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## Local structure around Gd in GdAl<sub>3</sub>Cl<sub>12</sub> glass and supercooled liquid: a Gd L<sub>III</sub>-edge EXAFS study

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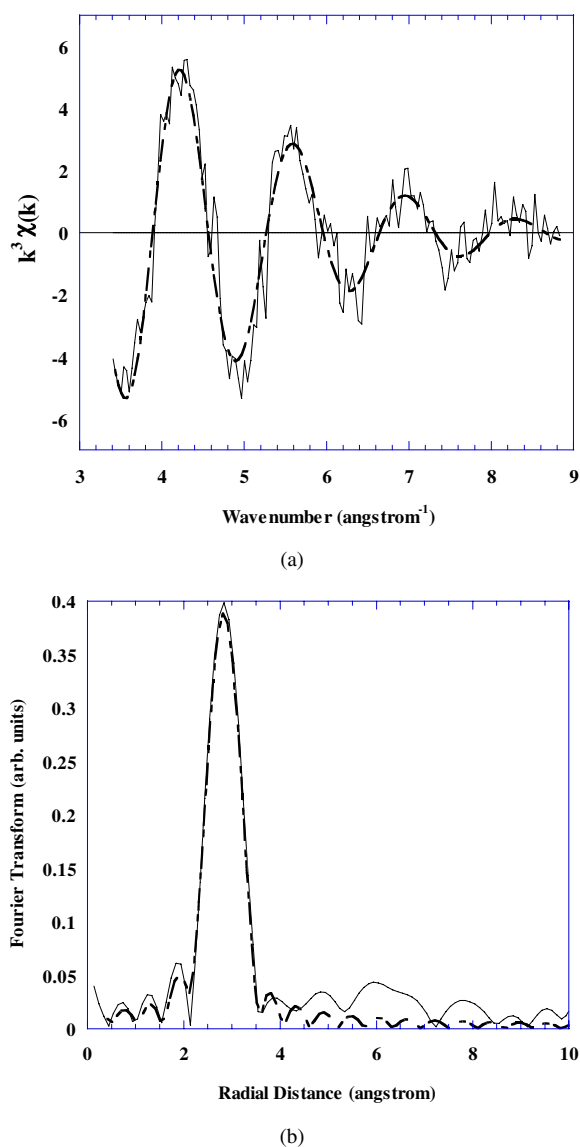
**Abstract.** The coordination environment around Gd<sup>3+</sup> ions in GdAl<sub>3</sub>Cl<sub>12</sub> glass and supercooled liquid has been studied using Gd L<sub>III</sub>-edge EXAFS spectroscopy. The Gd coordination environment in the glass is found to be similar to that in the GdAl<sub>3</sub>Cl<sub>12</sub> crystal with eight Cl nearest neighbours and four Al next-nearest neighbours. The Gd–Cl distance in the glass is the same as that in the crystal (~2.8 Å) although the Gd–Al distance in the glass (~3.85 Å) is longer than that in the crystal (~3.7 Å), indicating a less dense structure with a larger Gd–Cl–Al bond angle in the former. The Gd–Cl distance and coordination number are found to remain unchanged in the supercooled liquid at 60 °C. However, the absence of any Gd–Al second-neighbour shell in the EXAFS spectrum of the liquid indicates substantial increase in static disorder in the spatial disposition of AlCl<sub>4</sub> tetrahedra around Gd in the liquid. Such temperature dependent structural changes are suggested to be responsible for the marked fragility of this liquid.

Structural studies of liquids and glasses have been strongly motivated in the last few years by the need for understanding the temperature dependent structural changes in these amorphous materials [1–6]. This is mainly because of the important role played by such structural changes in controlling the physico-chemical properties of these systems relevant to their technological applications over a wide range of temperatures. From a fundamental point of view, glass formation upon cooling below the melting point is a long-standing research problem and a variety of universal phenomena and molecular mechanisms that accompany it are not yet fully understood [7].

The structural complexities in a number of crystalline and molten chloride and bromide salts have been found to be interesting from this standpoint. A number of studies based on vibrational Raman spectroscopy, neutron scattering and computer simulation have been undertaken in the past in order to establish the atomic structure of the MX<sub>3</sub> (M = Al, Ga, Fe, rare earth; X = halogen) molten salts [8–16]. Melting of the crystalline phases of these compounds is often found to be accompanied by large structural and volume changes [10, 11, 17, 18]. At the other extreme, ZnCl<sub>2</sub> provides an example of a halide salt which shows remarkable similarity in the short-range structure between its crystalline, glassy and liquid phases [19]. The halide molten mixtures in the binary LnX<sub>3</sub>–AlX<sub>3</sub> systems have been found to be novel glass-formers in recent studies [20, 21]. These studies have used vibrational Raman spectroscopy in order to establish the glass-forming composition ranges and to elucidate the structure of the glasses and liquids. Moreover, recent dynamic light scattering studies have

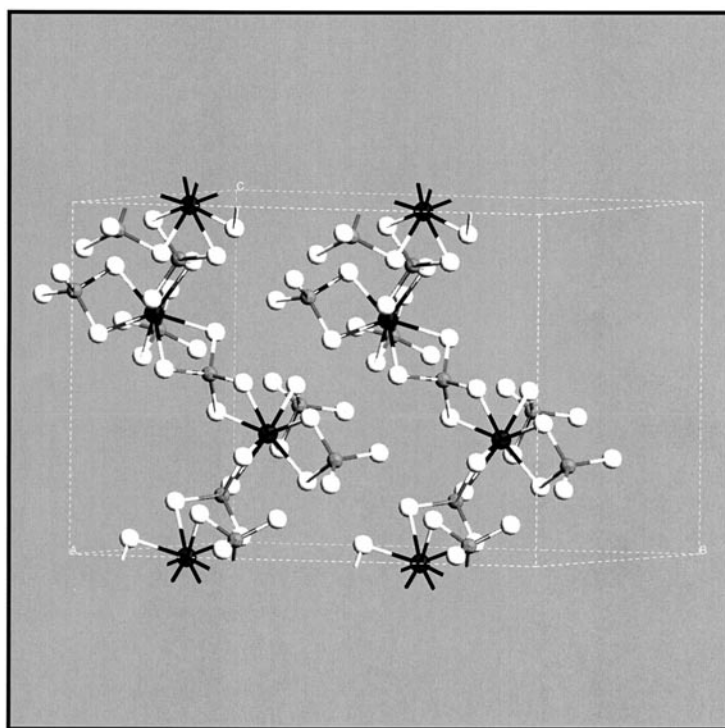
revealed important distinctions in the dynamic behaviour exhibited by different lanthanide glass-forming liquids [22]. These systems are important non-classical solvents and take part in industrial separation and extraction processes [20]. Their suitability for industrial use critically depends on their transport properties that are in turn expected to be closely linked with the temperature dependence of the short-range structural aspects in the glasses and liquids [2, 23].

In this study we have investigated the local coordination environments around the Gd atoms in the crystalline, glassy and the supercooled state for the composition  $\text{GdAl}_3\text{Cl}_{12}$  with Gd  $L_{III}$ -edge extended x-ray absorption fine structure (EXAFS) spectroscopy. This system has been chosen as it is one of the most stable glass-formers in the binary  $\text{LnX}_3\text{-AlX}_3$  mixtures that crystallizes stoichiometrically, thereby allowing a direct structural comparison between the crystal, glass and liquid of the same composition. The glass transition temperature  $T_g$  for the  $\text{GdAl}_3\text{Cl}_{12}$  liquid has been estimated to be  $\sim 35^\circ\text{C}$  from recent photon correlation spectroscopic measurements of the structural relaxation times [22]. The chemicals used for the preparation of the samples are extremely hygroscopic and all handling took place in a dry and oxygen-free nitrogen environment.  $\text{AlCl}_3$  (Fluka/Pure Inc. >99%) was purified by repeated slow sublimations in Pyrex tubes sealed *in vacuo*.  $\text{GdCl}_3$  (Cerac Pure, 99.9%) was purified by dynamic sublimation at  $800^\circ\text{C}$  and  $\sim 10^{-7}$  mbar. Fused silica tubes filled with stoichiometric amounts of the component were placed on a vacuum line and sealed with a butane torch. After slowly heating the samples in the temperature range  $200\text{--}350^\circ\text{C}$  for a few hours,  $\text{GdCl}_3$  was dissolved in liquid  $\text{Al}_2\text{Cl}_6$  and clear solutions were obtained, which filled more than two-thirds of the cells' volume. The glass was formed upon rapid cooling of the liquids in water at room temperature and remained stable for months/years. Slow cooling of the liquid and/or devitrification of the glass gave the crystalline  $\text{GdAl}_3\text{Cl}_{12}$  compound. More details about the preparation of the samples can be found elsewhere [21]. For EXAFS spectroscopy all samples were ground to fine powder and were transferred into  $10\ \mu\text{m}$  thick glass capillaries that were subsequently sealed using a light flame. Gd  $L_{III}$ -edge EXAFS spectra were collected at station 9.3 at the Daresbury Laboratory Synchrotron Radiation Source (SRS). An Si(220) monochromator was used and all spectra were obtained in the transmission mode.  $\text{GdCl}_3$  and  $\text{GdAl}_3\text{Cl}_{12}$  crystals have been used as model compounds. The Gd-EXAFS spectra for the  $\text{GdAl}_3\text{Cl}_{12}$  glass and  $\text{GdCl}_3$  and  $\text{GdAl}_3\text{Cl}_{12}$  crystals were obtained at ambient temperature. The Gd EXAFS spectrum of the  $\text{GdAl}_3\text{Cl}_{12}$  liquid was obtained *in situ* by heating the capillary tube containing the glass sample with a steady flow of hot air. Such a set-up allowed us to obtain temperatures up to  $100^\circ\text{C}$  with a maximum temperature gradient of  $5^\circ\text{C}$  across the length of the sample. Unfortunately, the  $\text{GdAl}_3\text{Cl}_{12}$  liquid was found to crystallize at temperatures above  $T_g$  over the time scale required for EXAFS data collection, typically 8 to 10 hours. However, we were able to avoid this problem by averaging data at  $60^\circ\text{C}$  on multiple samples over a shorter time scale. The EXAFS data have been analysed using the Daresbury laboratory EXBROOK and EXCURV92 software packages. The raw absorption spectra were background subtracted using the EXBROOK package. The  $k^3$ -weighted EXAFS oscillations were then fitted using the least-squares fitting routine EXCURV92. This routine is based on the curved-wave theory of EXAFS [24]. The three structural parameters that are varied in order to obtain the best fit are (i) the radial distance  $R$  of the atomic neighbours in a coordination shell of the central Gd atom, (ii) the coordination number  $N$  and (iii) the Debye–Waller factor  $2\sigma^2$ . The appropriateness of the calculated phase shifts for various atom pairs containing Gd has been tested by fitting the Gd EXAFS spectra of  $\text{GdCl}_3$  and  $\text{GdAl}_3\text{Cl}_{12}$  crystalline compounds. However, it must be noted that in EXAFS data analysis the coordination number and the Debye–Waller factor are correlated quantities and the quality of the fit can be kept unchanged by simultaneously increasing or decreasing both of these quantities over some limited range. The related uncertainties in the coordination numbers for Gd in these materials have been found to be of the order of  $\pm 1$ .



**Figure 1.** (a)  $k^3$ -weighted Gd  $L_{III}$ -edge EXAFS and (b) the corresponding Fourier-transformed partial radial distribution function for Gd ions at room temperature in the  $GdCl_3$  crystal. Solid lines represent experimental data and dashed lines correspond to least-squares fits using EXCURV92 (see text for details).

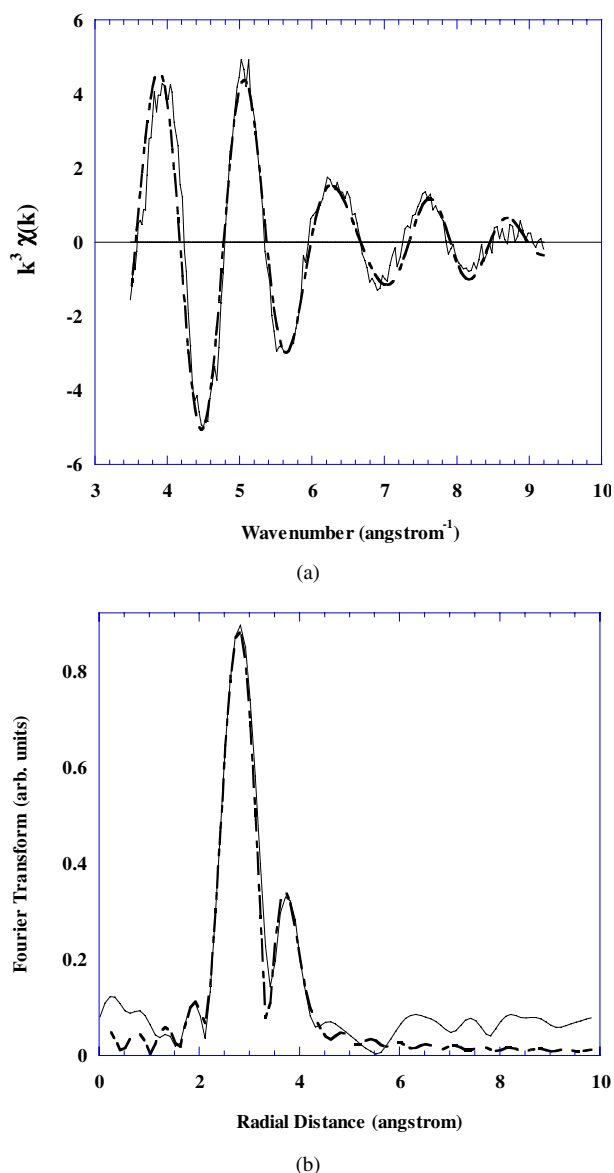
The experimental Gd EXAFS spectrum and its Fourier transform for the  $GdCl_3$  crystal are shown in figure 1. The best fit results in a Gd–Cl shell with 9 Cl at a distance of 2.85  $\text{\AA}$  with a Debye–Waller factor of 0.045  $\text{\AA}^2$  (figure 1). In a previous x-ray diffraction study it has been shown that the Gd ion in  $GdCl_3$  is surrounded by 9 Cl ions of which 6 Cl are at a distance of 2.822  $\text{\AA}$  while the other 3 Cl are situated at a distance of 2.918  $\text{\AA}$  [25]. Although the two types of Cl could not be resolved in the EXAFS spectrum, the average Gd–Cl distance as well as the coordination number are found to agree well with the x-ray results. Unfortunately, to



**Figure 2.** A perspective view of the crystal structure of isostructural  $\text{LnAl}_3\text{Cl}_{12}$  ( $\text{Ln} = \text{Y}$ , rare earths) compounds [26]. The Ln, Al and Cl atoms are shown in black, dark grey and light gray respectively.

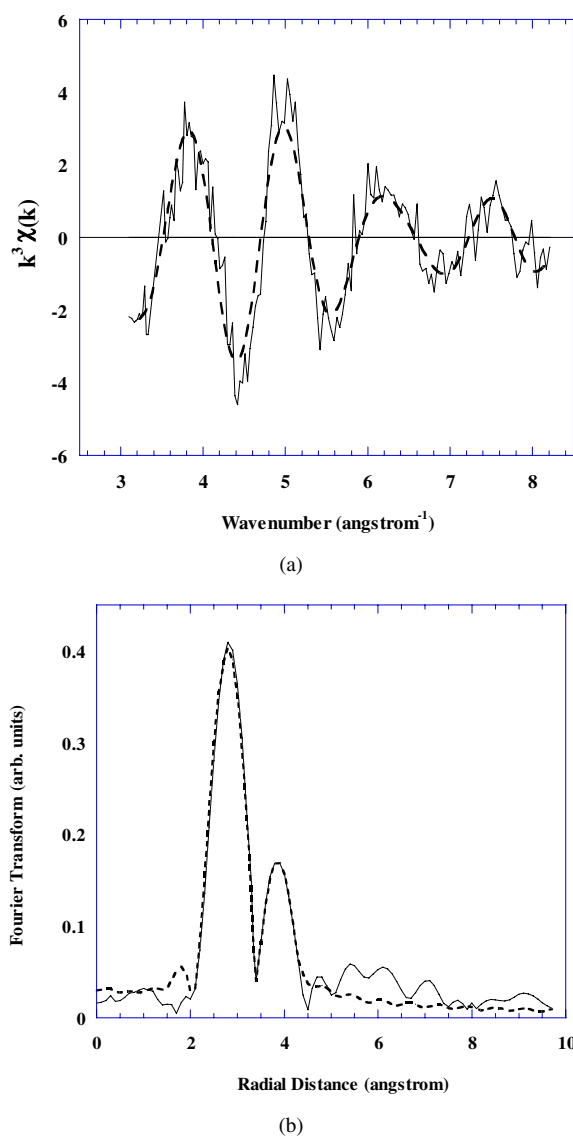
our knowledge, no x-ray diffraction structural refinement data on the  $\text{GdAl}_3\text{Cl}_{12}$  crystal exist in the literature. However, the crystal structures of isostructural  $\text{DyAl}_3\text{Cl}_{12}$ ,  $\text{HoAl}_3\text{Cl}_{12}$  and  $\text{YAl}_3\text{Cl}_{12}$  compounds are well known from previous studies [26]. In these crystal structures each rare earth atom is coordinated to eight Cl atoms through edge-sharing with four  $\text{AlCl}_4$  tetrahedra (figure 2). Two of these tetrahedra undergo double edge-sharing with two adjacent rare earth—Cl polyhedra to form puckered chains along the crystallographic  $c$ -axis (figure 2). The average Dy—Cl, Dy—Al, Ho—Cl and Ho—Al distances in these crystals are 2.79, 3.67, 2.78 and 3.67 Å respectively, while the average Y—Cl distance is 2.78 Å [26]. The experimental EXAFS spectrum of the  $\text{GdAl}_3\text{Cl}_{12}$  crystal and its Fourier transform (figure 3) clearly indicate the presence of two shells in the partial radial distribution function of Gd. The first peak is best fit with a shell of 8 Cl at a distance of 2.80 Å with a Debye–Waller factor of  $0.042 \text{ \AA}^2$ . The second shell corresponds to four Al next-nearest neighbours at a distance of 3.70 Å with a Debye–Waller factor of  $0.05 \text{ \AA}^2$ . These results on crystalline compounds indicate the general validity of the electron scattering phase shifts for the Gd—Cl and Gd—Al atom pairs as calculated by the EXCURV92 package. These phase shifts have therefore been treated as transferable constants for the analysis of the Gd EXAFS spectra of  $\text{GdAl}_3\text{Cl}_{12}$  glass and liquid.

The experimental EXAFS spectrum and its Fourier transform for the  $\text{GdAl}_3\text{Cl}_{12}$  glass and liquid are shown in figures 4 and 5 respectively. The Fourier transform of the glass spectrum (figure 4(b)) shows two shells around the central Gd ion. The best fit results in a first shell of 8 Cl at a distance of 2.80 Å. The Debye–Waller factor for this shell is found to



**Figure 3.** (a)  $k^3$ -weighted Gd  $L_{III}$ -edge EXAFS and (b) the corresponding Fourier-transformed partial radial distribution function for Gd ions at room temperature in the  $\text{GdAl}_3\text{Cl}_{12}$  crystal. Solid lines represent experimental data and dashed lines correspond to least-squares fits using EXCURV92 (see text for details).

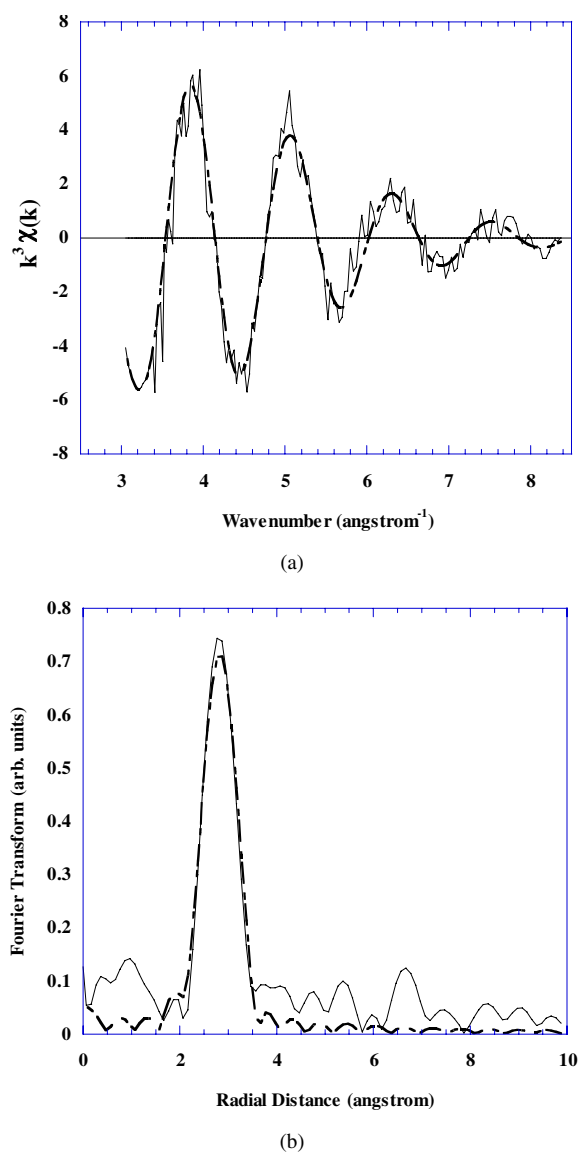
be  $0.044 \text{ \AA}^2$ . The second peak is best fit with a shell of 4 Al at  $3.85 \text{ \AA}$  with a Debye–Waller factor of  $0.05 \text{ \AA}^2$  (figure 4). The Gd coordination environment as well as the average degree of structural connectivity in the glass are therefore clearly similar to those in the corresponding crystal. This result is in agreement with a previous Raman spectroscopic study on the crystal, glass and liquid of  $\text{GdAl}_3\text{Cl}_{12}$  composition which indicates a general short-range structural similarity between these phases [20]. However, the EXAFS results indicate that the average Gd–Al distance in the glass is  $0.15 \text{ \AA}$  longer than that in the crystal. As the Gd–Cl average



**Figure 4.** (a)  $k^3$ -weighted Gd  $L_{III}$ -edge EXAFS and (b) the corresponding Fourier-transformed partial radial distribution function for Gd ions at room temperature in the  $\text{GdAl}_3\text{Cl}_{12}$  glass. Solid lines represent experimental data and dashed lines correspond to least-squares fits using EXCURV92 (see text for details).

distances are similar in both phases, the longer Gd–Al distance probably indicates a larger average Gd–Cl–Al bond angle in the glass compared to that in the crystal.

The experimental EXAFS spectrum of the  $\text{GdAl}_3\text{Cl}_{12}$  liquid collected at  $60^\circ\text{C}$  and its Fourier transform are shown in figure 5. The best fit results in a Gd–Cl shell similar to that observed in the crystal and the glass with 8 Cl at a distance of  $2.81 \text{ \AA}$  with a Debye–Waller factor of  $0.042 \text{ \AA}^2$  (figure 5). However, in contrast with the observations in the case of the  $\text{GdAl}_3\text{Cl}_{12}$  crystal and the glass, no Gd–Al second shell is observed in the partial radial distribution function of Gd ions in the liquid of the same composition at  $60^\circ\text{C}$  (figure 5(b)). This phenomenon has



**Figure 5.** (a)  $k^3$ -weighted Gd  $L_{III}$ -edge EXAFS and (b) the corresponding Fourier-transformed partial radial distribution function for Gd ions at 60°C in the  $GdAl_3Cl_{12}$  supercooled liquid. Solid lines represent experimental data and dashed lines correspond to least-squares fits using EXCURV92 (see text for details).

been found to be thermally reversible as the Gd–Al second shell reappears in the ambient temperature EXAFS spectrum of the glass on quenching the liquid. The unobservability of Al second neighbours in the Gd EXAFS spectrum of the liquid is most likely to be due to a strong static and/or thermal disorder in the topological disposition of Al atoms around Gd in the liquid. Such a disorder would increase the Debye–Waller factor of the Al second shell which may result in a Gd–Al peak too broad to be observable. However, the similar Debye–Waller factors for the Gd–Cl shell in the  $GdAl_3Cl_{12}$  glass and the liquid as well as the relatively



small temperature difference between the glass and the liquid spectra strongly indicate that thermal disorder is not likely to be the controlling factor for this phenomenon. As the number of Cl nearest neighbours around Gd remains unchanged on transformation of the glass into a supercooled liquid it is probably safe to conclude that the increased structural disorder in the liquid is not indicative of breaking of Gd–Al–Cl linkages.

In a previous Raman spectroscopic study it has been suggested that the basic building blocks in the  $\text{LnCl}_3\text{--AlCl}_3$  glasses and liquids are the  $\text{AlCl}_4$  tetrahedral units and occasional corner-shared  $\text{Al}_2\text{Cl}_7$  units that share edges with the Ln–Cl coordination polyhedra [20]. Therefore, the absence of the Gd–Al second shell in the  $\text{GdAl}_3\text{Cl}_{12}$  supercooled liquid can be related to a temperature dependent increase in static disorder in the spatial disposition of  $\text{AlCl}_4$  tetrahedral units around Gd in the liquid phase. It must be noted in this regard that the singly edge-shared  $\text{AlCl}_4$  tetrahedra in the  $\text{GdAl}_3\text{Cl}_{12}$  atomic structure are likely to have larger temperature dependent orientational degrees of freedom than that in the case of doubly edge-shared  $\text{AlCl}_4$  tetrahedra (figure 2). Such topological changes are likely to be an important source of configurational entropy which may give rise to a significantly non-Arrhenian temperature dependence of the structural relaxation time of the  $\text{GdAl}_3\text{Cl}_{12}$  liquid [27]. This is in contrast with the case of the topologically less flexible tetrahedral  $\text{ZnCl}_2$  structure where neutron diffraction results indicate strong structural similarity in the short and intermediate range between the glassy and the liquid phases [19]. Thus the freedom towards structural readjustment in response to temperature changes would render the liquids in the  $\text{GdCl}_3\text{--AlCl}_3$  system significantly more fragile than the tetrahedral network-forming  $\text{ZnCl}_2$  liquid [28]. Recent measurements of the structural relaxation times as a function of temperature with photon correlation spectroscopy have shown that this is indeed the case for  $\text{GdAl}_3\text{Cl}_{12}$  liquid [22]. The fragility index  $m$ , defined as  $m = d(\log \tau)/d(T_g/T)$  at temperatures near  $T_g$ , where  $\tau$  is the structural relaxation time and  $T$  is the absolute temperature, has a value of  $\sim 30$  for  $\text{ZnCl}_2$  whereas  $m \sim 60$  for the  $\text{GdAl}_3\text{Cl}_{12}$  liquid [3, 22]. It is tempting to hypothesize that the  $\text{GdAl}_3\text{Cl}_{12}$  liquid, and probably the  $\text{LnX}_3\text{--AlX}_3$  liquids in general, have bonding characteristics that would allow for temperature dependent changes in the short-range structure. As non-directional ionic bonding would impart more structural and topological degrees of freedom than directional covalent bonding, one possibility is that the  $\text{LnX}_3\text{--AlX}_3$  liquids are more akin to the Ca–K nitrate type of ionic glass-formers than  $\text{ZnCl}_2$ . However, a detailed verification of these hypotheses would require a more complete picture of the structure of these glasses and liquids that could be obtained by using a combination of techniques such as neutron diffraction and high energy x-ray anomalous scattering at the Gd K edge.

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