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**INTERMEDIATE- AND EXTENDED-RANGE  
ORDER IN PHOSPHATE GLASSES\***

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## Abstract

The structure of sodium ultraphosphate glasses,  $(\text{Na}_2\text{O})_x(\text{P}_2\text{O}_5)_{100-x}$  ( $x = 0, 10, 20$ ), and alkali metaphosphate glasses,  $\text{MePO}_3$  ( $\text{Me} = \text{Li, Na, K, Rb and Cs}$ ) have been studied by neutron diffraction. Structural features in the neutron structure factors  $S(Q)$  characteristic of intermediate-range ( $Q \lesssim 3 \text{ \AA}^{-1}$ ) order were identified. The feature of intermediate-range order in the pure phosphate glass ( $\text{v-P}_2\text{O}_5$ ) is accounted for by the  $\text{P}_4\text{O}_{10}$  molecule packing model. The addition of the alkali metal modifier, Na, has drastic affect on the intermediate-range structure due to destruction of the  $\text{PO}_4$  network structure. Around  $x \sim 50$  a new peak arises at lower  $Q$  than the intermediate-range order peak, which is found in the  $S(Q)$ 's of all alkali metaphosphate glasses, associated with extended-range order. The length scale of extended-range order increases with  $\text{Me}^+$  size. These phenomena can be explained by the behavior of oxygen atoms, i.e.  $\text{PO}_4$  chain-like units ordering around the  $\text{Me}^+$ .

## 1 Introduction

The structure of vitreous  $P_2O_5$  (v- $P_2O_5$ ) is thought to consist of a 3-dimensional (3-D) network of corner-sharing  $PO_4$  tetrahedra, each of which is decorated with a non-bridging  $P=O$  bond. As  $Me_2O$  ( $Me$  = a network modifying element such as an alkali metal) is introduced to v- $P_2O_5$  to form a binary glass  $(Me_2O)_x(P_2O_5)_{100-x}$ , a structural transformation from a  $P_2O_5$  3-D network to a  $MePO_3$  metaphosphate complex chain takes place through the generation of non-bridging oxygens [1]. Hence v- $P_2O_5$  and the ultra-phosphate glasses with  $x = 0 - 50$  are ideal systems to investigate the structural evolution of short-, intermediate- and extended-range order [2] in glasses. Nevertheless, because of their hygroscopic nature and volatility relatively little is known about their structures and properties. Recently synthetic and processing methods of preparing these glasses with high purity have been developed [3], and X-ray [4] and neutron diffraction [5] and spectroscopic [3,6,7] studies have been reported on some ultraphosphate systems, leading to a detailed description of the short-range order.

In this paper neutron scattering results for the structure of Na ultraphosphate glasses,  $(Na_2O)_x(P_2O_5)_{100-x}$  ( $x = 0, 10, 20$ ), and alkali metaphosphate glasses,  $MePO_3$  ( $Me = Li, Na, K, Rb$  and  $Cs$ ) are presented. The information obtained is compared with results on model calculations using  $P_4O_{10}$  molecular units in order to describe the intermediate-range order in v- $P_2O_5$ , and is discussed in terms of content and ionic radius of network modifier to understand the origin and nature of the intermediate- and extended-range order in alkali phosphate glasses. Neutron diffraction results for the  $P_4O_{10}$  crystal, which is made up of  $P_4O_{10}$  molecules [8], are also presented to compare the intermediate-range order in the glass and crystal.

## 2. Experimental procedures and method of analysis

### 2.1. *Sample preparations and neutron diffraction experiments*

Anhydrous glasses were prepared using procedures described previously [3]. The raw crystalline materials ( $P_2O_5$ ,  $LiPO_3$ ,  $NaPO_3$ ,  $KPO_3$ ,  $RbPO_3$  and  $CsPO_3$ ) were handled in an Ar dry-box atmosphere ( $O_2 + H_2O < 2$  ppm). To prevent silica contamination the glasses were

melted and quenched in vitreous carbon crucibles which were sealed in silica ampoules. Phosphate glasses were prepared with compositions  $(\text{Me}_2\text{O})_x(\text{P}_2\text{O}_5)_{100-x}$  with  $x = 0, 10, 20$  ( $\text{Me} = \text{Na}$ ) and  $x = 50$  ( $\text{Me} = \text{Li, Na, K, Rb, Cs}$ ). Results of chemical analysis of Na, K and P by atomic absorption spectrochemical analysis and ICP emission spectrophotometry showed that the batched composition was retained ( $\pm 1 \text{ mol\%}$ ) after melting.

Neutron diffraction measurements were made at the IPNS on the GLAD facility [9] using a large range of wave vector  $Q$  (up to  $30 \sim 40 \text{ \AA}^{-1}$ ). The glass samples were crushed and sealed into a thin-walled vanadium tubes in the dry-box. In the experiments, standard procedures were made to correct for background, multiple scattering, inelastic effect and absorption in the sample and to normalize the results. The neutron-weighted Faber-Ziman structure factors  $S(Q)$  are derived from the measured intensity  $I(Q)$  according to:

$$I(Q) = \langle \bar{b} \rangle^2 [S(Q) - 1] + \langle \bar{b}^2 \rangle, \quad (1)$$

where  $\bar{b}$  and  $\bar{b}^2$  are, respectively, the mean and mean-square neutron scattering length averaged over nuclear isotopes and spins and the brackets  $\langle \rangle$  represent averages over all atoms in the system. Total correlation functions in real space can be defined by Fourier transformation of the corresponding structure factors:

$$T(r) = 4\pi\rho^0 r + \frac{2}{\pi} \int_{Q_{\text{min}}}^{Q_{\text{max}}} [S(Q) - 1] \sin Qr \cdot Q \, dQ, \quad (2)$$

where  $\rho^0$  is the total number density.

## 2.2. Interpretation of the neutron data by the RPSU model

We used the Random Packing Structural Units (RPSU) model in the form introduced by Moss and Price [10] to explain the first sharp diffraction peak, which is a characteristic signature of intermediate-range order in glassy materials. The RPSU model, which was originally developed by Egelstaff et al. [11], uses structural units or molecules, distributed according to random packing of hard spheres, with either uncorrelated (random) or identical (parallel) orientation, which is based on the following neutron-weighted structure factor:

$$S(Q) = F_1(Q) + F_2(Q)[S_c(Q) - 1] + 1 + \frac{\langle \bar{b}^2 \rangle}{\langle \bar{b} \rangle^2}, \quad (3)$$

where  $F_1(Q)$  is the form factor of the isolated molecule,  $F_2(Q)$  is a different form factor expressing the correlation between randomly oriented molecules and  $S_c(Q)$  is the structure factor of the molecular centers, if we assume that positions and orientations of molecules are uncorrelated. If all molecules are oriented in the same direction (parallel configuration),

$$F_2(Q) = F_1(Q),$$

so that Eq. (3) becomes

$$S(Q) = F_1(Q)S_c(Q) + 1 + \frac{\langle \bar{b}^2 \rangle}{\langle \bar{b} \rangle^2}. \quad (4)$$

$S_c(Q)$  is assumed to be given by the structure factor for hard spheres,  $S_{hs}(Q)$ , i.e.,

$$S_c(Q) - 1 = (S_{hs}(Q) - 1) \exp\left(-\frac{\Delta_{hs}^2 Q^2}{2}\right).$$

$S_{hs}(Q)$  is calculated using a Percus-Yevick hard sphere model [12], which depends on the hard sphere diameter,  $\sigma$ , and packing fraction,  $\eta = \pi\sigma^3\rho^0/6n$ . An artificial damping factor,  $\Delta_{hs}$ , is introduced in order to reduce the oscillations in the high  $Q$  region due to the hard repulsive potential.

### 3. Results

#### 3.1. Structure factor of v-P<sub>2</sub>O<sub>5</sub>

Neutron structure factors obtained for v-P<sub>2</sub>O<sub>5</sub> and the P<sub>4</sub>O<sub>10</sub> crystal are shown in Fig. 1. They are plotted out only to  $Q = 15 \text{ \AA}^{-1}$  to emphasize the structural features which appear at low  $Q$ . The result for the v-P<sub>2</sub>O<sub>5</sub> is in good agreement with that of Wright et al. [14]. The most prominent features in the  $S(Q)$  from v-P<sub>2</sub>O<sub>5</sub>, at  $Q = 1.30$  and  $2.12 \text{ \AA}^{-1}$ , are due to the intermediate range order of the P-O network and correspond to correlation lengths  $L = 2\pi/Q =$

4.8 and 3.0 Å, respectively. The longer correlation length is characteristic of intermediate-range order in oxide and chalcogenide glasses [15]. The positions of these two peaks are close to those of Bragg reflections in the crystal at  $Q = 1.0 - 2.1 \text{ \AA}^{-1}$ , may be due to the correlations between  $\text{P}_4\text{O}_{10}$  molecules.

Figure 1 also shows  $S(Q)$ 's calculated for the RPSU model from Eqs. (3) and (4) with random and parallel configurations, respectively, taking the  $\text{P}_4\text{O}_{10}$  molecular structure of the crystal [8] and  $S_c(Q)$  with  $\sigma = 6.46 \text{ \AA}$ ,  $\eta = 0.683$  and  $\Delta_{hs} = 0.40 \text{ \AA}$ , where  $\rho^0 = 0.06771$  atoms  $\text{\AA}^3$  [8] and  $n = 14$ .  $\sigma$  is taken from the closest intermolecular distance:  $r_m = 7.46\sqrt{3}/2 \text{ \AA}$  because the crystal structure ( $R3c$ ) has an almost body-centered "pseudo unit cell" with  $a = b = c = 7.46 \text{ \AA}$ ,  $\alpha = \beta = \gamma = 87.3^\circ$ , containing two molecules [8,13];  $\eta$  is very close to the packing fraction for the body-centered cubic (bcc) cell. Comparing the calculated  $S(Q)$ 's with the observed ones has shown that the position of the first peak in the observed  $S(Q)$  for v- $\text{P}_2\text{O}_5$  can be accounted for by molecule-molecule correlations in terms of either randomly oriented or parallel oriented packing of  $\text{P}_4\text{O}_{10}$  molecules, suggesting that the character of the intermediate-range order of the glass is close to the  $\text{P}_4\text{O}_{10}$  crystal [8,13]. The position of the second peak, however, can not be reproduced by the randomly oriented packing model, so that the orientational correlations between  $\text{P}_4\text{O}_{10}$  molecule-like units in the  $\text{PO}_4$  network must be taken into account.

At higher momentum transfer ( $Q \gtrsim 4 \text{ \AA}^{-1}$ ) there is a remarkable similarity between the four curves in Fig. 1 because the well defined short-range structure of the  $\text{PO}_4$  tetrahedral groups. The small discrepancies reflect the differences in short-range order between the glass and molecular crystal. In order to investigate short-range atomic ordering, the form factor  $F_1(Q)$  of a  $\text{P}_4\text{O}_{10}$  molecule was fit to  $S(Q)$  for v- $\text{P}_2\text{O}_5$  in the  $Q$  range from 6 to  $30 \text{ \AA}^{-1}$ ; three short distances,  $\text{P}-\text{O}_{\text{NB}}$  ( $\text{O}_{\text{NB}}$ : non-bridging oxygen atom),  $\text{P}-\text{O}_B$  ( $\text{O}_B$ : bridging oxygen atom) and  $\text{P}-\text{P}$ , are parameters which define the  $F_1(Q)$  of a  $\text{P}_4\text{O}_{10}$  molecule with symmetry  $T_d(\bar{4}3m)$  [16]. The  $\text{P}-\text{O}_{\text{NB}}$  and  $\text{P}-\text{O}_B$  distances obtained are compared in Table 1 with those measured in  $\text{P}_2\text{O}_5$  by several studies. The values obtained here are almost identical to those measured in the previous study of Wright et. al [14]. Figure 2 shows the total correlation function  $T(r)$  obtained from

calculating  $S(Q)$  from Eq. (4) using the fitted  $F_i(Q)$  and  $S_c(Q)$  with  $\sigma = 6.36 \text{ \AA}$ ,  $\eta = 0.680$  (bcc structure) and  $\Delta_{hs} = 0.60 \text{ \AA}$ , where  $\rho^0 = 0.07083 \text{ atoms \AA}^{-3}$  (density of v-P<sub>2</sub>O<sub>5</sub> in the present study). The result is compared with  $T(r)$  for v-P<sub>2</sub>O<sub>5</sub> obtained from the experimental  $S(Q)$ . The good agreement for the first peak only suggests that the quality of this fit in the high  $Q$  region is determined almost completely by the first-neighbor P-O atom distribution.

### 3.2. Structure factors of alkali ultraphosphate glasses

Figures 3 shows the structure factors measured for the Na ultraphosphate glasses. The result for the Na metaphosphate glass is in good agreement with that of Suzuki et al. [17]. The addition of the Na modifier to v-P<sub>2</sub>O<sub>5</sub> has little affect on the short-range order (i.e. high  $Q$  region) where the basic PO<sub>4</sub> tetrahedral unit retained but drastic effects on the intermediate-range structure (i.e. low  $Q$  region). In particular, the two intermediate-range order peaks of v-P<sub>2</sub>O<sub>5</sub> at  $Q = 1.30$  and  $2.12 \text{ \AA}^{-1}$  are replaced by a single peak at  $Q_1 = 1.60 \text{ \AA}^{-1}$  for 20 mol% Na<sub>2</sub>O, corresponding to correlation lengths  $L_1 = 3.7 \text{ \AA}$ . These length is slightly smaller than the characteristic length for intermediate-range order in binary glasses [15], showing that P<sub>4</sub>O<sub>10</sub> molecular-like units are broken down into smaller units by the modifier cations. From 20 to 50 mol%, the intermediate-range order peak shifts to higher  $Q$ , indicating further destruction of the PO<sub>4</sub> linkage, and a new peak arises at  $Q_0 = 1.16 \text{ \AA}^{-1}$  for 50 mol% Na<sub>2</sub>O, implying order on an extended length scale  $L_0 = 5.8 \text{ \AA}$ . The appearance of the extended-range order suggests that the Na<sup>+</sup> first modifies the PO<sub>4</sub> network but then build up a new network. These structural changes are reflected in the physical properties, as discussed in Section 4.2.

### 3.3. Structure factors of alkali metaphosphate glasses

Figure 4 shows that the structure factors measured for several alkali metaphosphate glasses. All glasses have an extended-range order peak at  $Q_0 = 1.01 \sim 1.16 \text{ \AA}^{-1}$ , corresponding to a length scale  $L_0 = 5.2 \sim 6.3 \text{ \AA}$ . The effect of modifier ionic size on the peak positions is

clearly seen in Fig. 5, where the appropriate cation radii are calculated from the cation-oxygen nearest distances in the alkali phosphate crystals [18-22] and the ionic radius  $1.4 \text{ \AA}$  of  $\text{O}^{2-}$  [23]. The peak shifts to lower  $Q$  with increasing size of the  $\text{Me}^+$ , and changes rapidly at an ionic radius of about  $1.4 \text{ \AA}$ . On the other hand, the position of the intermediate-range order peak at  $Q_1 = 1.69 \sim 1.98 \text{ \AA}^{-1}$ , corresponding to a length scale  $L_1 = 3.2 \sim 3.7 \text{ \AA}$ , moves to higher  $Q$  up to the radius of  $\text{K}^+$  ( $\approx 1.46 \text{ \AA}$ ) and then shifts to lower  $Q$ , as also shown in Fig. 5. These characteristic changes in  $\text{Me}^+$  size dependencies around  $1.4 \text{ \AA}$  reflect the fact that the length scales for extended- and intermediate-range order in alkali metaphosphate glasses are related to the ratio of the  $\text{Me}^+$  size to the that of the oxygen.

#### 4. Discussions

##### 4.1. Intermediate-range order in $\text{v-P}_2\text{O}_5$

Although one might expect the structure of a glass to prefer random orientation, the results of Fig. 1 shows that the parallel configuration is more probable. This figure also shows a broad disagreement in the heights and widths of the intermediate-range order peaks between the calculated and experimental structure factors. This suggests that the  $\text{P}_4\text{O}_{10}$  molecule used has a too rigid and ordered structural unit and too high packing density. Actually the intramolecular-range ( $r \leq 6 \text{ \AA}$ ) structure of  $\text{v-P}_2\text{O}_5$  is highly modulated and presumably overlaps with intermolecular atomic distances ( $r \geq 3 \text{ \AA}$ ). Hence, a more sophisticated treatment of configurations and structural units is necessary to fully explain the intermediate range order in  $\text{v-P}_2\text{O}_5$ .

In addition to the molecular crystal form and the glass, there are two high temperature  $\text{P}_2\text{O}_5$  crystalline polymorphs,  $\text{o-P}_2\text{O}_5$  ( $Fdd2$ ) [24] and  $\text{o}'\text{-P}_2\text{O}_5$  ( $Pnma$ ) [25]. Meyer [7] suggests that the structure of  $\text{v-P}_2\text{O}_5$  may be described by substructures of the 3-D network of  $\text{o-P}_2\text{O}_5$ , on the basis of their infrared and other X-ray diffraction studies. The present study, however, shows that the features of the intermediate-range order in  $\text{v-P}_2\text{O}_5$  are characterized by the  $\text{P}_4\text{O}_{10}$  molecular model. The structure of  $\text{v-P}_2\text{O}_5$  would be explained better by optimization of

the  $P_4O_{10}$  structural units and their packing rather than by stereochemical modulation of the high temperature crystalline phases having structures with close packing of oxygen ions (see  $\rho^0$  in Table 1).

#### 4.2. Extended-range order in alkali phosphate glasses

The compositional dependence of the intermediate- and extended-range order reflects the behavior of the other physical properties such as glass transition temperature  $T_g$  [3,26]. Figure 6 shows a plot of  $T_g$  versus mol%  $Na_2O$  for  $Na$  ultraphosphate glasses [26,27].  $T_g$  shows a rapid drop up to 10 mol%  $Na_2O$ , which may correspond to the depolymerization of the 3-D network structure associated with the destruction of molecular-like structural units, and with the formation of non-bridging oxygen units [6].  $T_g$  reaches a minimum at  $\sim 20$  mol%  $Na_2O$  and thereafter increases, reflecting the 3-D network restructuring associated with the extended-range order. Hudgens et al. [3] suggested a comparable picture for  $Li$  ultraphosphate glasses on the basis of  $T_g$  and infrared measurements, in which the origin of the extended-range order is described by the entanglement of long  $PO_4$  chains. The present results clearly show that the extended-range order peak is affected by the  $Me^+$  size and concentration, so that the influence of  $MeO_n$  polyhedra (observed in silicate and phosphate crystals [28]), as well as the linkage of  $PO_4$  units, is a substantial factor in the extended-range ordering. The explanation of the extended-range order is in terms of increasing structural rigidity as shown in the increase of  $T_g$  with modifier concentration in  $Li$  and  $Na$  ultraphosphate glasses, however, appears to be inadequate for the larger alkali cation ultraphosphate glasses. This is because the  $T_g$  of alkali metaphosphate glasses decreases with increasing size of the alkali cations i.e. with decreasing charge density around the cations [27]. Moreover, the  $T_g$ 's of alkaline-earth ( $Mg$ ,  $Ca$ ,  $Sr$ ) metaphosphate glasses are higher than those of alkali metaphosphate glasses [27] although the extended-range order peak is not as clearly observed [29]. Accordingly, it is necessary to take into account the charge density in order to understand the generic relationships between extended-range order and physical properties in binary ultraphosphate glasses. The effect of charge density on extended-range order

will be discussed elsewhere in connection with neutron scattering results on alkaline-earth phosphate glasses [29].

In Rb germanate glasses, Price et al. found that the extended-range order is associated with a topological ordering of the oxygen atoms around the modifier cations and with a chemical ordering of two cations [2]. It appears that a similar situation applies to extended-range order in alkali phosphate glasses, with ordering of  $\text{PO}_4$  chain-like units around modifier cations and association of  $\text{MeO}_n$  polyhedra. The rapid changes around an ionic radius of 1.4 Å in Fig. 5 are related to the variation in oxygen atom ordering as a function of the ratio of  $\text{Me}^+$  size to  $\text{O}^2$  size.

## Conclusions

Intermediate-range order in  $\text{v-P}_2\text{O}_5$ , characterized by two neutron diffraction peaks at  $Q = 1.30$  and  $2.12 \text{ \AA}^{-1}$ , is substantially represented by an RPSU model based on parallel oriented  $\text{P}_4\text{O}_{10}$  molecular units. A more precise structural model will require consideration of orientational correlations between them and optimization of their arrangement in the glass structure.

The addition of an alkali metal modifier Na has drastic effects on the intermediate-range structure due to depolymerization of  $\text{PO}_4$  network and reconstruction of the network associated with extended-range order. The extended-range order in alkali metaphosphate glasses, characterized by diffraction peaks at  $Q$  values below those of typical intermediate-range order peaks, can be associated with ordering of  $\text{PO}_4$  chain-like units around the  $\text{Me}^+$  and aggregation of  $\text{MeO}_n$  polyhedra. This picture satisfactorily represents the network depolymerization and reconstruction processes corresponding to the drastic changes in glass transition temperature  $T_g$  (minimum in  $T_g$  at about 20 mol%  $\text{Na}_2\text{O}$ ), and the increase in the length scale of extended-range order with increasing  $\text{Me}^+$  size. It is necessary to take into account the charge density around the modifier cations and the relative cation to oxygen ion size for a complete structural description of the ultraphosphate and metaphosphate glasses.

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Table 1. Mean P-O, P-O<sub>NB</sub> (O<sub>NB</sub>: non-bridging oxygen atom) and P-O<sub>B</sub> (O<sub>B</sub>: bridging oxygen atom) distances in P<sub>2</sub>O<sub>5</sub> glasses and crystals and the average atom number densities ( $\rho^0$ ).

Chemical formula	P-O (Å)	P-O <sub>NB</sub> (Å)	P-O <sub>B</sub> (Å)	$\rho^0$ (atoms Å <sup>-3</sup> )	Reference
P <sub>2</sub> O <sub>5</sub> (glass)	1.539	1.420 ± 0.010*	1.579 ± 0.010*	0.07083	this work
P <sub>2</sub> O <sub>5</sub> (glass)	1.538	1.426 ± 0.005	1.576 ± 0.005	-	[14]
P <sub>4</sub> O <sub>10</sub> (crystal)	1.550	1.432	1.590	0.06771	[8]
P <sub>2</sub> O <sub>5</sub> (o-, crystal)	1.543	1.445	1.576	0.08033	[24]
P <sub>2</sub> O <sub>5</sub> (o', -, crystal)	1.539	1.444	1.570	0.08696	[25]

\*) The quality of fit was  $R_x = \left( \frac{\sum_i [S_{\text{exp}}(Q_i) - S_{\text{fit}}(Q_i)]^2}{\sum_i S_{\text{exp}}^2(Q_i)} \right)^{1/2} = 3.1$  (%) in the range  $Q = 6 - 30$  Å<sup>-1</sup>.

## Figure captions

Figure 1: Experimental neutron structure factors  $S(Q)$  of v- $P_2O_5$  and  $P_4O_{10}$  crystal, and calculated ones of the RPSU model based on random and parallel oriented  $P_4O_{10}$  molecules. The inset values are peak heights of the first peaks in the calculated  $S(Q)$ . The dotted lines are a guide to the eye only.

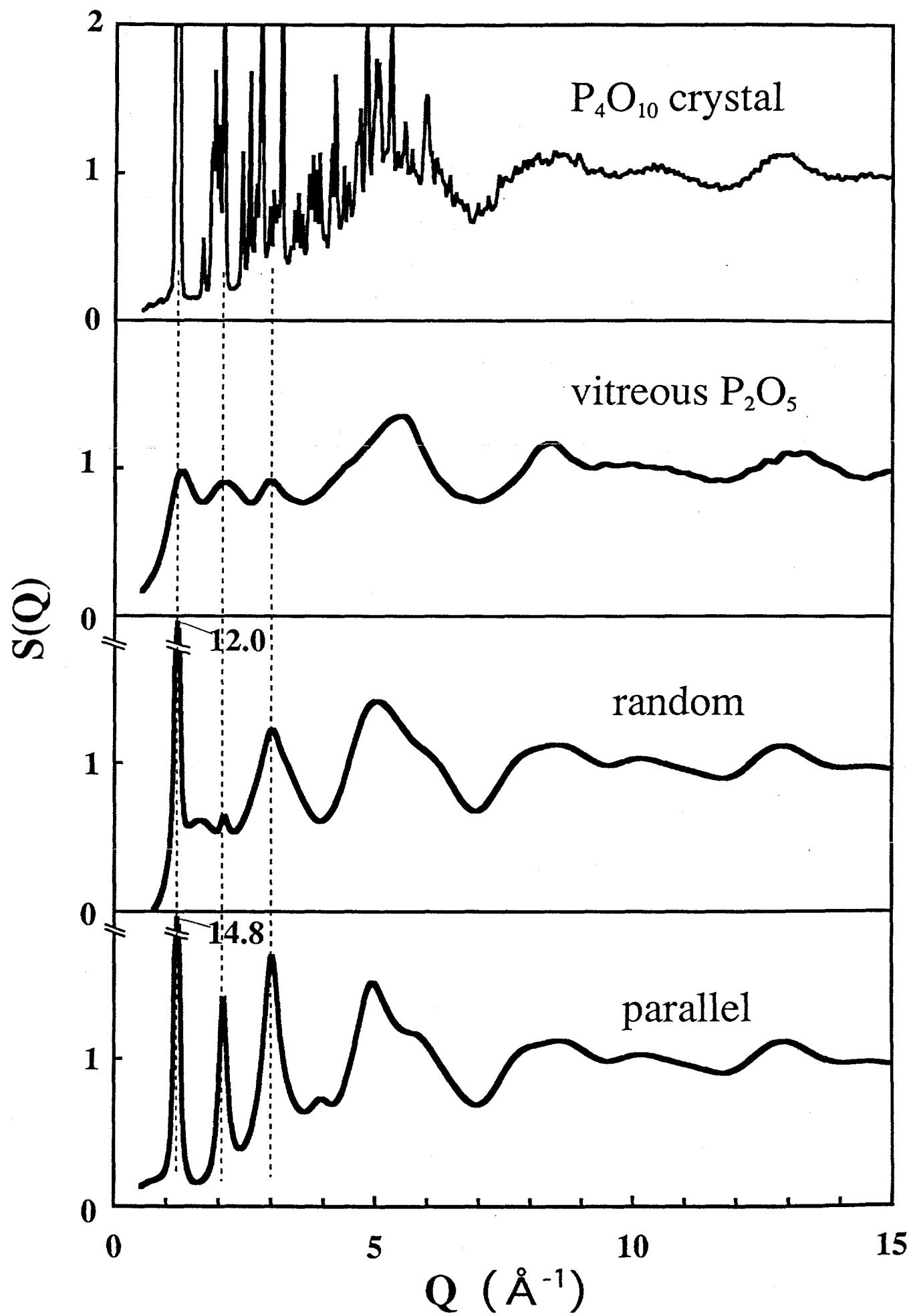
Figure 2: Comparison of the total correlation function  $T(r)$  of v- $P_2O_5$  with the one (solid curve) obtained from the calculated  $S(Q)$  for the RPSU model of parallel oriented optimized- $P_4O_{10}$  molecules; this is calculated using a fitted  $F_1(Q)$  to  $S(Q)$  of v- $P_2O_5$  and parameters outlined in Sec. 3.1 and Table 1. Lorch function was used in the Fourier transforms with  $Q_{\max} = 30 \text{ \AA}^{-1}$ .

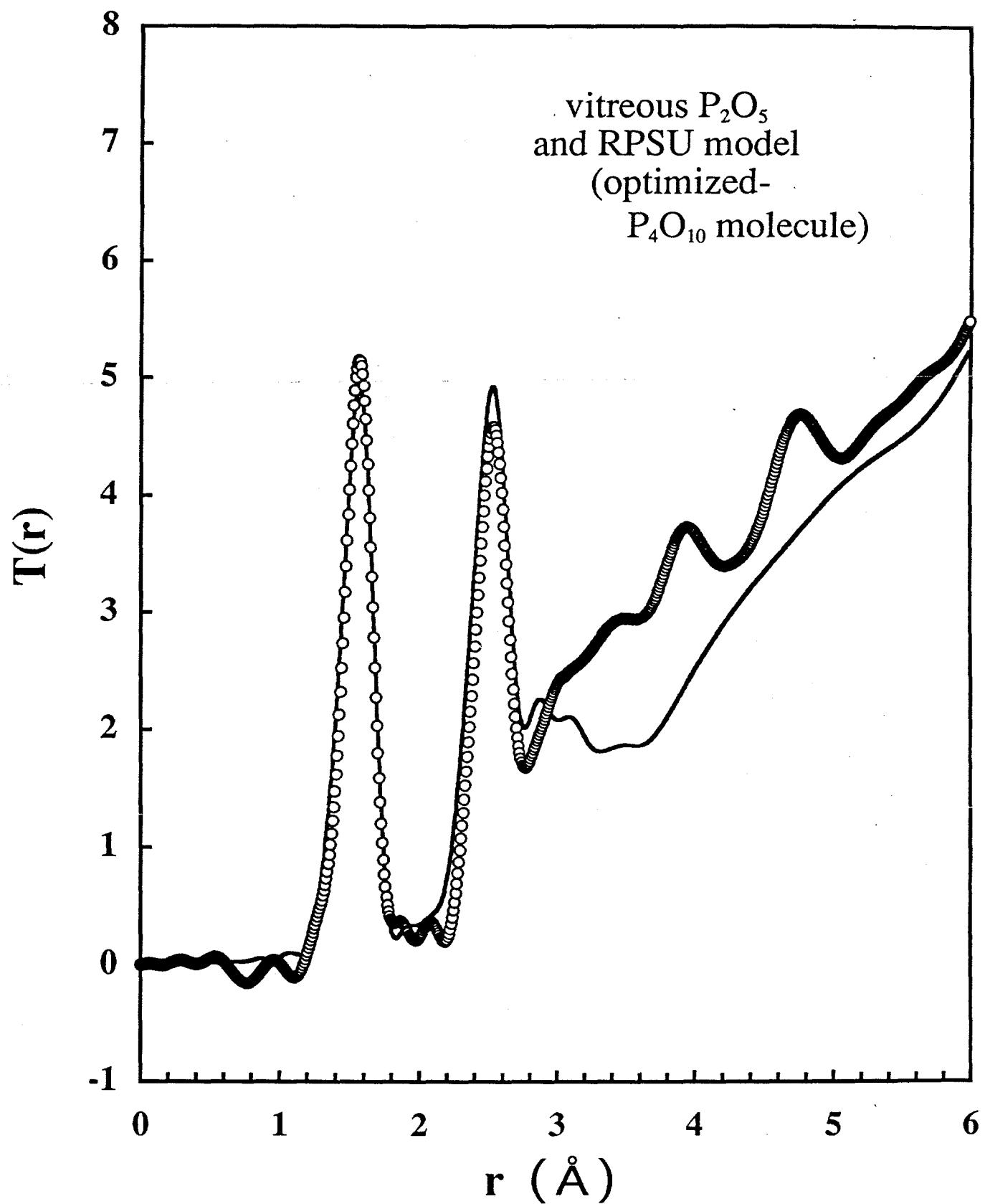
Figure 3: Neutron structure factors  $S(Q)$  of  $(Na_2O)_x(P_2O_5)_{100-x}$  glasses; successive curves are displaced upward by 0.5 unit for clarity. The allows are a guide to the eye only.

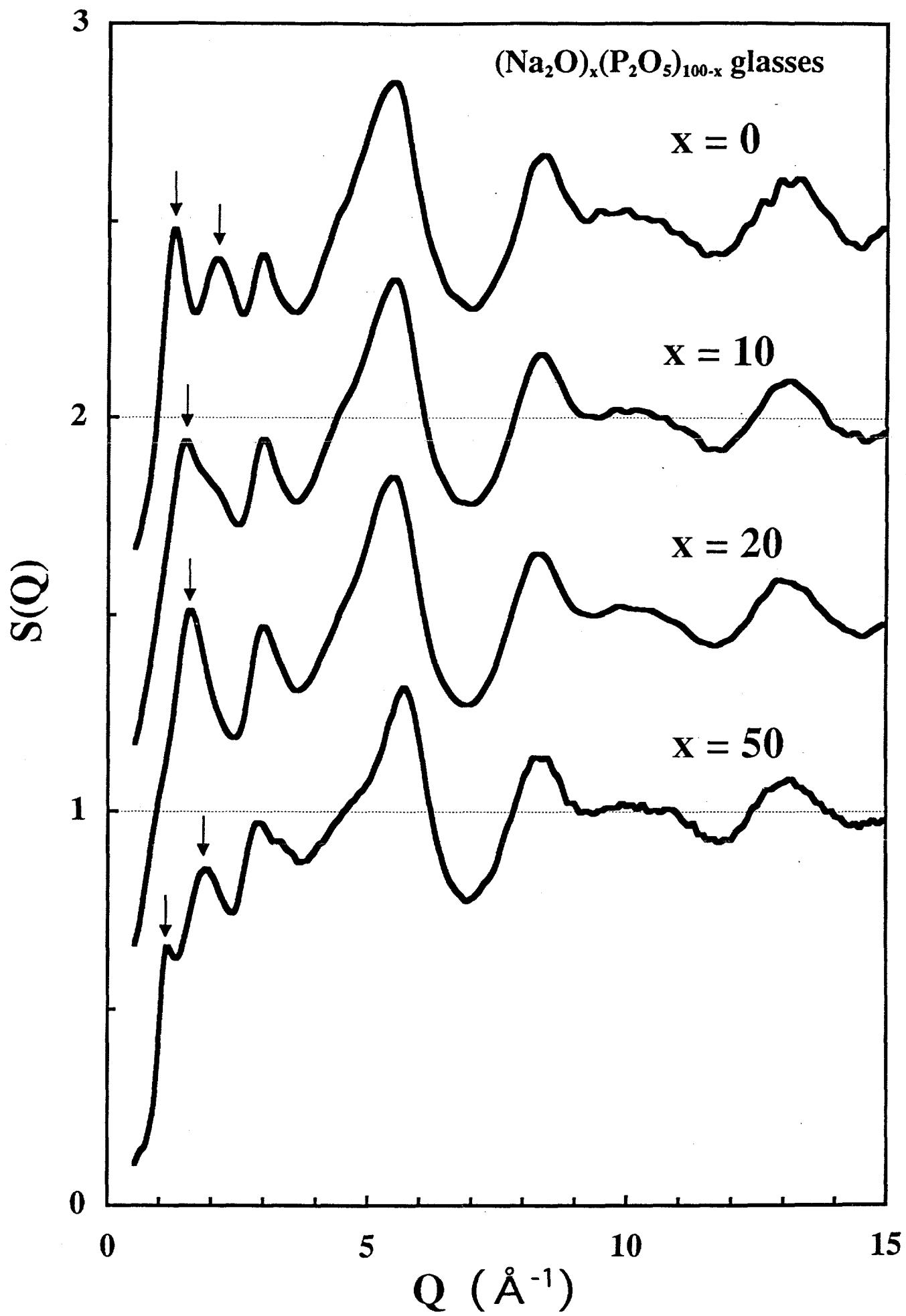
Figure 4: Neutron structure factors  $S(Q)$  of  $(Me_2O)_{50}(P_2O_5)_{50}$  glasses (Me: Li, Na, K, Rb, Cs); successive curves are displaced upward by 1.0 unit for clarity. The dotted line is a guide to the eye only.

Figure 5: Positions of  $Q_0$  of the extended-range order (ERO) peak and  $Q_1$  of the intermediate-range order (IRO) peak in the structure factors  $S(Q)$  of  $(Me_2O)_{50}(P_2O_5)_{50}$  glasses (Me: Li, Na, K, Rb, Cs). The lines joining the points are a guide to the eye only.

Figure 6: Glass transition temperature  $T_g$  of glasses in the series  $(Na_2O)_x(P_2O_5)_{100-x}$ . The data are taken from Ref. [26] and [27]. The solid curve joining the points is a guide to the eye only.







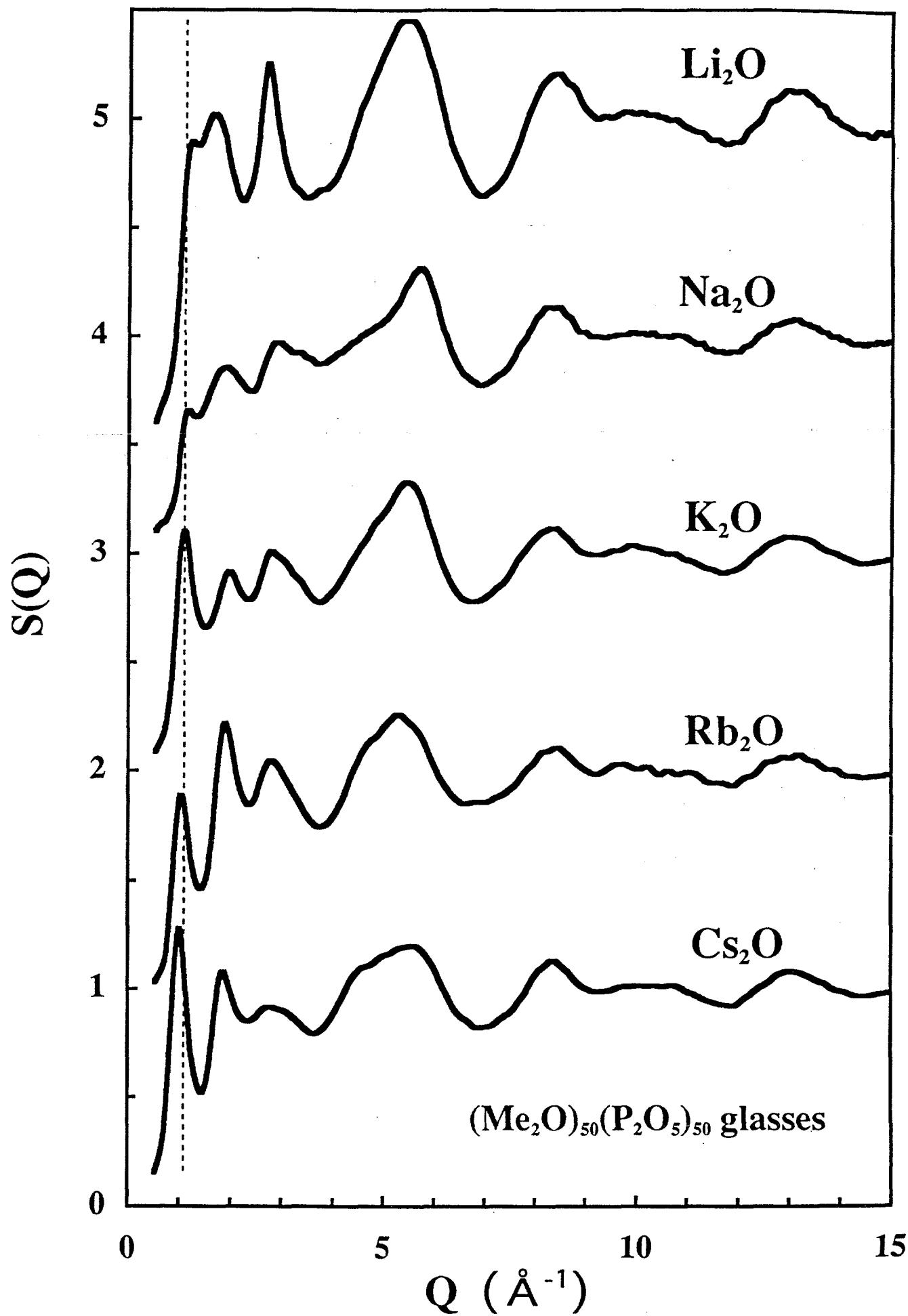


Figure 5, K. Suzuya et al.

