Anomalous temperature dependence of the first diffraction peak in the superionic glass $(AgI)_x(AgPO_3)_{1-x}$

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We report neutron-scattering measurements on the first sharp diffraction peak in the superionic conducting glass $(AgI)_x(AgPO_3)_{1-x}$ as a function of composition x from 0.0 to 0.7. The temperature variation is studied in detail between 300 K and 500 K, a range that spans the calorimetric glass transition. This peak reflects structure in the phosphate network with periodicity $d \approx 10$ Å and correlation length ≈ 25 Å. The intensity of the first sharp diffraction peak shows an anomaly as a function of temperature at a temperature about 6–11 % higher than T_g as measured calorimetrically. This is tentatively ascribed to the diffraction intensity reflecting the onset of α relaxation, while the calorimetric data reflects the onset of β relaxation.

I. INTRODUCTION

Glasses with high ionic conductivity have attracted much interest in recent years because of their possible application in batteries, fuel cell technologies, and sensors, as well as the fundamental interest in understanding the transport mechanism in disordered materials.[1–4] Fast ion conducting (FIC) glasses have been investigated as materials for solid-state electrolytes and, among these, Ag^+I^--containing ones have been discovered with ionic conductivities as high as 0.01 S cm^{-1} at room temperature. FIC glasses generally consist of three components: a glass network former, metal oxides or metal sulfides acting as a glass network modifier, and a dopant salt such as AgI. $(AgI)_x(AgPO_3)_{1-x}$ has been studied for various values of x by several different methods. Pure AgPO$_3$ shows very low ionic conductivity; the ionic conductivity in AgI is significant, but not as high as in the mixed salts at ambient temperature.[5–7] The electrical properties suggest that conduction occurs by diffusion of silver ions that percolate through clusters of AgI embedded in a fixed glassy matrix of AgPO$_3$.[5] Analysis of Brillouin[8,9] and neutron-scattering[10,11] data also suggested such clusters in the glass structure. Reverse Monte Carlo (RMC) modeling[12–15] of $(AgI)_x(AgPO_3)_{1-x}$ confirms that the glass structure typically consists of a ''network'' component, e.g.,

phosphate chains, and a ''salt'' component, which are strongly interlinked. Salt doping is known to expand the network structure, leading to an increase in the accessible free volume and the number of conduction pathways and, hence, to the observed increase in the ionic conductivity.

Neutron diffraction has been widely used to study the structure of silver-containing glasses, such as AgI doped into a three-dimensional random network (Ag$_2$O-2B$_2$O$_3$), into long polymeric chains (AgPO$_3$), or into isolated anions (Ag$_2$MoO$_4$).[10–15] In all these neutron studies, the structure factor exhibits a strong and relatively sharp diffraction peak at anomalously low values of the scattering vector $Q(0.6 < Q < 0.8$ Å^{-1}). This peak is not observed in the corresponding undoped glasses and is indicative of some form of intermediate range order (IRO) with a periodic length scale of $d = 2\pi/Q$,[16,17] which is of the order of 10 Å. In the literature, some authors[12–15,18] refer to this peak as the first sharp diffraction peak (FSDP), while others[19,20] refer to it as a prepeak and reserve the term first sharp diffraction peak for the first peak in pure AgPO$_3$, at about 2.1 Å^{-1}. Arbitrarily, we will follow the former of these examples and refer to the peak as the first sharp diffraction peak. There is a second length scale associated with the first sharp diffraction peak, which is related to the length D over which the periodicity persists, and is given by $D = 2\pi/\Delta Q$ where ΔQ is the half

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width at half maximum of the peak.[18,21–23] For $(AgI)_x(AgPO_3)_{1-x}$, we will show that this length is of the order of 25 Å.

The FSDP typically shows behavior different from that of the other peaks in the structure factor of a glass, with respect to its variation with temperature and composition. An example of this is in As_2Se_3 and As_xS_{1-x} glasses[24] where a surprising increase in the intensity was observed with increasing temperature, while the intensity of the other diffraction peaks decreased. This result was attributed to the existence of local layering in these glasses. Another example of anomalous temperature dependence of the first sharp diffraction peak is observed in the liquid $GeSe_2$.[25,26] The height of the FSDP in the liquid at 1084 K is 10% less than in the glass at 10 K, indicating that the intermediate range order is largely preserved on melting.[25] However, the origin of the first sharp diffraction peak in these materials is different from that in our system.

The first sharp diffraction peak in superionic conducting glasses of composition $(AgI)_x(AgPO_3)_{1-x}$ is strong and has already been the subject of several neutron-diffraction investigations.[10–15,19,20,27–29] However, the temperature dependence of its structure factor has previously only been studied over a limited temperature range for one composition, $x=0.5$.[28] This study found no significant temperature dependence of the FSDP at this composition near the glass transition. In the present paper we present an extensive neutron-diffraction study for $x=0.0$, 0.3, 0.5, and 0.7 at various temperatures. Where overlap occurs, our neutron work agrees with the earlier work, but this new study shows that the story is much richer than revealed by the earlier work, with anomalies in the temperature dependence of the scattering intensity at temperatures 6–11 % above the calorimetric glass transition temperature. In order to relate the results of these measurements to the thermal behavior, we also made calorimetric measurements using differential scanning calorimetry.

The paper is arranged as follows: Sec. II will briefly describe the experimental methods. The thermal data will be presented and discussed in Sec. III. In Sec. IV the temperature dependence of the neutron-diffraction pattern for all compositions will be presented and discussed. Further discussion and conclusions will be given in Secs. V and VI.

II. EXPERIMENT

Usually as-purchased AgI is a mixture of β and γ phases at room temperature. The pure-β phase has a simple transition to the α phase at about 147 °C on heating. The γ phase transforms first to the β, then to the α phase.[30,31] In order to obtain the pure-β phase, the AgI (Aesar 99.98%) was first purified and dried, and then dissolved in a concentrated solution of KI. The mixture was filtered, and then water was added to precipitate AgI. The AgI was dried in an oven at 100 °C for a few hours, then cooled and stored in a dessicator before being used.

$(AgI)_x(AgPO_3)_{1-x}$ glasses were prepared with AgI concentrations of 0%, 30%, 50%, and 70%, by the following procedure. Appropriate amounts of β-AgI, $AgNO_3$, and $(NH_4)H_2PO_4$ were weighed to produce the desired composition, mixed and ground together in a mortar. The mixtures

were heated in porcelain crucibles at a rate of 100 °C/h to 600 °C for $AgPO_3$ and to 700 °C for AgI-$AgPO_3$ mixtures. The melt was left at this temperature for 2 h. The glass specimens were made by casting the melts into shallow and deep holes in a piece of Teflon, and directly quenching into liquid nitrogen. The thin circular disk samples were used for the differential scanning calorimetry (DSC) measurements, and the long cylindrical rods for the neutron measurements. A clear, yellowish, yellowish, and brownish transparent glass was obtained for $x=0.0$, 0.3, 0.5, and 0.7, respectively. The sample preparation was performed in the Neutron Scattering Laboratory, Materials Science Research Center, Batan, Indonesia.

For the DSC measurements, 20–50-mg samples were enclosed in a small aluminum pan and placed into a platinum sample holder. An empty reference alumunium pan was placed into an identical sample holder. They were subjected to identical thermal processes and the difference in heat flow of the two was monitored by a differential thermocouple. The sample was heated from room temperature up to 500 °C with a heating rate of 15 °C/min. All measurements were done under flowing argon gas in order to keep the sample from absorbing moisture from air. These measurements were performed at the Brockhouse Institute for Materials Research in McMaster University.

Neutron-diffraction measurements were performed at the NRU research reactor at the Chalk River Laboratories, Chalk River, Canada using the DUALSPEC high-resolution powder diffractometer with a neutron wavelength of 1.257 Å. The samples were contained in a thin-walled vanadium cylindrical holder of inner diameter 5 mm, which was placed in a furnace. The data were corrected for the background scattering, the scattering by the empty vanadium holder, the detector efficiency, and absorption. The details of the measurement and data correction procedures were as described previously.[32]

III. THERMAL DATA

Figures 1(a), 1(b), 1(c), and 1(d) show the DSC scans for $(AgI)_x(AgPO_3)_{1-x}$ with $x=0.0$, 0.3, 0.5, and 0.7 , respectively. The scans show the calorimetric glass-liquid transition on heating, which is an endothermic change in the DSC signal. The vertical arrows on the plots mark the onset temperature T_g of the calorimetric glass transition at 436, 397, 361, and 348 K for $x=0.0$, 0.3, 0.5, and 0.7, respectively. The heat flows at $T_g(x)$ for these compositions are 0.075, 0.069, 0.039, and 0.024 W/g, respectively.

It has been suggested previously[33,34] that the amount of AgI that crystallizes during annealing is such that the mole fraction of AgI dissolved in the glassy matrix is constant for $x>0.55$.[35] Further amounts of AgI dopant will form a crystalline precipitate. Neither the DSC nor the neutron measurements indicate the presence of any AgI precipitate in the sample with $x=0.5$, in agreement with this suggestion.

IV. NEUTRON-DIFFRACTION DATA

A. Analysis of the neutron structure factor for $(AgI)_x(AgPO_3)_{1-x}$

Figure 2 shows the structure factor $S(Q)$ for $x=0.0$, 0.3, 0.5, and 0.7 at several temperatures. Our data for $x=0.3$ and
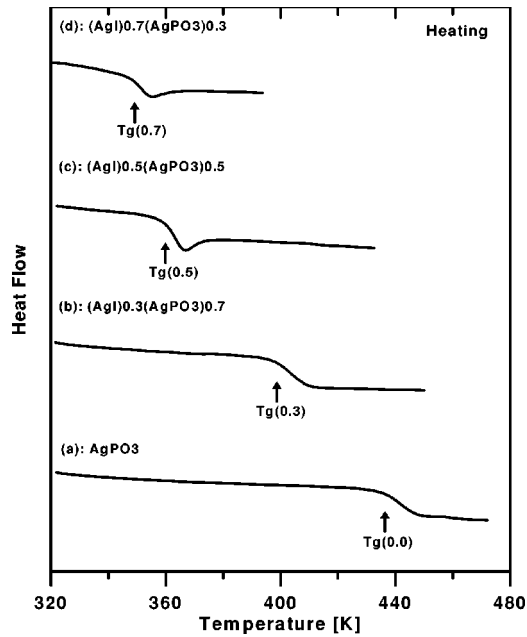
FIG. 1. The DSC scans for $(AgI)_x(AgPO_3)_{1-x}$ glasses measured for a heating rate of 15 °C/min. The arrows show the temperature of the onset of the glass transition.

for $x=0.5$ at room temperature is in agreement with that given by Tachez *et al.*[11] and by Rousselot and co-workers.[19,20] For $x=0$, there are differences at $Q < 1.5$ Å^{-1} where we observe more scattering than Rousselot *et al.*[19,20] The $S(Q)$ for doped and undoped glasses ($x < 0.7$) are similar at high $Q(Q>1.5$ Å$^{-1})$, since the scattering in this region mostly reflects the short-range covalent bonding, which is largely unchanged by addition of AgI. However, for the samples with AgI doping there are large changes at low Q where the first sharp diffraction peak is apparent at a Q value of about 0.7 Å^{-1} and there is a pronounced minimum in the scattering at a Q value of about 1.3 Å^{-1}. These features are absent in the corresponding base glass AgPO$_3$. At room temperature, the intensity of the first sharp diffraction peak increases from $x=0.3$ to $x=0.5$ but then decreases for $x=0.7$. However, for $x=0.7$ there is a rapid increase in its intensity on heating to 404 K, while for $x=0.3$ and $x=0.5$ the intensity is not strongly dependent on temperature. The minimum at 1.3 Å^{-1} is only weakly temperature dependent at all compositions.

For $x=0.7$, there is Bragg scattering superimposed on the diffuse glass-scattering pattern. This Bragg scattering corresponds to crystalline AgI, indicating that this sample is a mixture of $(AgI)_x(AgPO_3)_{1-x}$ glass and precipitated AgI. The sharp increase in intensity of the FSDP just before the appearance of a second crystalline phase may be a precursor of the crystallization process.

In this paper we concentrate on the temperature dependence of the first sharp diffraction peak in the range of Q from 0.3 to 1.2 Å^{-1}. The FSDP can be described quantitatively[18] by fitting with a Lorentzian curve $S(Q) \sim A(Q) \times \{\Delta Q/[(Q-Q_0)^2+\Delta Q^2]\}+B$, where B is the background and $A(Q)$, ΔQ, and Q_0 are the peak height intensity, half-width at half maximum, and position, respectively.
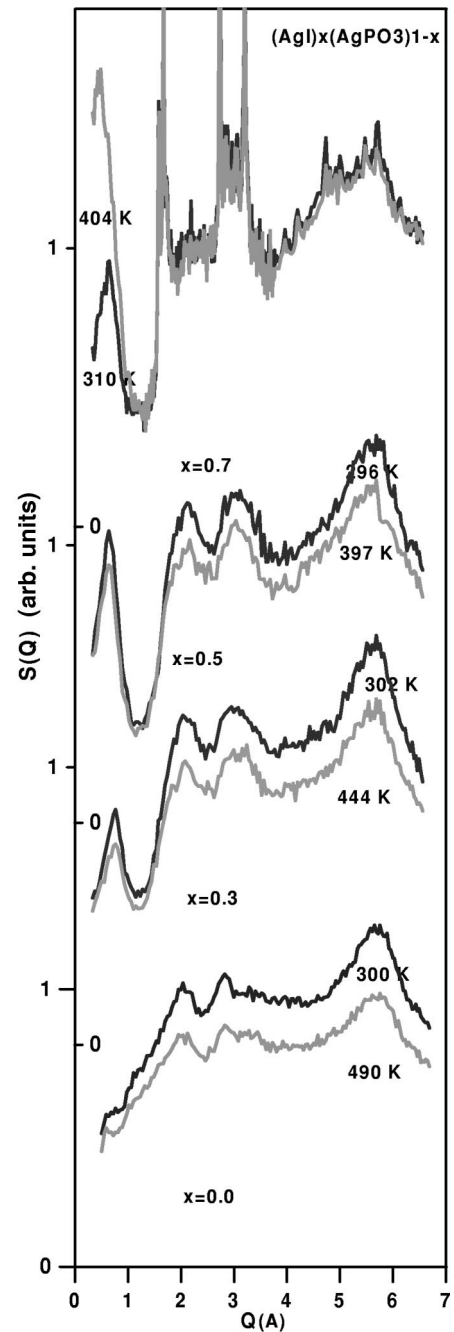

FIG. 2. The structure factor $S(Q)$ for $(AgI)_x(AgPO_3)_{1-x}$ at different temperatures and compositions.

B. Temperature dependence for AgPO$_3$

Figure 2 ($x=0.0$) shows $S(Q)$ for AgPO$_3$ glass for temperatures below and above the glass transition temperature (433 K). In this glass, there is no first sharp diffraction peak, and the diffraction pattern is similar for the glass and liquid phases. Overall, the pattern does not change much with temperature, but there is a decrease in intensity as the temperature is raised above the glass transition.

C. Temperature dependence of the FSDP intensities for $(AgI)_{0.3}(AgPO_3)_{0.7}$

Figure 2 ($x=0.3$) shows $S(Q)$ for this material at two different temperatures on heating. The patterns are similar in
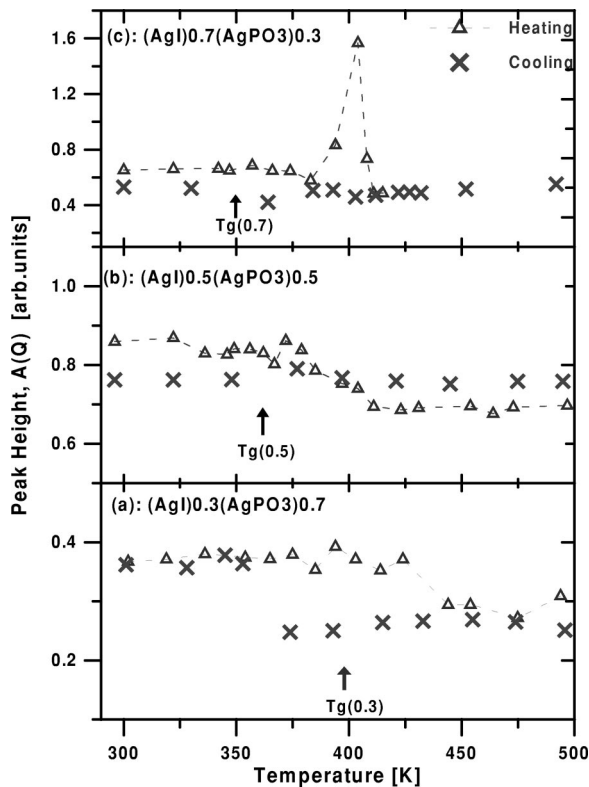
FIG. 3. The peak height of the first sharp diffraction peak for different compositions of $(AgI)_x(AgPO_3)_{1-x}$ as a function of temperature on heating (triangles) and cooling (crosses). The arrows show the glass transition temperatures as measured by DSC.

the glassy state at 302 K and in the liquid state at 444 K, but there is a general decrease in peak height at the higher temperature, as observed for $AgPO_3$. In contrast to $AgPO_3$, the patterns show a clear FSDP and a pronounced minimum at about 1.3 Å^{-1}. Figure 3(a) shows the fitted peak height as a function of temperature. Upon heating, the peak height of the FSDP changes very little until about 425 K when there is a small downward step, which we associate with a glass transition process. However, this step occurs at a higher temperature than the calorimetric glass transition at $T_g(0.3)$ = 397 K. Because the neutron measurements correspond to a lower heating rate than for the DSC measurements, they would be expected to give a glass transition temperature slightly lower than the DSC T_g, if anything.

Upon cooling the sample, the height of the first sharp diffraction peak remains the same until about 370 K when there is an increase in intensity. This change can be identified with the glass transition on cooling.

D. Temperature dependence of the FSDP intensities for $(AgI)_{0.5}(AgPO_3)_{0.5}$

Figure 2 ($x=0.5$) shows $S(Q)$ for this composition in the glassy state at 296 K and in the liquid state at 397 K. The pattern changes little with temperature except that the scattering is generally less at the higher temperature, as expected from the Debye-Waller factor. The peak heights obtained from Lorentzian fits are shown in Fig. 3(b) as a function of temperature upon heating and cooling. As also observed in earlier neutron-scattering measurements between 293 K and

403 K,[28] there is no change in peak intensity when the temperature is increased through the calorimetric glass transition temperature, $T_g(0.5)=361$ K. There is, however, a decrease in peak intensity on heating between 380 and 410 K. As for $x=0.3$, the glass transition seen in the diffraction pattern occurs at a temperature somewhat higher than indicated by the calorimetric data.

On cooling, the peak intensity remains essentially constant right down to room temperature, where it is different than observed for the starting sample. The starting sample was first quenched to 77 K and then warmed to room temperature, so it appears that changes in the sample must take place on cycling below 300 K.

E. Temperature dependence of the FSDP intensities for $(AgI)_{0.7}(AgPO_3)_{0.3}$

The stucture factor $S(Q)$ for this material is shown in Fig. 2 ($x=0.7$). As remarked previously, this sample is partially crystalline at all temperatures that we studied. At 310 K, the first sharp diffraction peak and the glass scattering in general is quite apparent but weaker than observed for samples with $x=0.3$ and 0.5. This is to be expected since a significant part of the sample volume is occupied by crystalline material.

At 419 K, a crystallization is present, from a phase of unknown composition. We deliberately crystallized some of our $AgPO_3$ sample and this did not give the new phase observed at 419 K. This new crystalline phase first appears at a temperature of 411 K on heating and persists through 494 K. Our next measurement at 544 K showed no sign of the phase, and it did not reappear on cooling. This crystallization must involve only a relatively small volume fraction of the material since its presence has little or no effect on the glass scattering for $Q>1.5$ Å^{-1}. Pure AgI in the α, β, or γ phases has no Bragg peaks for $Q<1.5$ Å^{-1}. The scattering from the AgI precipitate should thus not distort our results for the FSDP in this sample.

Figure 3(c) shows the peak height of the FSDP as obtained from the Lorentzian fits. The intensity remains constant on heating through the calorimetric glass transition (348 K), but it increases dramatically at about 400 K and then decreases rapidly as the Bragg peaks appear from crystallization. The dramatic increase in intensity may be a precursor to the crystallization process rather than a glass transition effect, and we are unsure as to the correct explanation of the observed behavior. On cooling back to room temperature, the height of the first sharp diffraction peak changes relatively little. As for the $x=0.5$ sample, the peak height does not return to its initial value at room temperature, presumably for similar reasons.

F. Temperature dependence of the FSDP correlation length and periodic length scale

Figures 4(a) and 4(b) show the correlation length, $D=2\pi/\Delta Q$, and the periodic length scale, $d=2\pi/Q_0$, from the Lorentzian fits, for various composition as a function of temperature. At room temperature, the correlation length decreases with increasing concentration from $x=0.3$ through $x=0.5$ to $x=0.7$, while the periodic length scale increases with increasing x, as shown in Fig. 4(b). At and above the solubility limit ($x=0.55$), the length scales are only weakly
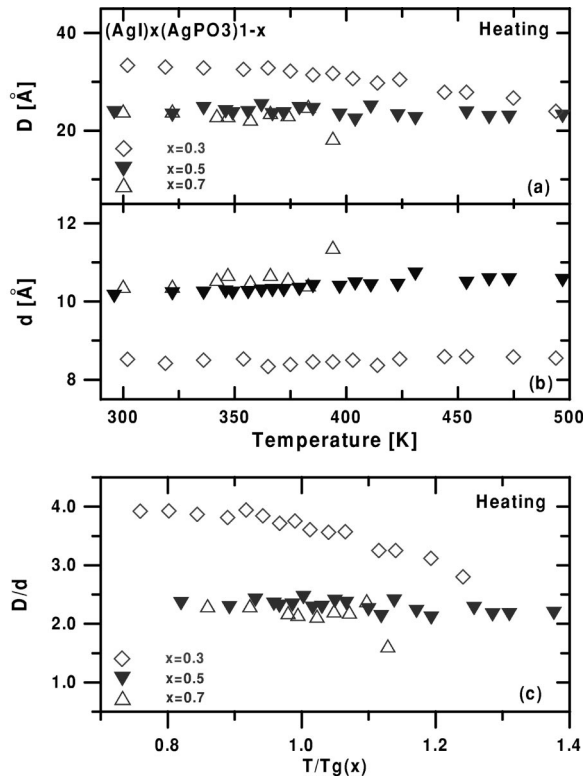
FIG. 4. (a) The correlation length D and (b) the length scale d of the first sharp diffraction peak for different composition of $(AgI)_x(AgPO_3)_{1-x}$ as a function of temperature upon heating; (c) the size ratio D/d plotted against the reduced temperature $T/T_g(x)$.

nitude greater than this, so the effects observed reflect temperature dependencies of the intermediate range order, not of the density of the whole glass.

It is interesting to look for a relationship between the correlation length and the periodic length scale of the first sharp diffraction peak as a function of temperature and composition. As mentioned in the previous section, the width of the peak reflects a correlation length within the glass while the position of the peak reflects a repetitive characteristic distance between structural units. The size ratio $Q_0/\Delta Q$, or equivalently the ratio D/d, is the ratio of these two lengths. It has been found for many glasses that $Q_0/\Delta Q$ is usually in the range from 3 to 5.[18] This means that the correlation length D of vitreous structures, i.e., the scale of intermediate-range order, is closely related to a characteristic periodic distance d of the underlying structural units which produce the FSDP.[18] The size ratio $Q_0/\Delta Q$ or D/d is plotted as a function of reduced temperature $T/T_g(x)$ in Fig. 4(c). The ratio varies between about 2 and 4 for our data. Its value is essentially constant at about 2.3 for the glasses with $x=0.5$ and $x=0.7$. If the saturation concentration for AgI dissolved in $AgPO_3$ is about 0.55,[35] these two glasses are relatively similar in composition, so it is not surprising that they show similar size ratios. The temperature independence of the size ratio might be taken to indicate that it is close to an optimum value. For $x=0.3$, the ratio is larger and varies between 2.5 and 4.0; in this case D is larger and d is smaller. Since this composition contains more phosphate and less iodide, it may be that the larger D reflects a larger spatial extent of the phosphate network, while the smaller value of d reflects a change in the spatial packing of this network.

V. DISCUSSION

In Fig. 5 we combine the data from Figs. 1 and 3 for different compositions by plotting (a) the thermal data and (b) the peak height, normalized to unity at room temperature, as a function of $T/T_g(x)$. For both the thermal data and the peak height, the three compositions show the same behavior as a function of the reduced temperature. For the calorimetric data, the only change of heat flow is at the glass transion temperature T_g, i.e., where the reduced temperature is equal to 1. For the peak height, there is no change at T_g on heating, but there is a drop in peak height between $T=1.06T_g$ and $T=1.11T_g$. It is as though the diffraction measurements are sensitive to a different transition temperature than the calorimetric measurements.

There is a possible explanation for this in terms of the established theory[36] of the glass transition that identifies two relaxation modes in glasses, α relaxation that involves slow diffusive motions and β relaxation that involves jump diffusion. The theory predicts that, on cooling, α relaxation processes freeze out first, followed by the freezing out of β processes at the calorimetric glass transition temperature T_g. Mode-coupling theory[36] quantifies this picture and predicts that the α relaxation processes freeze out at a temperature T_c that is about 10% higher than T_g. This difference in temperature is similar to that which we observe between the neutron and the DSC measurements. Thus, a possible explanation of the observations is that the intensity of the FSDP is more sensitive to α relaxation while the calorimetric data is more

composition dependent. Our results agree with those of Rousselot and co-workers[19,20] for the same material, but show a difference from those for the related glasses $(AgI)_x(Ag_2O\text{-}2B_2O_3)_{1-x}$,[29] where the position of the FSDP does not change with composition, and the length scale is about 8 Å^{-1}. The result shown in Fig. 4(b) indicates that structural periodicities of about 5–10 Å are built up when AgI is introduced into the base glass. This indicates ordering on a longer scale than in ordinary glasses, and is often referred to as intermediate-range order.[16,17]

Figure 4(a) shows that the correlation length for $x=0.3$ decreases almost linearly from 35 Å at room temperature to about 25 Å at the highest temperature studied. Figure 4(b) shows that the periodicity for this glass has little variation with temperature for d about 8.5 Å. As shown also in Figs. 4(a) and 4(b), for the glass with $x=0.5$ there is a slight decrease of the correlation length from about 25 to 23 Å and an increase of d from 10.1 to 10.6 Å over the range for heating. For $x=0.7$, the correlation length remains constant at about 24 Å on heating from 300 K to 390 K, and then decreases before crystallization takes place. The length scale also remains constant at about 10.5 Å on heating from 300 K to 390 K. It then increases sharply to about 14 Å at 410 K, followed by a rapid decrease as the sample crystallizes (not shown in the figure). The variation with temperature of the first sharp diffraction peak for $x=0.7$ is not understood.

We should also mention that unpublished work by one of us (N.I.) shows that the coefficient of linear thermal expansion of all these glasses is small, of order 1.5×10^{-6} K^{-1}. The temperature variation of d is one to two orders of mag-
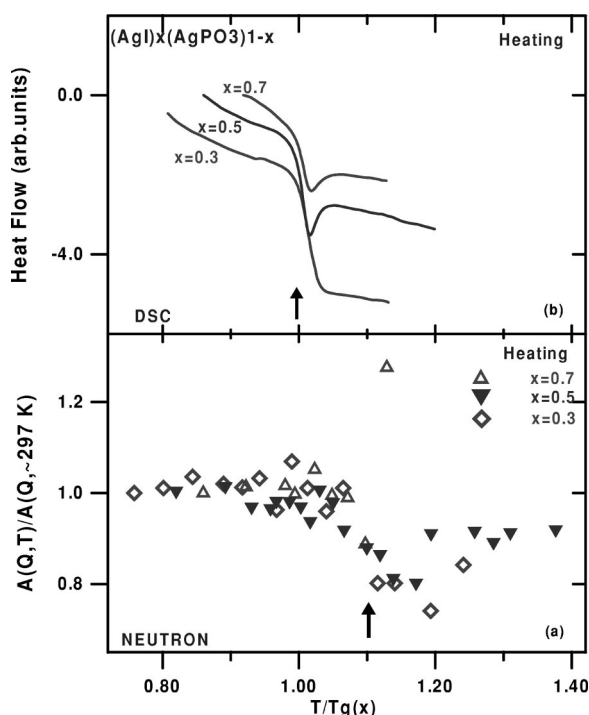
FIG. 5. The comparison between (a) the normalized peak height and (b) the thermal data for different compositions of $(AgI)_x(AgPO_3)_{1-x}$ plotted against the reduced temperature $T/T_g(x)$. The only feature in the thermal data is the onset of the glass transition temperature at $T/T_g(x) = 1$. The peak height plot is universal. There is no indication of a change at T_g, but there is a marked decrease between $T = 1.06T_g$ and $1.11\ T_g$.

sensitive to the switching on or off of β relaxation. Since α relaxation involves a cooperative motion of many atoms and β relaxation involves a change in position of maybe just one ion, it is likely that the diffraction pattern will be more sensitive to α processes than to β processes. In contrast, the larger energies associated with jump diffusion might mean that the specific heat is more sensitive to β processes.

VI. CONCLUSIONS

We have measured the evolution with temperature of the neutron-diffraction pattern of the superionic conducting glass $(AgI)_x(AgPO_3)_{1-x}$ for $x = 0.0$, 0.3, 0.5, and 0.7. Generally the doped glasses exhibit a first sharp diffraction peak at $Q \sim 0.6–0.8\ Å^{-1}$ and there is a pronounced minimum in the diffraction pattern at a Q value of about 1.3 $Å^{-1}$, as shown in Fig. 2. The results show that the intensity of the FSDP increases with increasing amount of AgI, while the position of the peak decreases meaning that the length scale increases. Our intensity data for both heating and cooling show a trend

similar to that of the other existing data for $x < 0.55$, i.e., before the solubility limit is reached.[33–35] For $x = 0.7$, i.e., above the solubility limit, the intensity of the FSDP decreases. This is probably linked to the presence of a crystalline component, which reduces the fraction of glassy material in the sample, and hence, the scattering.

As noted in the Introduction, it has been suggested that the first sharp diffraction peak arises from either small clusters of AgI within the phosphate network[10,19] or from a characteristic length scale of the phosphate network itself. The fact that there is no natural periodicity as large as 10 Å in AgI leads one to favor the latter explanation. This suggests that the FSDP arises because there is IRO in the phosphate chains, which remain covalently bonded but are pushed further apart by the dopant salt as explained by the RMC model.[15]

There is a universal behavior of the temperature dependence of the FSDP intensities on heating [Fig. 5(a)]. The intensity shows an anomalous decrease at a temperature about 6–11 % higher than T_g as measured calorimetrically [Fig. 5(b)]. This is tentatively ascribed to the diffraction intensity reflecting the onset of α relaxation, while the calorimetric data reflects the onset of β relaxation.

In this study, as a result of carrying out both neutron-diffraction and differential scanning calorimetric measurements on samples of identical composition and obtaining diffraction patterns for four compositions over a wide range of temperatures, and especially for temperatures above the calorimetric glass transition temperature T_g, we have shown that the superionic glass system $(AgI)_x(AgPO_3)_{1-x}$ exhibits a much richer variation of behavior than revealed by earlier, more restricted studies. Of particular significance is the fact that our diffraction results exhibit anomalous behavior at temperatures 6–11 % above T_g, strongly suggesting that the neutron scattering and calorimetric measurements are primarily sensitive to the α and β relaxation processes, respectively, and supporting the prediction of the mode-coupling theory of glasses.

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