The structure of LiAlCl₄ has been investigated by neutron diffraction of isotopically enriched samples. The lithium contribution to the scattering has been removed by using a "null" scattering sample, of ⁶Li and ⁷Li. We have derived three partial structure factors S_{LiA} (k), S_{ClCl}(k) and S_{AlCl}(k) and their Fourier transforms, the partial radial distribution functions (rdf's), g_{LiA}(r) and g_{AlCl}(r) and g_{ClCl}(r) are at 3.51, 2.13 Å, respectively. The coordination numbers obtained by integrating to the first minima are about 6, and 4, respectively. As anticipated, the existence of extremely well defined AlCl₄⁻ tetrahedra has been established, with little if any Al-Cl-Al bridging between tetrahedra in this melt. The results are similar to those predicted from molecular dynamical calculations on model systems.

INTRODUCTION

Ordered or complexing molten salt mixtures have aroused the interest of thermo-dynamicists and structural chemists alike since the thermodynamic and physical properties of these mixtures have strong compositional dependencies which are not completely understood. There is no statistical mechanical theory for the precise description of binary complexing systems such as LiF-BeF₂ or LiCl-AlCl₃. In order to deduce useful concepts and theories for such systems, much more information on the structural and thermodynamic characteristics are needed.

With this in mind, we set out to investigate the structure of the melt LiAlCl₄, as a first step in the characterization of a particular binary complexing salt pair.
at different compositions. This type of melt has been central to recent molecular dynamical (MD) studies carried out by Saboungi et al.\textsuperscript{1} who demonstrate that the structure is a very strong function of interionic potential. We have been able to confirm the expected presence of AlCl\textsubscript{4} tetrahedra in this melt and to make detailed comparison with MD calculations.

We find broad agreement with the MD results which are based on a simplified Tosi-Fumi potential for a melt analogous to NaAlCl\textsubscript{4}. The height of the first peak in the measured partial radial distribution function, $g_{\text{AlCl}_4}(r)$, is unusually large. This was not detected in recent X-ray results on this melt\textsuperscript{2} which are otherwise consistent with our results. In what follows we describe our neutron diffraction measurements as well as the partial structure factors and radial distribution functions (rdf’s) for AlAl, ClCl, and AlCl pairs deduced from the measurements.

**EXPERIMENT**

The sample parameters pertaining to the experiment are shown in Table 1; the sample temperature was 200°C. As with previous experiments by the group at Bristol,\textsuperscript{4} the partial structure factors $S_{\alpha\beta}(k)$ (where $\mathbf{k}$ is the momentum transfer in the scattering process) can be separated from three independent total structure factors, $F(k)$, obtained from at least three samples of a given chemical composition with each sample having a different isotopic composition. $F(k)$ is the quantity obtained directly from a single neutron diffraction experiment on a liquid with a particular isotopic composition.

In the case of LiAlCl\textsubscript{4}, the Li contribution to the scattering has been removed using null-scattering lithium, a mixture of $^6$Li and $^7$Li (see Table 1). The melt is then seen by the neutron beam as a simple two species melt, where

$$F(k) = c_{\text{Al}}^2 f_{\text{Al}}^2 [S_{\text{AlAl}}(k) - 1] + c_{\text{Cl}}^2 f_{\text{Cl}}^2 [S_{\text{ClCl}}(k) - 1] + 2c_{\text{Al}}c_{\text{Cl}}f_{\text{Al}}f_{\text{Cl}}[S_{\text{AlCl}}(k) - 1]$$

for example

$$F_{\text{nat}}(k) = 0.0033[S_{\text{AlAl}}(k) - 1] + 0.408[S_{\text{ClCl}}(k) - 1] + 0.0734[S_{\text{AlCl}}(k) - 1]$$

where $c_{\alpha}$ is the atomic fraction of species $\alpha$, $f_{\alpha}$ is its neutron coherent scattering length, and $S_{\alpha\beta}(k)$ is a partial structure factor. The Fourier transform of $F(k)$ produces the total radial distribution function $G(r)$ using the relation

$$G(r) = \frac{1}{2\pi^2 pr} \int_{0}^{\infty} k^2 \sin kr F(k) dk.$$

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Similarly, the partial structure factors relate to the partial rdf's, \( g_{\alpha\beta}(r) \), through

\[
g_{\alpha\beta}(r) = 1 + \frac{1}{2\pi^2\rho_r} \int_0^\infty k \sin(kr) \left( S_{\alpha\beta}(k) - 1 \right) dk
\]

where \( \rho \) is the ionic number density. To separate out the \( S_{\alpha\beta}(k) \), \( f_{Cl} \) was changed by isotopic substitution, using \( \text{naf} \text{Cl} \), \( \text{mix} \text{Cl} \), and \( \text{37Cl} \), where \( \text{naf} \text{Cl} \) is composed largely of \( \text{35Cl} \), and \( \text{mix} \text{Cl} \) is a mixture of natural Cl with \( \text{37Cl} \). The parameters for these three compositions are given in Table 1. A natural sample (not containing the null Li) was also investigated. All the measurements were carried out on the D4 diffractometer at the reactor facility of the Institut Laue-Langevin (ILL) in Grenoble, France using a neutron wavelength of 0.7A.

**SAMPLE PREPARATION**

Samples of \( \text{oLi}^*\text{Cl} \) and \( \text{Al}^*\text{Cl}_3 \) were synthesized at Bristol, using \( \text{Na}^*\text{Cl} \) salt as the starting material, where \( ^*\text{Cl} \) denotes an isotope of chlorine. The \( \text{Al}^*\text{Cl}_3 \) sample was supplied by Anderson Physics Laboratories (Champaign, Illinois, USA), and the \( \text{oLiAlCl}_4 \) was prepared at the Argonne National Laboratory. The chloride isotopes were supplied as \( \text{Na}^*\text{Cl} \), by the Oak Ridge National Laboratory.

Labeled hydrochloric acid was made by cationic exchange using an Amberlite IR 120(H) ion exchange resin as follows:

\[
\text{Resin} + \text{H}^+\text{(aq)} + \text{Na}^*\text{Cl(aq)} \rightarrow \text{Resin} + \text{Na} + \text{H}^*\text{Cl(aq)}
\]

The \( \text{oLi}^*\text{Cl} \) samples were then produced through the reaction:

\[
\text{oLiOH(aq)} + \text{H}^*\text{Cl(aq)} \rightarrow \text{oLi}^*\text{Cl(aq)} + \text{H}_2\text{O}
\]

The \( \text{oLi}^*\text{Cl} \) solutions were dehydrated by gentle heating on a vacuum line. Residual water content was checked by examination of the infrared absorbance at 3440 cm\(^{-1}\) of a deuterium oxide (heavy water) solution of the dried salt.

The \( \text{Al}^*\text{Cl}_3 \) salts were produced from \( \text{Ag}^*\text{Cl} \) salt and Al pieces via the following reaction:

\[
3\text{AgCl} + \text{Al} \rightarrow 3\text{Ag} + \text{AlCl}_3
\]

The containment apparatus is shown in Fig. 1.

Ag\(^*\text{Cl} \) (formed from the \( \text{Na}^*\text{Cl} \)) powder was fused under vacuum in the graphite crucible. Clean dry Al pieces were placed in the side arm of the quartz reaction vessel and the evacuated vessel sealed.

All the aluminum pieces were then tipped into the graphite crucible. The main tube was heated to 700\(^\circ\text{C}\)-the reaction started when the silver chloride melted (455\(^{\circ}\text{C}\)). The aluminum chloride which formed sublimed and was collected in the cooler side arm. After cooling, the side arm containing the Al\(^*\text{Cl}_3 \) was removed from the main tube, ready for mixing with the \( \text{oLi}^*\text{Cl} \).
RESULTS

The F(k) for the four LiAlCl$_4$ samples are shown in Fig. 2 and their transforms to G(r) in Fig. 3. The three partial structure factors S$_{\text{AIAl}}$(k), S$_{\text{ClCl}}$(k), and S$_{\text{AICl}}$(k), and partial rdf's g$_{\text{AIAl}}$(r), g$_{\text{ClCl}}$(r), and g$_{\text{AICl}}$(r) deduced from the measurements are given in Figs. 4 and 5. MD results for g$_{\text{AIAl}}$(r), g$_{\text{ClCl}}$(r) and g$_{\text{AICl}}$(r) are also shown for comparison in Fig. 5. We have checked that the S$_{\alpha\beta}$(k) correctly generate the measured F(k) for all three samples where the lithium contribution was zero. The agreement can be seen in Figs. 2a-c. We summarize the structural parameters in Table 2. Finally, Fig. 6 shows the running coordination number, n$_{\alpha\beta}$(r), for both the neutron diffraction measurements and the molecular dynamical calculations. The running coordination number is defined as the average number of ions of type $\beta$ within a radius r from an ion of type $\alpha$.

DISCUSSION

The Cl-Cl interaction

The g$_{\text{ClCl}}$(r) peak height of 3.0, with a maximum at 3.51Å and a smaller shoulder, peaking at 4.0Å, are consistent with the rdf simulated by using potential c (but are also close to that from potential d with both potentials c and d giving rise to tetrahedral A-X symmetry, where A is a triply charged cation and X is a singly charged anion). The ClCl coordination number, Z$_{\text{ClCl}}$, (the number of Cl atoms within a radius from a particular Cl which is given by the distance to the first minimum in the rdf for the ClCl pair) has a significant uncertainty because of the asymmetry of the peak shape which leads to a strong dependence on the method of evaluation. Comparison of values of Z$_{\text{ClCl}}$ obtained using various methods of evaluation, is shown in Table 3. Fig. 6b shows the more informative running coordination number for neutron and MD work, n$_{\alpha\beta}$(r) and indicates overall agreement. The slightly lower value for the MD work is related to the narrower first peak in the rdf (see Table 4).

The shoulder at about 4.0 to 4.5Å reflects the strong attraction of the highly charged aluminum ion. The Cl$^-$ ions tend to pack tightly about polyvalent cations thus maximizing the number of Cl$^-$ ions around the Al$^{3+}$ ion. Integrating under the curve out to the long r side of the shoulder gives a coordination number of 9-10, see Fig. 6b.

The Al-Cl interaction

As regards the cross term, the g$_{\text{AICl}}$(r) has the expected narrow first peak at 2.13Å, with a large maximum reaching to 9.3. This falls to very small values before rising again at about 3.7Å. This value of 2.13Å, along with the Cl-Cl separation of 3.51Å, indicates a tetrahedral distribution of Cl$^-$ ions about Al$^{3+}$.
ions ($\sqrt{8/3} = 1.63, 3.51/2.13$ (experiment) $= 1.65 \pm 0.03$). As has been discussed\(^1\), one can consider that the chloride ions are sitting in a deep potential well and are tightly bound. A comparison of the measured and molecular dynamically calculated running coordination numbers $n_{AlCl}(r)$ is shown in Fig. 6c. The value of about 4 for the nearest neighbor coordination number of Al by Cl is consistent with our deduction of the presence of $AlCl_4^-$ tetrahedra. The structureless form of the $g_{AlAl}(r)$ curve suggests that there are very few Al-Cl-Al bridges.

A final point to note is the partial charge cancellation effect when $g_{ClCl}(r)$ and $g_{AlCl}(r)$ are superimposed. This is also evidenced by the corresponding peak and trough in the $S_{ClCl}(k)$ and $S_{AlCl}(k)$, respectively, at about 2.1Å\(^{-1}\).

The Al-Al interaction

If we now consider the $S_{AlAl}(k)$ for the Al-Al pair, we see that the $S(k)$ and consequently $g(r)$ are relatively structureless, resembling the Ni-Ni structure factor in aqueous NiCl\(_2\) solutions. Isolation of this $S(k)$ and $g(r)$ was very difficult because of the very low weighting in the simultaneous equations being solved, and because of its lack of structure. Consistent with this lack of structure, the equilibrium constant for the reaction

$$2AlCl_4^- \rightleftharpoons Al_2Cl_7^- + Cl^-$$

is known to be so small that essentially no Al-Al pairs should be present at 4.3Å.

The r-space information we obtained merely indicates a curve rising from zero around 4.0Å, increasing to no more than about 1.5 units, and falling back to the $r = \infty$ asymptotic value by about 9Å, results which are not inconsistent with the $g_{AlAl}(r)$ calculated by molecular dynamics.

The Li-Cl interaction

Comparison of our results for $nat$Li$Al^{nat}$Cl\(_4\), and the $^{6}$LiAl$^{nat}$Cl\(_4\), in principle, should provide information on the LiCl pair distribution function. Because of the relative insensitivity of the experimental results to this interaction the statistical noise led to ambiguity in the results. Further work with substitution of Li isotopes would be needed to deduce the LiCl pair distribution function.

Other concentrations

Molecular dynamical simulations of more acid melts are under way,\(^5\) and we intend to carry out neutron experiments on more acid mixtures, especially to study the expected increase in the number of Al-Cl-Al bridges.

To complete our experimental work, we should use lithium isotopes to improve the Li-Cl separation, although absorption by $^{6}$Li might well limit our success.

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CONCLUSIONS

The AlCl\textsuperscript{4} tetrahedra known to be present in the equimolar melt LiCl-AlCl\textsubscript{3} appear to be tightly bound moieties as has been observed in MD simulations. This conclusion follows from the large first peak height in the rdf for AlCl pairs. The partial structure factors of Al-Al, Cl-Cl and Al-Cl have been determined. Reliable information on $g_{LiCl}(r)$ could not be extracted because of statistical noise in the data.

As expected, Al-Cl-Al bridging between tetrahedra was not observed. An increase in bridging is expected with an increase in melt acidity as has been observed in MD calculations\textsuperscript{5}. The MD potentials c and d used by Saboungi et al. simulate our experimental results reasonably well with potential c being somewhat better. This conclusion was also deduced from X-ray results\textsuperscript{2}.

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Table 1. Parameters used in the data analysis.

| Parameter                                      | Value     |
|------------------------------------------------|-----------|
| Temperature (°C)                               | 200       |
| Density (g cm\(^{-3}\))                       | 1.6\(^3\) |
| Number density (Å\(^{-3}\))                    | 0.032     |
| Cl isotopes                                    | nat, 38, mix, all-natural, \(^6\)Li, \(^7\)Li |
| Scattering cross section (barns atom\(^{-1}\)) | 9.12, 1.72, 5.42, 9.61, 1.19, 1.4  |
| Absorption cross section (barns atom\(^{-1}\))| 106.97, 86.78, 96.88, 34.14, 507.6, 70.5 |
| Aluminum scattering length (x 10\(^{-12}\)cm) | 0.345, 0.345, 0.345, 0.345, 0.345 |
| \(^{nat}\)Li scattering length (x 10\(^{-12}\)cm) | -0.203, -0.203, -0.203, -0.203, -0.203 |
| Anion scattering length (x 10\(^{-12}\)cm)     | 0.958, 0.363, 0.660, 0.958, --, -- |

\(^{6}\)Li : \(0.54^{6}\)Li + 0.46\(^7\)Li

\(^{nat}\)Li : \(0.075^{6}\)Li + 0.925\(^7\)Li
Table 2. $^7$LiAlCl$_4$ structural parameters. $r_{\alpha\beta}$ is the position of the first peak maximum in $rg_{\alpha\beta}(r)$, or in $g_{\alpha\beta}(r)$, as indicated. The coordination number of $\beta$ about $\alpha$ is given by $Z_{\alpha\beta}$, using either the method of integrating under the symmetrized first peak in $rg(r)$, i.e., symmetrical distribution in $rg(r)$ is assumed, or the method of integrating to the first minimum in $g_{\alpha\beta}(r)$, as indicated.

|       | $r_{\alpha\beta}$(Å) |       | $Z_{\alpha\beta}$ |
|-------|----------------------|-------|------------------|
|       | $rg(r)$ | $g(r)$ | $rg(r)$ | $g(r)$ |       |
| Cl-Cl | 3.51 ± 0.03 | 3.50 | 4.54 ± 0.8 | ~6(to 4.1Å) |       |
| Al-Cl | 2.13 ± 0.03 | 2.12 | 3.80 ± 0.4 | 3.81 ± 0.03 |       |
| Al-Al | --         | 4.56 | --         | --         | --     |

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Table 3. Comparison of diffraction and computer experimental results for the structural parameters. Ion-ion separation from the first maximum in $g_{a\beta}(r)$ (fm) or symmetrical $rg_{a\beta}(r)$ is given by $r(\AA)$ as indicated. Coordination number is given as indicated by either integration to first minimum in $g_{a\beta}(r)$, (FM), or integration using symmetrical first peak in $rg_{a\beta}(r)$.

|       | molecular dynamics (ref.1) | this work | X-ray diffraction (ref.2) |
|-------|--------------------------|-----------|---------------------------|
|       | c                        | d         |                           |
| Cl-Cl |                          |           |                           |
| $r(\AA)$ | $\sim 3.47$ | $\sim 3.55$ | $3.51 \pm 0.03$ | $3.50$ |
|       | fm                      | fm        | $rg(r)$                  | $rg(r)$ |
| $Z$   | 3.5                      | 4         | $4.5 \pm 0.8$           | $\sim 6$ |
|       | FM                      | FM        | $rg(r)$                  | FM       |
|       |                         |           |                           |
| Al-Cl |                          |           |                           |
| $r(\AA)$ | 2.1 - 1.2$^\dagger$ | 2.13 $\pm$ 0.03 | 2.15                     |
|       | fm                      | $rg(r)$   | $rg(r)$                  |
| $Z$   | 4                        | 4         | $3.8 \pm 0.4$           | 4.1      |
|       | FM                      | FM        | $rg(r)$                  | $rg(r)$  |

$^\dagger$(defined from experiment)
Table 4. Comparison of the first peak height and full widths at half maximum for $g_{CI\text{Cl}}(r)$ and $g_{AI\text{Cl}}(r)$.

|        | peak height | FWHM |
|--------|-------------|------|
| Cl-Cl  | this work   | 3.0  | 0.56 |
|        | MD          |      |      |
|        | pot c       | 3.40 | 0.42 |
|        | pot d       | 3.95 | 0.35 |
| Al-Cl  | this work   | 0.3  | 0.34 |
|        | MD          |      |      |
|        | pot c       | 16   | 0.25 |
|        | pot d       | 18.5 | 0.32 |
Experimental setup for AlCl₃ powder production. Reaction was carried out at 450°C.
Fig. 2. Total structure factors, $F(k)$, for LiAlCl$_4$, (a) $^{37}$LiAlCl$_4$; (b) $^{37}$LiAl$^{miz}$Cl$_4$; (c) $^{37}$LiAl$^{nat}$Cl$_4$; (d) $^{nat}$LiAl$^{nat}$Cl$_4$. The full curves show the $F(k)$ reconstructed using the $S_{\alpha\beta}(k)$ shown in Fig. 4. The statistical error of an average data point in $F(k)$ is $\pm 0.002$. 

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Fig. 3. Total radial distribution functions, $G(r)$, obtained from the $F(k)$ shown in Fig. 2. (a) $^{37}\text{Li}^{Al}Cl_4$; (b) $^{6}Li^{Al}\text{nat}Cl_4$; (c) $^{6}Li^{Al\text{nat}}Cl_4$; (d) $^{nat}Li^{Al\text{nat}}Cl_4$. 
Fig. 4. Partial structure factors, $S_{\alpha\beta}(k)$. (a) $S_{AlAl}(k)$; (b) $S_{ClCl}(k)$; and (c) $S_{AlCl}(k)$. 
Fig. 5. Partial radial distribution functions, $g_{\alpha \beta}(r)$. (a) $g_{\text{AlAl}}(r)$; (b) $g_{\text{CICl}}(r)$; and (c) $g_{\text{AlCl}}(r)$. N: neutron experiment; C: MD result, potential c; D: MD result, potential d.
Fig. 6. Dependence of the running coordination numbers on r (a) Al-Al pairs; (b) Cl-Cl pairs; (c) Al-Cl pairs. N: neutron experiment; C: MD result, potential c; D: MD result, potential d.