentum transfer $q$.

Here we contribute to the understanding of the mechanism of fast alkali relaxation by means of quasielastic neutron scattering on lithium, sodium, and potassium disilicate melts. The intrinsic $q$ resolution of quasielastic neutron scattering and the variation of incoherent and coherent scattering lengths for the different alkali atoms allows one to elucidate in great detail the peculiar dynamics of these systems. The experiments reveal the self- and pair correlators indeed decaying on different time scales. We find that the incoherent Na contribution to the density correlation function decays on a 10 ps time scale. In the small $q$ limit its relaxation time corresponds to the alkali self-diffusion coefficient. Coherent

contributions to the signal are not observed up to 60 ps, hence relaxation of pair correlations must be at least an order of magnitude slower in accordance with the MD simulation on sodium disilicate.[7] Our inelastic neutron scattering experiments show that the alkali ions in binary silicate melts indeed diffuse via diffusion channels in a relatively immobile Si-O network.

The binary alkali silicates $^7$Li$_2$O 2SiO$_2$, Na$_2$O 2SiO$_2$, and K$_2$O 2SiO$_2$ were investigated by means of quasielastic neutron scattering. The latter two samples were synthesized from pure SiO$_2$, Na$_2$CO$_3$, and K$_2$CO$_3$ powders at 1250 °C under air in a Pt crucible. In $^7$Li$_2$O 2SiO$_2$ $^6$Li was replaced by the isotope $^7$Li due to the large absorption cross section of $^6$Li. This sample was provided by Paul Heitjans from the University of Hanover. For homogenization the samples were annealed at 1300 °C for 12 h. Weight measurements before and after annealing showed sodium and potassium evaporation being negligible. The inelastic neutron scattering experiments were performed using Pt sample holders that provide a hollow cylindrical sample geometry of 30 mm height, 22.5 mm outer diameter, and 1.25 mm wall thickness. This sample geometry results in a 5%–8% scatterer, where multiple scattering only has a minor effect on the signal.

The experiments on $^7$Li$_2$O 2SiO$_2$ and K$_2$O 2SiO$_2$ were performed on the crystal time-of-flight spectrometer IN6 at the Institute Laue-Langevin (ILL). An incident neutron wavelength of $\lambda = 5.9$ Å yielded an accessible time range up to 30 ps [50 $\mu$ev full width at half maximum (FWHM)]. The experiment on Na$_2$O 2SiO$_2$ was performed on the disk chopper time-of-flight spectrometer IN5 with an incident neutron wavelength of $\lambda = 8$ Å. This setup gave access to time scales of up to 60 ps (35 $\mu$eV FWHM) and a dynamic structure factor at a $q$ value as low as $0.25$ Å$^{-1}$. Moreover, spectra from an earlier IN6 experiment[9] on Na$_2$O 2SiO$_2$ have been analyzed allowing for an extended $q$ range of up to 2 Å$^{-1}$ at a relaxed energy resolution of 88 $\mu$eV FWHM. Measurements were performed at 300 K and in the melt up to 1600 K on both instruments.

Data reduction was performed using the Frida-1 program.[11] It includes normalization to a vanadium standard, background subtraction, correction for self-absorption as well as container scattering and interpolation to constant
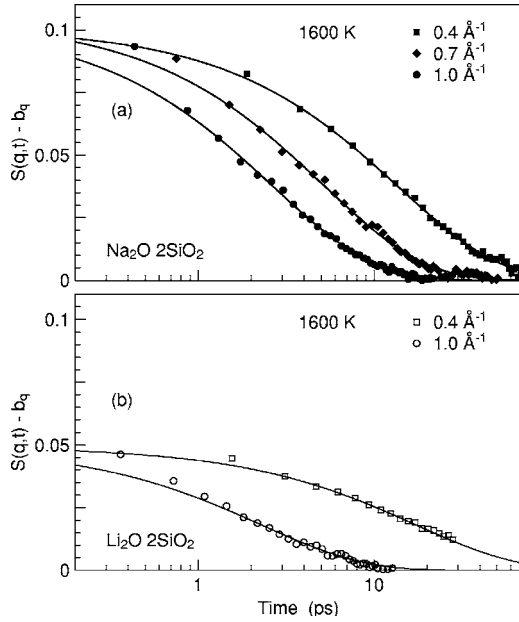
FIG. 1. Density correlation functions of (a) sodium and (b) lithium disilicate melts in the fast alkali relaxation regime. The solid lines represent fits with a stretched exponential function [Eq. (1)]. For clarity the elastic contribution $b_q$ to the spectra was subtracted. Corresponding to the ratio of the incoherent scattering cross sections of the alkali atoms the amplitude of the alkali relaxation is about a factor of two smaller in $^7$Li$_2$O 2SiO$_2$ than in Na$_2$O 2SiO$_2$.

wave numbers $q$. The dynamic structure factor $S(q,\omega)$ was further transformed by means of Fourier deconvolution into the density correlation function $S(q,t)$,[12] where only the neutron energy gain side is used for the Fourier transformation. In the following our discussion is based on $S(q,t)$. For a visualization of $S(q,\omega)$ as it is measured in our experiments the interested reader is referred to our previous paper on sodium disilicate.[9] Elastic structure factors $S(q,\omega=0)$ were obtained by integrating the dynamic structure factor over the instrumental energy resolution function. To a good approximation this quantity is proportional to the product of the static structure factor $S(q)$ and the Debye-Waller factor $f_q$.[13]

Figure 1 shows the density correlation function of the sodium and lithium disilicate melts for different $q$. Below $\sim 0.8$ ps the broad band of vibrational excitations leads to a rapid dephasing of correlations and hence a decrease in $S(q,t)$ by a value that is proportional to $1-f_q$. Above $\sim 0.8$ ps the relaxation of the alkali atoms leads to a decrease towards a plateau. We will show that this relaxation of the alkali atoms corresponds to their long range diffusive motion. The plateau corresponds to the elastic contribution to the signal of the relatively immobile Si-O network that exhibits a structural relaxation on a 10 ns time scale.[9] In the following, we demonstrate that coherent alkali contributions to the scattering also add to this plateau.

Beyond 0.8 ps the spectra are well described by a stretched exponential function

$$F(q,t) = b_q + a_q \cdot \exp\{-(t/\tau_q)^\beta\}, \qquad (1)$$

where $a_q$ is the amplitude of the fast alkali relaxation and $\tau_q$ its relaxation time. The quantity $b_q$ represents the elastic con-

TABLE I. Coherent $\sigma_c$ and incoherent $\sigma_i$ cross sections of the investigated alkali atoms in barn ($10^{-24}$ cm$^2$) (Ref. 15).

|            | Li         | Na       | K         |
|------------|------------|----------|-----------|
| $\sigma_c$ | 0.619(11)  | 1.66(2)  | 1.69(2)   |
| $\sigma_i$ | 0.78(3)    | 1.62(3)  | 0.27(11)  |

tribution to the signal. In the investigated $q$ and temperature range we found a stretching exponent $\beta = 0.75 \pm 0.05$ to describe the data. Above $\sim 1$ Å$^{-1}$ the derived amplitudes $a_q$ turn increasingly overestimated upon increasing $q$, because the sodium relaxation times are approaching the times of atomic vibrations. The strength of the atomic vibrations scales according to Debyes law as $[1-\exp(-q^2\langle u^2 \rangle)]$ with the mean square displacement $\langle u^2 \rangle$. We estimate from the data the effect on the amplitude $a_q$ to be about 20% at 2 Å$^{-1}$. In turn, the overestimation of the amplitude leads to an underestimation of the relaxation time that also approximates about 20% at 2 Å$^{-1}$.

Relaxation times of the fast alkali relaxation in lithium disilicate are about a factor of two smaller than relaxation times in sodium disilicate (Fig. 1). This indicates a Li diffusivity that is two times larger than that for Na. This finding is in agreement with conductivity data that shows Li, Na, and K diffusivities only varying within a factor of four in the melt.[14] Although conductivity data predict the potassium diffusion and thus the relaxation times at 1600 K to be in the range of our quasielastic neutron scattering measurement, a quasielastic signal could not be resolved (not shown). This is attributed to the small incoherent cross section $\sigma_i$ (compare Table I) for scattering on potassium (see discussion below).

Figure 2(a) depicts the fit amplitudes $a_q$ and $b_q$ derived for Na$_2$O 2SiO$_2$. The elastic amplitude $b_q$ depends on $q$ with a broad maximum between 0.9 Å$^{-1}$ and 1.5 Å$^{-1}$. It is proportional to the elastic structure factor. In contrast, the amplitude $a_q$ of the sodium relaxation is fairly constant over the measured $q$ range. The mean relaxation time $\langle \tau_q \rangle$ exhibits a continuous decrease with increasing $q$ [Fig. 2(b)]. For small $q$ the mean relaxation time is proportional to $q^{-2}$ [see inset of Fig. 2(b)].

Discussing our data we note again that the amplitude $a_q$ of the sodium relaxation in Na$_2$O 2SiO$_2$ shows no pronounced oscillations in $q$ [Fig. 2(a)]. This is characteristic for an incoherent scatterer exhibiting long range atomic transport.[16] In case of coherent scattering on diffusing particles in viscous liquids[17–19] the static structure factor $S(q)$ of the diffusing constituents is proportional to the quasielastic amplitude $a_q$. In addition, the relaxation time $\langle \tau_q \rangle$ shows variations that are in phase with the static structure factor.

Consequently for the alkali silicates $a_q$ and $\tau_q$ are expected to show oscillations that are in phase with the partial alkali-alkali structure factor if coherent scattering processes add to the signal. Lacking a measured alkali-alkali partial structure factor in these melts one cannot conclude on the exact strength of the coherent oscillations in $a_q$ and $\tau_q$. Nevertheless, the amplitude $a_q$ of the alkali relaxation [Fig. 2(a)] should display large variations over the measured $q$ range, since the coherent scattering cross sections for sodium and
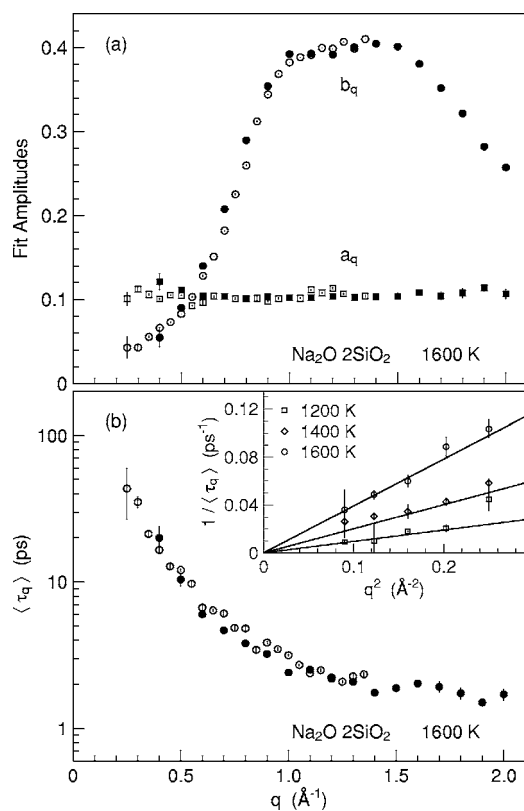
FIG. 2. Amplitude $a_q$ of the sodium relaxation, elastic amplitude $b_q$, and mean relaxation time $\langle \tau_q \rangle$ in sodium disilicate at 1600 K. Open symbols were obtained from IN5 data, closed symbols were obtained from Ref. 9 via fits with Eq. (1). (a): $a_q$ is $q$ independent. $b_q$ is proportional to the elastic structure factor. (b): $\langle \tau_q \rangle$ exhibits a continuous decrease with increasing $q$. For small wave numbers $\langle \tau_q \rangle \propto q^{-2}$ holds (inset).

lithium are similar to their respective incoherent cross sections (Table I). Moreover, following an estimation based on the partial structure factors obtained from the simulation,[10] one expects oscillations in $a_q$ that exceed 100% at 0.9 Å$^{-1}$. Such an oscillating behavior of $a_q$ is not observed in the measured data.

Further strong evidence, that the fast sodium relaxation indeed only displays incoherent contributions, lies in the comparison of the $a_q$'s of lithium, sodium, and potassium silicates. In good agreement with the ratio of the incoherent cross sections of $^7$Li and of Na the relaxation amplitude $a_q$ of the lithium disilicate melt [Fig. 1(b)] is also reduced by a factor of two in comparison with sodium disilicate [Fig. 1(a)]. The incoherent cross section of potassium is six times smaller than that for sodium. Hence, in agreement with our conclusions, in potassium disilicate a quasielastic contribution to the signal can hardly be resolved, although the coherent cross section of potassium exhibits a similar value compared to sodium.

The mean relaxation time $\langle \tau_q \rangle$ of the fast sodium diffusion shown in Fig. 2(b) also does not display any systematic oscillations that are proportional to the partial structure factor as expected for coherent scattering.[18,19]

The $q$ dependence of the relaxation amplitude, the relaxation time, and the comparison of the relaxation amplitudes
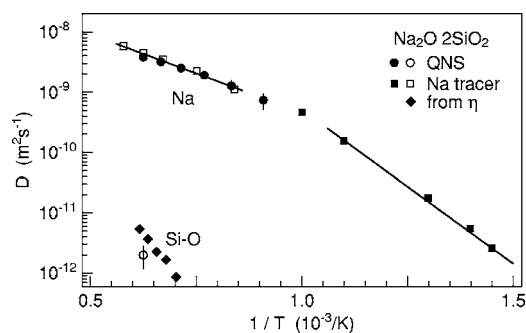


FIG. 3. Diffusion in sodium disilicate: sodium diffusion coefficients obtained by tracer diffusion (filled squares) (Ref. 25) and (open squares) (Ref. 1) compare well to sodium self-diffusion coefficients obtained by quasielastic neutron scattering (QNS) (closed circles). Even in the melt sodium diffuses orders of magnitude faster than Si-O. Diffusion coefficients estimated from neutron backscattering data (Ref. 9) (open circles) and calculated via the Stokes-Einstein relation from viscosity data (Ref. 4) (diamonds).

of different alkali silicates demonstrate that the observed fast sodium relaxation on the accessible time scale up to 60 ps comprises only incoherent scattering contributions. Coherent contributions to the fast alkali relaxation are not observed. Therefore, coherent alkali pair correlations must decay with relaxation times that are larger than the time scales accessible in our experiment. Hence, the decay of the incoherent self-correlations of the alkali atoms is decoupled by at least an order of magnitude from the coherent pair correlations. Summing up the previous paragraphs our data clearly demonstrate that the relaxation time of the alkali self-correlation function as seen by incoherent neutron scattering is decoupled of the corresponding pair correlation function as seen by coherent scattering.

As it is shown in the simulation by Horbach and co-workers[7,20] a sodium diffusion mechanism acting along a network of channels requires such a decoupling. On the contrary a decoupling of the time scales for the decay of the coherent and the incoherent correlators by at least an order of magnitude is not observed for bulk diffusion.[21] It is also not observed for diffusion inside a sphere which is the corresponding structure if we were dealing with Na atoms segregated in clusters. Here, even the contrary is observed in a zeolite material providing cages for the diffusing species.[22] For the one-dimensional (1D) and the single file case detailed nuclear magnetic resonance and neutron scattering studies were reported for zeolites.[23,24] However, the surrounding matrix is completely frozen and not only separated by three orders of magnitude in relaxation time as in the alkali silicate melts. Thus the results on the self- and pair dynamics in these systems cannot be directly compared to the silicate melts. For the alkali silicate melts subject to this study the incoherent scattering on the alkali atoms corresponds to their fast diffusion within the channels, the coherent scattering to the rearrangement of the channels on the time scale of the Si-O network relaxation.

In the following we discuss transport coefficients for the sodium disilicate melt shown in Fig. 3. We remind the reader that the inset of Fig. 2(b) depicts the relaxation rate $(1/\langle \tau_q \rangle)$

scaling with $q^2$. For incoherent scattering this allows to derive the self-diffusion coefficient $D = 1/(\langle \tau_q \rangle q^2)$ on an absolute scale.[16] We further note that for the lithium disilicate sample the accessible $q$ and time range of our measurement does not allow one to extract a Li self-diffusion coefficient with high accuracy. Values for the Na self-diffusion coefficients vary between $0.7 \pm 0.2 \cdot 10^{-9}$ m$^2$ s$^{-1}$ at 1100 K and $3.8 \pm 0.3 \cdot 10^{-9}$ m$^2$ s$^{-1}$ at 1600 K following an Arrhenius law. Na self-diffusivities derived by QNS and tracer diffusion[1] are equal within the experimental error. This demonstrates that the fast sodium relaxation observed on a 10 ps time scale and at the microscopic length scale of our quasielastic neutron scattering experiment corresponds to the long range sodium diffusion.

Furthermore, this finding indicates that all Na atoms participate in the fast long range diffusion. Tracer diffusion gives the macroscopic average of the self-diffusion of all Na atoms, while in our neutron scattering experiment we only detect fast relaxations up to 60 ps. Consequently, the amplitude $a_q$ of the fast alkali relaxation is temperature independent in the investigated temperature range from 1100 to 1600 K (not shown). This result conflicts with the picture derived from a MD simulation on sodium tetra silicate,[26] where substantial amounts of Na atoms have been identified to be outside of the diffusion channels and to exhibit relaxation times that approach the large Si-O network relaxation time.

From the incoherent alkali relaxation we are not able to extract a characteristic length scale for this channel network. However, inelastic neutron scattering also gives access to the elastic structure on an intermediate length scale. A comparison of MD simulation and neutron scattering for sodium silicates[10] showed a prepeak in the elastic structure factor around 0.9 Å$^{-1}$ marking characteristic interchannel distances. We note that the neutron scattering structure factors in alkali silicates represent a sum of six partial structure factors that are weighed with the neutron scattering cross sections. Incoherent scattering results in a flat background in $S(q, \omega = 0)$.

Figure 4 shows a comparison of the elastic structure factors of Li, Na, and K disilicate melts at 1600 K. Potassium disilicate exhibits a pronounced peak at about 0.85 Å$^{-1}$ in agreement with results of a recent neutron diffraction experiment on KS2 (Ref. 27). In sodium disilicate in the total neutron scattering structure factor the prepeak only appears as a shoulder around 0.9 Å$^{-1}$—in lithium disilicate only as an extra intensity around 1 Å$^{-1}$. The prepeak position shifts to larger wave numbers with a decreasing size of the alkali atoms as expected for a decreasing interchannel distance.

Lithium, sodium, and potassium silicate melts exhibit a similar nonlinear behavior of viscosity upon alkali oxide concentration and a fast alkali ion diffusion.[3] Together with the observed prepeak in the elastic structure factor in potassium disilicate, this indicates that the potassium atoms diffuse along channels as well. Although such a prepeak is not
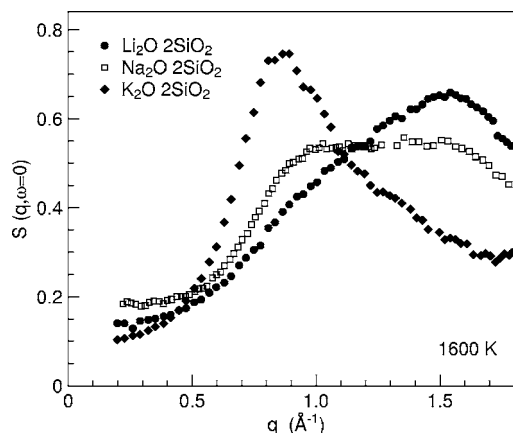


FIG. 4. Elastic structure factor of K$_2$O 2SiO$_2$, Na$_2$O 2SiO$_2$, and $^7$Li$_2$O 2SiO$_2$ at 1600 K. The prepeak most pronounced in K$_2$O 2SiO$_2$ decreases with the size of the alkali atoms. The prepeak position shifts to smaller wave numbers in the order $^7$Li$_2$O 2SiO$_2$ > Na$_2$O 2SiO$_2$ > K$_2$O 2SiO$_2$.

clearly seen in the elastic structure factor of lithium disilicate, a MD simulation on lithium silicate melts also revealed the existence of lithium diffusion channels.[28] Therefore, lithium, sodium, and potassium silicate melts exhibit the same underlying mechanism for the fast alkali diffusion via diffusion channels.

Our measured data are in agreement with the results of the MD simulations on sodium disilicate melts.[7] In the simulation the Na self-correlation function decays on the time scale of the fast sodium ion diffusion, whereas Na-Na pair correlations decay on the 10 ns time scale of the Si-O network relaxation. The $q$ dependence of the measured mean relaxation time of the fast sodium relaxation qualitatively agrees with the one observed in the MD simulation.[7] However, in the experiment it is about an order of magnitude smaller.

In conclusion, our quasielastic neutron scattering experiments on lithium, sodium, and potassium disilicate melts show, model independent, that the alkali ions diffuse via alkali rich channels in a relatively immobile Si-O network. A characteristic length scale for this network of channels is marked by prepeaks in the elastic structure factors with positions that shift to larger $q$ values with a decreasing alkali ion radius. The diffusion via these channels results in a decoupling of incoherent from coherent correlations of the alkali relaxation. The observed fast relaxation process that leads to long range atomic transport is incoherent over the dynamic range of our experiment of up to 60 ps. This is evidenced by relaxation amplitudes that are $q$ independent and whose values scale with the incoherent scattering cross sections of the different alkali atoms and relaxation times that exhibit no coherent oscillations.

*Present address: Department of Applied Physics, Chalmers University of Technology, Göteborg, Sweden

†Electronic address: ameyer@ph.tum.de

[1] Y. P. Gupta and T. B. King, Trans. Metall. Soc. AIME **239**, 1701 (1967).

[2] Y. Oishi, R. Terai, and H. Ueda, in *Mass Transport Phenomena in Ceramics*, edited by A. R. Cooper and A. H. Heuer (Plenum Press, New York, 1975).

[3] O. V. Mazurin, M. V. Streltsina, and T. P. Shvaiko-Shvaikovskaya, *Handbook of Glass Data, Part A: Silica Glass and Binary Silicate Glasses* (Elsevier, Amsterdam, 1983).

[4] R. Knoche, D. B. Dingwell, F. A. Seifert, and S. L. Webb, Phys. Chem. Miner. **116**, 1 (1994).

[5] C. A. Angell, P. A. Cheeseman, and S. Tamaddon, J. Phys. NC-9, **43**, 381 (1982).

[6] G. N. Greaves, J. Non-Cryst. Solids **71**, 203 (1985).

[7] J. Horbach, W. Kob, and K. Binder, Phys. Rev. Lett. **88**, 125502 (2002).

[8] P. Jund, W. Kob, and R. Jullien, Phys. Rev. B **64**, 134303 (2001).

[9] A. Meyer, D. B. Dingwell, and H. Schober, Europhys. Lett. **59**, 708 (2002).

[10] A. Meyer, J. Horbach, W. Kob, F. Kargl, and H. Schober, Phys. Rev. Lett. **93**, 027801 (2004).

[11] http://sourceforge.net/projects/frida.

[12] For a detailed discussion of the Fourier deconvolution procedure and the range of reliability of the resulting data we refer to: J. Wuttke, W. Petry, G. Coddens, and F. Fujara, Phys. Rev. E **52**, 4026 (1995).

[13] F. Kargl and A. Meyer, Chem. Geol. **213**, 165 (2004).

[14] R. E. Tickle, Phys. Chem. Glasses **8**, 101 (1967).

[15] H. Rauch and W. Waschkowski, *Landolt-Bornstein, New Series I/*, edited by H. Schopper, 16A (Springer, Berlin, 2000).

[16] A. Meyer, Phys. Rev. B **66**, 134205 (2002).

[17] U. Bengtzelius, W. Götze, and A. Sjölander, J. Phys. C **17**, 5915 (1984).

[18] F. Mezei, W. Knaak, and B. Farago, Phys. Scr. **T19**, 363 (1987).

[19] A. Tölle, J. Wuttke, H. Schober, O. G. Randl, and F. Fujara, Eur. Phys. J. B **5**, 231 (1998).

[20] J. Horbach and W. Kob, J. Phys.: Condens. Matter **14**, 9237 (2002).

[21] J. Wuttke, W. Petry, and S. Pouget, J. Chem. Phys. **105**, 5177 (1996).

[22] H. Jobic, J. Kärger, and M. Bée, Phys. Rev. Lett. **82**, 4260 (1999).

[23] K. Hahn, J. Kärger, and V. Kukla, Phys. Rev. Lett. **76**, 2762 (1996).

[24] H. Jobic, K. Hahn, J. Kärger, M. Bée, A. Tuel, M. Noack, I. Girnus, and G. J. Kearley, J. Phys. Chem. B **101**, 5834 (1997).

[25] J. R. Johnson, R. H. Bristow, and H. H. Blau, J. Am. Ceram. Soc. **34**, 165 (1951).

[26] E. Sunyer, P. Jund, and R. Jullien, J. Phys.: Condens. Matter **15**, S1659 (2003).

[27] O. Majérus, L. Cormier, G. Calas, and B. Beuneu, Chem. Geol. **213**, 89 (2004).

[28] H. Lammert and A. Heuer, Phys. Rev. B **70**, 024204 (2004).