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Structure of KCl–BiCl₃ ionic glasses by neutron diffraction

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Abstract. The structure of the ionic glasses (KCl)_x(BiCl₃)_{1-x}, where $x = 0.35, 0.40, 0.45$, has been measured at 20 K by using neutron diffraction. The results show that BiCl₃ units exist as the predominant structural motifs at all compositions, give a Bi–Cl nearest-neighbour distance of 2.53(2) Å, and an angle Cl–Bi–Cl of 89(2)°. The nearest-neighbour K–Cl correlations occur at about 3.1 Å. The first sharp diffraction peak observed in the total structure factors is attributed to Bi–Bi correlations and the shift in its position to smaller scattering vector values with increased x is attributed to an enlarged separation of the BiCl₃ units with enhanced KCl content.

1. Introduction

The object of this paper is to present neutron diffraction results on the structure of the glasses (KCl)_x(BiCl₃)_{1-x} where $x = 0.35, 0.40$ and 0.45 . Motivation for their study is provided by the observation that it is possible to continuously change the vitreous state from the halide glasses (KCl)_x(BiCl₃)_{1-x} to the pure chalcogenide glass As₂S₃ by addition of the latter compound (Gan 1992). Hence, the KCl–BiCl₃–As₂S₃ system offers the opportunity to progressively advance from an ‘ionic’ regime, for which there are interaction models that are good candidates for reproducing the microscopic structure and dynamics (Wilson and Madden 1994, Madden and Wilson 1996), to the ‘covalent’ regime, for which Car–Parrinello-type *ab initio* molecular dynamics methods look promising (see e.g. Massobrio *et al* 1998)‡. Furthermore, the effect of adding As₂S₃ is to increase the glass transition temperature T_g and render the materials far less hygroscopic which is of importance if they are to be used for practical applications (Gan 1992).

Glass formation in the (KCl)_x(BiCl₃)_{1-x} system is reported to occur in the range $0.25 \leq x \leq 0.45$ (Ziegler and Angell 1982) from melts that are good examples of ‘fragile’ liquids (Torell *et al* 1984, Angell 1988). The glasses have low T_g values in the range 25–45 °C, are transparent in the visible and IR range, have a high refractive index and low Abbe number (Angell and Ziegler 1981, Ziegler and Angell 1982), and may be doped with Nd³⁺ to give laser glasses with a large stimulated emission cross section (Weber *et al* 1982). Several of the elastic properties of the glasses have been obtained from Brillouin scattering studies (Torell 1983) and Raman spectra have been interpreted in terms of the existence of a variety of polyhedral units (Fung *et al* 1973, Jiang *et al* 1991). Further information on the glass structure does not, however, appear to exist.

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‡ Following Madden and Wilson (1996), we regard an ‘ionic’ system as one whose properties are reproduced by an interaction model based on discrete closed-shell ions with integer charges, and a ‘covalent’ system as one whose interactions arise from the formation of chemical bonds involving the sharing of pairs of electrons between atoms. Many properties conventionally attributed to ‘covalency’ may be explained in terms of ‘ionic’ interactions provided that effects such as polarization, compression and deformation are taken into explicit account.

2. Theory

In a neutron diffraction study on $(\text{KCl})_x(\text{BiCl}_3)_{1-x}$ glasses the total structure factor $F(k)$ derived from the coherent scattered intensity can be expressed as

$$F(k) = A[S_{KK}(k) - 1] + B[S_{BiBi}(k) - 1] + C[S_{ClCl}(k) - 1] + D[S_{KCl}(k) - 1] \\ + E[S_{KBi}(k) - 1] + F[S_{BiCl}(k) - 1] \quad (1)$$

where $A = c_K^2 b_K^2$, $B = c_{Bi}^2 b_{Bi}^2$, $C = c_{Cl}^2 b_{Cl}^2$, $D = 2c_K c_{Cl} b_K b_{Cl}$, $E = 2c_K c_{Bi} b_K b_{Bi}$ and $F = 2c_{Bi} c_{Cl} b_{Bi} b_{Cl}$. Here $S_{\alpha\beta}(k)$ denotes a Faber–Ziman partial structure factor, k is the scattering vector, and c_α , b_α denote the atomic fraction and coherent scattering length of chemical species α respectively. The values of the A – F coefficients, calculated using $b_K = 3.67(2)$ fm, $b_{Bi} = 8.532(2)$ fm and $b_{Cl} = 9.5770(8)$ fm (Sears 1992), are given in table 1 from which it can be seen that the diffraction patterns are dominated by the Cl–Cl and Bi–Cl correlations.

Table 1. The weighting coefficients on the $S_{\alpha\beta}(k)$ contributing to the total structure factor $F(k)$ for each of the $(\text{KCl})_x(\text{BiCl}_3)_{1-x}$ glasses.

x	A (mbarn)	B (mbarn)	C (mbarn)	D (mbarn)	E (mbarn)	F (mbarn)
0.35	1.52(1)	28.24(1)	445.54(5)	52.0(3)	13.08(7)	224.35(6)
0.40	2.10(2)	25.59(1)	433.52(5)	60.4(3)	14.68(8)	210.66(5)
0.45	2.84(2)	22.91(1)	420.90(5)	69.1(4)	16.13(9)	196.41(5)

The total pair distribution function corresponding to the total structure factor is given by

$$G(r) = A[g_{KK}(r) - 1] + B[g_{BiBi}(r) - 1] + C[g_{ClCl}(r) - 1] + D[g_{KCl}(r) - 1] \\ + E[g_{KBi}(r) - 1] + F[g_{BiCl}(r) - 1] \quad (2)$$

where $g_{\alpha\beta}(r)$ denotes a partial pair distribution function. The mean number of particles of type β contained in a volume defined by two concentric spheres of radii r_i and r_j , centred on a particle of type α , is given by

$$\bar{n}_\alpha^\beta = 4\pi n_0 c_\beta \int_{r_i}^{r_j} r^2 g_{\alpha\beta}(r) dr \quad (3)$$

where n_0 is the atomic number density of the glass.

3. Experimental details

The glasses were prepared using high purity KCl (99.999%, Aldrich) and BiCl_3 (99.999%, Aldrich). The KCl was dried for 36 h at 130 °C under vacuum and the BiCl_3 was dried for 36 h under vacuum at room temperature over the desiccant P_2O_5 . The salts were then loaded into silica cells of 5 mm inner diameter and 1 mm wall thickness, using a procedure designed to avoid contamination (Penfold and Salmon 1989), and sealed under chlorine gas, at a pressure of ≈ 0.5 atm at room temperature, to suppress the formation of reduced bismuth species (Angell and Ziegler 1981). The samples were then heated in a rocking furnace at 1 °C min^{-1} to 400 °C, where the chlorine vapour pressure was estimated to be 1.1 atm, left at this temperature for 12 h, and quenched into an ice/salt-water mixture at

-5 °C. The glasses were transparent with a slight yellow-greenish tinge and did not have the red coloration which is indicative of reduced bismuth species (Angell and Ziegler 1981). They were stored at 0 °C because of the low T_g values.

The thermal properties of the glassy samples were measured using a TA Instruments Thermal Analyst 2000 differential scanning calorimeter operating at a scan rate of 10 °C min^{-1} . The onset and midpoint T_g values were $47(1)$ °C and $48(1)$ °C for $x = 0.35$, $50(1)$ °C and $52(1)$ °C for $x = 0.40$, and $55(1)$ °C and $56(1)$ °C for $x = 0.45$ where the errors refer to the spread of values obtained from several different measurements. These T_g values are higher than those reported by Ziegler and Angell (1982) which may arise from the fast quench rate used in the present work. The scans indicated stress relaxation in the supercooled liquid regime and all three samples showed crystallization exotherms. The $x = 0.35$ glass showed two melting points at $157(2)$ °C and $172(2)$ °C while the $x = 0.40$ glass had a single melting point at $155(2)$ °C in excellent agreement with the phase diagram reported by Addison and Halstead (1966) for the $(KCl)_x(BiCl_3)_{1-x}$ pseudo binary tie line. The $x = 0.45$ glass showed a single melting point at $155(2)$ °C rather than the two expected from the phase diagram. The enthalpies of the melting transitions were $14(3)$ J g^{-1} ($T_m = 157$ °C) and $47(3)$ J g^{-1} ($T_m = 172$ °C) for $x = 0.35$, $58(3)$ J g^{-1} for $x = 0.40$, and $53(3)$ J g^{-1} for $x = 0.45$.

The neutron diffraction experiments were performed using the LAD instrument at the ISIS pulsed neutron source, Rutherford Appleton Laboratory. The samples were contained in vanadium cans of 8.8 mm inner diameter and 0.1 mm wall thickness and were cooled to 20 K using a closed cycle refrigerator to suppress both the thermal disorder and the possibility of devitrification. The complete experiment comprised the measurement of the diffraction patterns for the samples in their container, the empty container, the background scattering with nothing placed in the refrigerator, and a vanadium rod of $8.31(4)$ mm diameter for normalization purposes. The data analysis was made using the ATLAS suite of programs (Soper *et al* 1989) and the cross sections were calculated using the values of Sears (1992).

LAD comprises 14 groups of detectors at scattering angles of $\pm 5^\circ$, $\pm 10^\circ$, $\pm 20^\circ$, $\pm 35^\circ$, $\pm 60^\circ$, $\pm 90^\circ$ and $\pm 150^\circ$ corresponding to instrumental resolution functions ($\Delta k/k$) of 11%, 6%, 2.8%, 1.7%, 1.2%, 0.8% and 0.5% respectively. The final $F(k)$ were constructed by merging all those diffraction patterns from the different groups that showed good agreement. It was checked that the resultant $F(k)$ tend to the correct high- k limit, obey the usual sum rule relation and that there is good overall agreement between $F(k)$ and the back-Fourier transform of the corresponding $G(r)$ after the unphysical low- r oscillations are set to their calculated limiting $G(0)$ value (Salmon and Benmore 1992). The density of the $x = 0.40$ glass at room temperature (Weber *et al* 1982) was extrapolated to 20 K by using a temperature dependence estimated from the density of the molten phase (Addison and Halstead 1966). The liquid state density data were also used to estimate the density of the other glasses. The corresponding n_0 at 20 K are 0.0270 Å $^{-3}$ ($x = 0.35$), 0.0264 Å $^{-3}$ ($x = 0.40$) and 0.0259 Å $^{-3}$ ($x = 0.45$). Full details of the experiment are given by Wasse (1998).

4. Results

The measured $F(k)$ for the $(KCl)_x(BiCl_3)_{1-x}$ glasses are shown in figure 1 and have similar features. Each function has a first sharp diffraction peak (FSDP) which shifts its position k_{FSDP} from $1.32(3)$ Å $^{-1}$ to $1.17(3)$ Å $^{-1}$ via $1.23(3)$ Å $^{-1}$ as x is increased and which becomes more clearly defined. The total structure factor was also measured for a sample

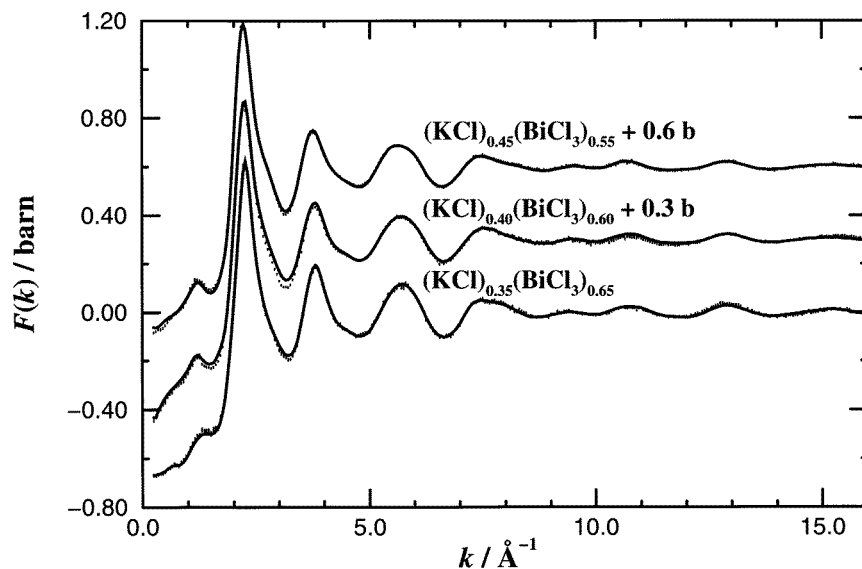


Figure 1. The measured total structure factors $F(k)$ for the $(\text{KCl})_x(\text{BiCl}_3)_{1-x}$ glasses at 20 K where $x = 0.35, 0.40$ or 0.45 . The bars represent the statistical errors on the data points and the solid curve is the back-Fourier transform of the corresponding $G(r)$ given by the solid curve in figure 2.

Table 2. The peak positions, coordination numbers and angles obtained from the measured $G(r)$ for the $(\text{KCl})_x(\text{BiCl}_3)_{1-x}$ glasses.

x	r_1 (Å)	r_2 (Å)	r_3 (Å)	r_4 (Å)	$\bar{n}_{\text{Bi}}^{\text{Cl}}$	Angle Cl–Bi–Cl (°)
0.35	2.54(2)	3.07(3)	3.53(3)	5.46(2)	3.0(2)	88(2)
0.40	2.53(2)	3.11(3)	3.55(3)	5.46(2)	3.0(2)	89(2)
0.45	2.53(2)	3.09(3)	3.56(3)	5.47(2)	3.0(2)	89(2)

of $(\text{KCl})_{0.25}(\text{BiCl}_3)_{0.75}$ prepared in an identical manner to the $x = 0.35$, $x = 0.40$ and $x = 0.45$ glasses. Small Bragg peaks were observed, i.e. the glass-forming region for KCl–BiCl₃ mixtures prepared using the method described in section 3 is smaller than quoted by Angell and Ziegler (1981).

The corresponding $G(r)$ functions, shown in figure 2, are dominated by the Cl–Cl and Bi–Cl correlations as seen from the weighting factors given in table 1. The overall features are comparable and the peaks occur at similar positions (see table 2).

The first peak in the $G(r)$ functions at $r_1 = 2.53(2)$ Å, covering the range $2.33 \lesssim r$ (Å) ≤ 2.82 for all three glasses, is assigned to Bi–Cl correlations by comparison with the structure of crystalline BiCl₃ wherein bismuth is surrounded by three chlorine atoms, in a distorted trigonal pyramidal arrangement, at a distance between 2.468(4) Å and 2.518(7) Å and a further five chlorine atoms at a distance between 3.216(9) Å and 3.450(9) Å (Nyburg *et al* 1971, 1972). With this identification, a coordination number of $\bar{n}_{\text{Bi}}^{\text{Cl}} = 3.0(2)$ is obtained for each of the glasses. The Bi–Cl distance is smaller than the sum of the ionic radii for Bi³⁺ (1.03 Å) and Cl[−] (1.81 Å) (Müller 1991) and is comparable to the sum of covalent radii for Bi (1.52 Å) and Cl (0.97 Å) (Cotton *et al* 1995), i.e. the structure is substantially different from that expected on the basis of a rigid ion model for the interactions

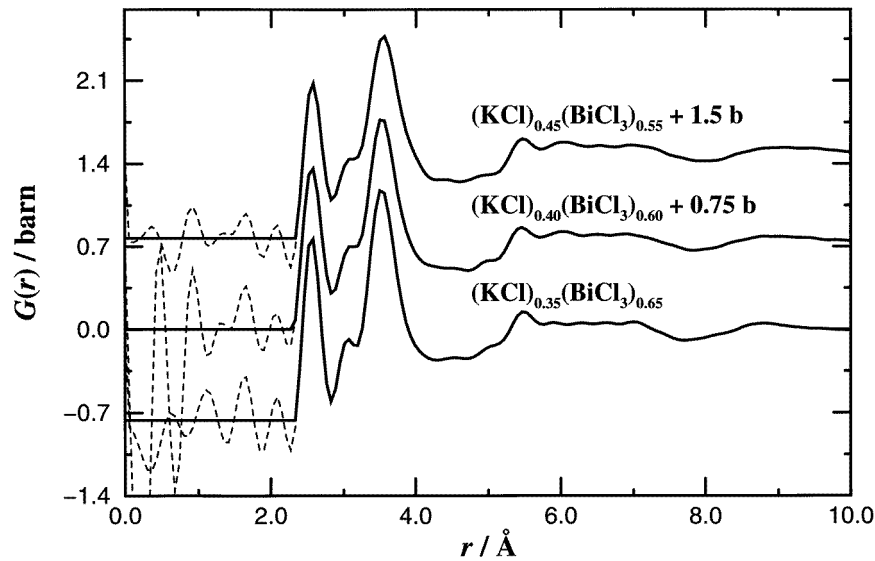


Figure 2. The total pair distribution functions $G(r)$ for the $(\text{KCl})_x(\text{BiCl}_3)_{1-x}$ glasses at 20 K, where $x = 0.35, 0.40$ or 0.45 , obtained by Fourier transforming the $F(k)$ given by the error bars in figure 1. The unphysical low- r oscillations about the $G(0)$ limits are shown by the broken curves.

(see Madden and Wilson 1996).

The second peak in the $G(r)$ functions at $r_2 \approx 3.1 \text{ \AA}$ occurs close to the sum of the ionic radii for K^+ (1.38 \AA) and Cl^- (1.81 \AA) (Müller 1991) and near to the position of the first peak in $g_{\text{KCl}}(r)$ at 2.98 \AA in molten KCl at $847 \text{ }^\circ\text{C}$ (Hily *et al* 1994). By comparison with the structures of molten KCl (Hily *et al* 1994) and molten BiCl_3 (Fukushima and Suzuki 1976, Price *et al* 1993) it is assigned to K–Cl correlations, i.e. although the K–Cl correlations receive a small weighting in each of the $G(r)$ functions they appear to be discernible. This is demonstrated in figure 3 where $G(r)$ for glassy $(\text{KCl})_{0.35}(\text{BiCl}_3)_{0.65}$ is compared with the combination

$$G^*(r) = 0.732 {}^{\text{BiCl}_3}G(r) + 1.5[g_{\text{KK}}(r) - 1] + 67[g_{\text{ClCl}}(r) - 1] + 52[g_{\text{KCl}}(r) - 1] \quad (4)$$

where ${}^{\text{BiCl}_3}G(r)$ is the measured total pair distribution function (in mbarn) for molten BiCl_3 at $270 \text{ }^\circ\text{C}$ (Fukushima and Suzuki 1976) and the $g_{\alpha\beta}(r)$ are the measured partial pair distribution functions for molten KCl at $847 \text{ }^\circ\text{C}$ (Hily *et al* 1994). The coefficients in equation (4) are chosen to give weighting factors on the partial pair distribution functions in $G^*(r)$ (namely 1.5 mbarn for $g_{\text{KK}}(r)$, 33 mbarn for $g_{\text{BiBi}}(r)$, 445 mbarn for $g_{\text{ClCl}}(r)$, 52 mbarn for $g_{\text{KCl}}(r)$, 224 mbarn for $g_{\text{BiCl}}(r)$ and 0 mbarn for $g_{\text{KBi}}(r)$) that are comparable to those in $G(r)$ (see table 1). Although the glass structure is unlikely to result from an exact superposition of the pair distribution functions of the melts, for which there is also considerable thermal broadening, the comparison shows that the second peak in $G(r)$ for the glasses is likely to result from K–Cl correlations.

The most intense peak in the $G(r)$ functions at $r_3 \approx 3.55 \text{ \AA}$ will, by comparison with the crystal structure of BiCl_3 , have a strong contribution from the Cl–Cl correlations. If the peak position is attributed to the Cl–Cl distance within a BiCl_3 pyramidal unit then an angle Cl–Bi–Cl of $89(2)^\circ$ is estimated which is within the range expected from the structure of crystalline BiCl_3 (Nyburg *et al* 1971, 1972).

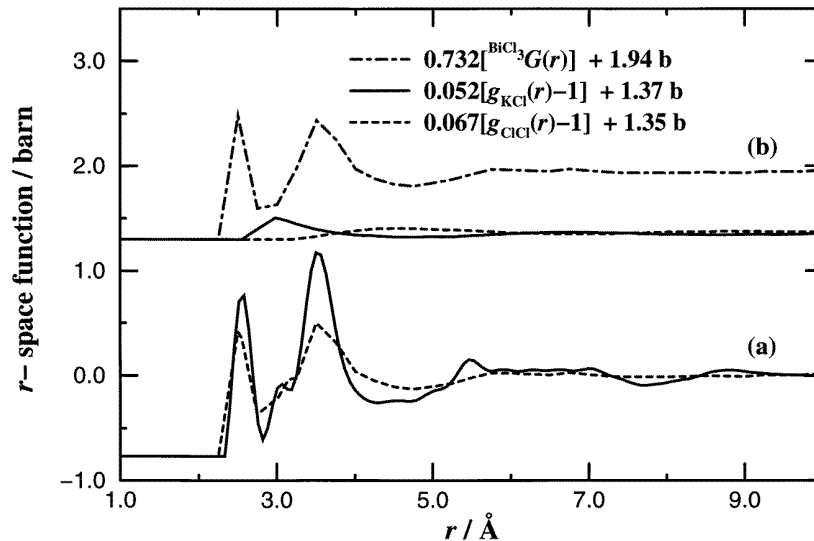


Figure 3. (a) Comparison of the experimental total pair distribution function $G(r)$ for glassy $(\text{KCl})_{0.35}(\text{BiCl}_3)_{0.65}$ (solid curve) with $G^*(r)$ as defined by equation (4) (broken curve). (b) The contributions to $G^*(r)$ from the total pair distribution function ${}^{\text{BiCl}_3}G(r)$ for molten BiCl_3 (chain curve) and the partial pair distribution functions $g_{\text{KCl}}(r)$ (solid curve) and $g_{\text{ClCl}}(r)$ (broken curve) for molten KCl (see text).

5. Discussion

The neutron diffraction results show that structural motifs of the type BiCl_3 appear in all three of the $(\text{KCl})_x(\text{BiCl}_3)_{1-x}$ glasses, an observation which also holds for molten BiCl_3 (Fukushima and Suzuki 1976, Price *et al* 1993). By comparison, the Raman spectra for molten BiCl_3 and molten and glassy KCl– BiCl_3 mixtures are similar (Fung *et al* 1973, Jiang *et al* 1991). The data for molten BiCl_3 have been interpreted in terms of the existence of BiCl_3 units of C_{3v} symmetry interacting with their surroundings while the data for the molten and glassy KCl– BiCl_3 mixtures have been interpreted in terms of the formation of BiCl_4^- and BiCl_6^{3-} anionic species (Fung *et al* 1973). The spectra for glassy KCl– BiCl_3 mixtures have also been interpreted in terms of the existence of BiCl_8^{5-} polyhedra of a type comparable to those found in crystalline BiCl_3 (Jiang *et al* 1991). The neutron diffraction results for the $(\text{KCl})_x(\text{BiCl}_3)_{1-x}$ glasses do not support the existence of a substantial number of higher species of the type BiCl_n^{3-n} where $n > 3$ unless the Bi–Cl bond lengths occur at a distance greater than 2.82 \AA , i.e. beyond the first minimum in the measured $G(r)$ functions.

In molten BiCl_3 the FSDP appearing in the measured total structure factor at $k_{\text{FSDP}} \approx 1 \text{ \AA}^{-1}$ has, by means of applying the method of isomorphous substitution in neutron diffraction, been identified with the Bi–Bi correlations (Fukushima and Suzuki 1976). This assignment of the FSDP to metal–metal atom correlations is consistent with several experiments on the structure of molten divalent metal halide systems (see e.g. Salmon 1992) and with the calculated structure of molten YCl_3 (Tosi *et al* 1991). By comparison with the data for molten BiCl_3 , the FSDP in the $(\text{KCl})_x(\text{BiCl}_3)_{1-x}$ glasses is also attributed to the correlations between bismuth-centred BiCl_3 units. The decrease in its position with increasing x then implies that the separation of the BiCl_3 units increases as KCl is added (Salmon 1994).

In molten RbCl–ZnCl₂ mixtures, k_{FSDP} also moves to a smaller value as RbCl is added to ZnCl₂ and the appearance of an FSDP at high RbCl concentrations is attributed to the correlations between ZnCl₄²⁻ ions, the network of pure ZnCl₂ having been disrupted by the large Rb⁺ ions (Wilson and Madden 1994). While there are similarities between the origin of the FSDP and its behaviour with respect to composition in the KCl–BiCl₃ and RbCl–ZnCl₂ mixtures, substantial differences between the structures of these two systems is expected on both the short and intermediate range distance scales. For example, the bismuth–chlorine interaction in molten BiCl₃ (Fukushima and Suzuki 1976, Price *et al* 1993) has a substantially larger ‘covalent’ component than the zinc–chlorine interaction in molten ZnCl₂ (Biggin and Enderby 1981) as manifest by a smaller coordination number ($\bar{n}_{Bi}^{Cl} = 3$, cf. $\bar{n}_{Zn}^{Cl} = 4$), a Bi–Cl distance which is incommensurate with the sum of the cation and anion radii, and a smaller Pauling electronegativity difference between the chemical species (Huheey *et al* 1993). Furthermore, although molten BiCl₃ is fairly viscous when compared with most molten metal halides, it is far less viscous than ZnCl₂ and it also has a substantial electrical conductivity (Akdeniz and Tosi 1992). Additionally, the ratio of the ionic radii for Rb⁺ and Zn²⁺ is much larger at 2.05 than the corresponding ratio for K⁺ and Bi³⁺ at 1.34 (Müller 1991). It will therefore be interesting to discover the extent to which ionic interaction models that include an account of ionic polarization phenomena (Madden and Wilson 1996) can reproduce the observed structure of the glassy KCl–BiCl₃ mixtures.

6. Conclusions

The neutron diffraction results for the (KCl)_x(BiCl₃)_{1-x} glasses show that BiCl₃ units exist as the predominant structural motifs over the range $0.35 \leq x \leq 0.45$ and are consistent with a pyramidal geometry wherein the angle Cl–Bi–Cl is 89(2)°. The first peak in $g_{KCl}(r)$ appears at about 3.1 Å, a value comparable to that found in molten KCl. The FSDP in the total structure factors is attributed to the Bi–Bi correlations between the bismuth-centred BiCl₃ structural motifs and the shift in k_{FSDP} to smaller k -values with increased x is attributed to an enlarged separation of the BiCl₃ units with enhanced KCl content.

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