Evidence of Long Range Ordering in Molten MgCI$_2$

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Letter

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The low Q rise in the structure factor, $S_T(Q)$, of molten MgCl$_2$ observed by Day and McGreevy for $Q < 0.3$ Å^{-1} has been confirmed by small angle neutron scattering using the D17 diffractometer at the Institut Laue Langevin. This feature is found to have a possible maximum value at $Q \simeq 0.1$ Å^{-1} indicating long range ordering with a correlation length $\simeq 60$ Å. The results are found to be inconsistent with the possibility of oxygen contamination, so the ordering must be inherent to the liquid structure.

Key Words: Correlation length, small angle scattering.

Neutron diffraction studies of molten alkaline earth chlorides using the technique of isotopic (Cl) substitution have shown that the structures of BaCl$_2$ and SrCl$_2$ have similar isomorphous short range order (SRO) with approximately eightfold cubic coordination.[1,2] The correlation length, as in most simple liquids, is $\simeq 6$ Å. CaCl$_2$ has a similar anion structure ($g_{--}(r)$) but a different cation structure ($g_{++}(r)$) with the cations occupying "nearest-neighbour" sites in the anion sub-structure rather than "next-nearest-neighbour" sites.[3] MgCl$_2$ has different anion and cation structures; $g_{+-}(r)$ is well defined with a fourfold coordination.[4] This may be considered to be somewhere between a distorted square planar arrangement and a deficient asymmetric octahedron, distorted from the octahedral layer structure in the crystal. Molten ZnCl$_2$ has a similar cation radius to MgCl$_2$ and is also fourfold coordinated, but here the arrangement is definitely tetrahedral,[5] as it is in the various crystalline glassy phases. Molten NiCl$_2$ has less well defined tetrahedral coordination.[6]

The cation-cation structure factors, $S_{++}(Q)$, of MgCl$_2$ and ZnCl$_2$ both show "pre-peaks" or "first sharp diffraction peaks" at $Q \simeq 1$ Å^{-1}, indicative of intermediate range ordering (IRO) between local coordination shells. The correlation length of this ordering, determined by the

width of the peak, is $\simeq 20$ Å. (This is not a precise "correlation length" as in e.g. Ornstein–Zernicke theory, but is intended to give a microscopic idea of the structural significance of the "pre-peak".) Day and McGreevy[7] have measured the total structure factors of $CaCl_2$ and $MgCl_2$ down to $Q = 0.17$ Å^{-1} and find an anomalous rise in $S_T(Q)$ for $MgCl_2$ for $Q < 0.3$ Å^{-1}, indicating long range ordering (LRO); a rise does not occur in $CaCl_2$. Recent measurements on molten $ZnCl_2$[8] show a rise for $Q < 0.05$ Å^{-1}. Such rises are well known for systems approaching a critical point, e.g. for phase separation in the binary alloy LiNa.[9] However for an ionic system like $MgCl_2$ the requirement of long range charge neutrality means that $S_T(Q)$ must decrease to the value determined by the isothermal compressibility at $Q = 0$. This indicates that there must be a maximum in the region $Q < 0.17$ Å^{-1}. In order to confirm this we have undertaken a small angle neutron diffraction study of molten $MgCl_2$.

A sample of anhydrous $MgCl_2$ was prepared using the method detailed by Bunten et al.[10] This was sealed in a rectangular silica cell of approximate dimensions 10 mm × 50 mm and thickness 2 mm, the thickness of the glass faces being 0.5 mm and of the sample 1 mm. The small sample thickness was necessary in order to avoid strong absorption of the long wavelength neutrons. The container was then mounted in a boron nitride holder that obscured the edges from the neutron beam and also reduced background scattering. This was mounted within a furnace heated by passage of a high current through a thin cylindrical Niobium foil coaxial with the sample. Measurements were made using the D17 small angle diffractometer at the Institut Laue Langevin in Grenoble with an incident wavelength of 11 Å. The 64 × 64 cm^2 area detector was offset at an angle of 10° to the beam at a distance of 1.47 m, giving a range $0.01 < Q < 0.2$ Å^{-1}; however the spread of the incident beam (collimation 1 × 1 cm^2) limited this to $Q > 0.03$ Å^{-1}. The intensity was summed radially around the appropriate Debye-Scherrer cones using software. The sample temperature was 1023 ± 2 K (melting point 987 K). Measurements were also made of scattering from the empty sample container, the empty furnace, and from the container filled with water, all at ambient temperature.

Relative to the high level of background (furnace) scattering the container scattering was found to be negligible. The true scattering from the sample (I_S) could therefore be determined from the experimentally measured sample (I_S^E) and background (I_B^E) intensities using the expression

$$I_S^E = A_{SSC}I_S + A_{SC}I_B^E \tag{1}$$

where A_{SSC} is the absorption coefficient for scattering by the sample and absorption by the sample and container (scattering angle dependent) and A_{SC} is the absorption coefficient of the sample and container for normal incidence. The scattering from water was similarly corrected and found to be flat over most of the Q range, deviations at low Q being due to the incident beam and at high Q to inelastic effects. The flat level was then used for normalisation via the incoherent cross-section of water. Multiple scattering was calculated to be $< 1\%$.

The calculated total structure factor $S_T(Q)$ for molten MgCl₂ is shown in Figure 1, together with the result of Day and McGreevy.[7] Considering the high level of background scattering in the present experiment the level of agreement is surprisingly good (there are no adjustable parameters in either case). $S_T(Q)$ does not continue to increase as rapidly at low Q but flattens below $Q \simeq 0.15 \text{ Å}^{-1}$. The data indicate a maximum value at $\simeq 0.1 \text{ Å}^{-1}$ but within the errors it is possible that the maximum occurs at $Q = 0$.

One possible origin of this feature may be low level oxide contamination. MgCl₂ is highly hygroscopic and is very difficult to prepare in a completely anhydrous form. Residual Mg(OH)₂ decomposes at high temperature to leave MgO which has a significantly higher melting point than MgCl₂ and hence would remain in the melt as small
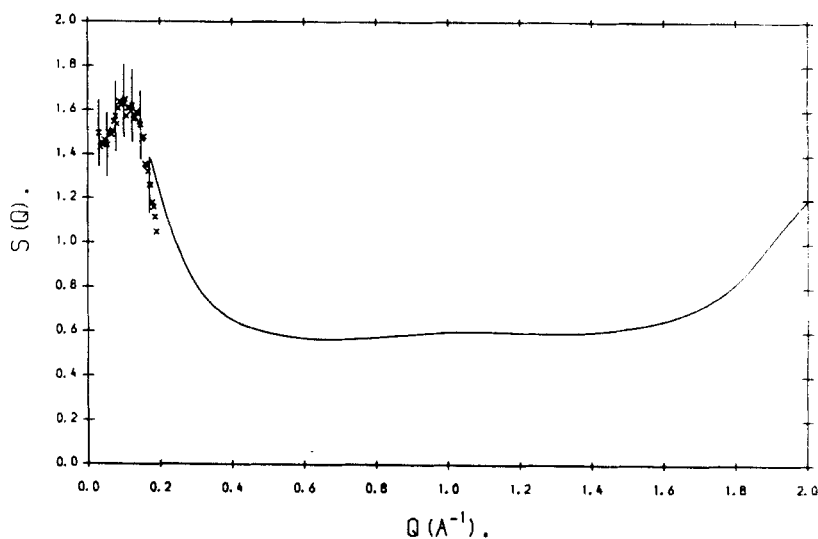

Figure 1 Total structure factor for molten MgCl₂ measured using D1B (solid curve) and D17(X) diffractometers.

particles. Such particles are well known to produce small angle scattering. For evenly distributed, well defined, spherical particles $S_T(Q \to 0)$ should have the form

$$S_T(Q \to 0) = S_0 + A \exp(-Q^2 R_g^2/3) \tag{2}$$

where S_0 ($= 0.443$) is the inherent scattering from $MgCl_2$ determined by the incoherent and coherent cross-sections and the isothermal compressibility. The Gaussian width is determined by R_g, the radius of gyration of the particles, and A by their volume fraction and scattering density. The maximum in $S_T(Q)$ therefore occurs at $Q = 0$. Fitting this expression we find 3 % (mole fraction) of MgO particles with a radius of 7 Å. If the particles are not spherical or well defined, and hence the form of Eq. (2) is somewhat different, this can nevertheless be considered a measure of their average size. If $S_T(Q)$ has a maximum at $Q \simeq 0.1 \text{ Å}^{-1}$, as the data seem to indicate, then the impurity particles will have an average separation $\simeq 60$ Å. The calculated density of impurities will be slightly lower, and their average radius will be similar. From experience with light scattering studies of $MgCl_2$ we know that oxide particles in contaminated samples are easily visible; such particles would have a large radius of gyration and hence give small angle scattering with a width in Q lower by several orders of magnitude. They would have to be in addition to the 3 % calculated above. An oxide contamination of a few % can be achieved even by the crudest drying methods, so the sample used here, which has been sublimed, should have a much lower level, and hence the results are inconsistent with the low Q rise being caused by oxide contamination. The same arguments also apply to hydroxide contamination.

We therefore conclude that the low Q rise in $S_T(Q)$ is unlikely to be due to oxide contamination and is an inherent feature of the liquid structure. A peak at $\simeq 0.1 \text{ Å}^{-1}$ indicates LRO with a spacing $\simeq 60$ Å. It has already been pointed out that the SRO correlation length of the local coordination shell is $\simeq 6$ Å and the IRO correlation length between coordination shells is $\simeq 20$ Å (only for liquids with a structure factor "pre-peak"). The present result then indicates that these IRO regions are themselves ordered on this longer length scale. Inelastic neutron scattering[11] and Raman scattering[10] give characteristic lifetimes of SRO and IRO as $\simeq 1$ ps and $\simeq 0.3$ ps respectively. No information is available on possible lifetimes of LRO and is probably not attainable using present inelastic neutron scattering spectrometers. However it is possible that the LRO is due to short lived dynamical fluctuations and should not be considered from a static structural point of view. Assuming that these are (sinusoidal) number density fluctua-

tions the required amplitude is 4.5 % of the mean density. Since MgCl$_2$ has an anomalously high compressibility,[12] almost an order of magnitude larger than for most molten salts (note that the value of S_0 is largely determined by incoherent scattering), and the volume change on melting is extremely large ($\simeq 30\%$), the energetics of such a density fluctuation may not be so unfavourable. In addition it is interesting to note that the velocity of sound is found to be almost independent of temperature from both ultrasonic[12] and Brillouin scattering[13] measurements. This is also anomalous.

In order to further understand the origin of this LRO it is necessary to perform diffraction experiments at lower Q and to confirm that $S_T(Q)$ does indeed decrease to the predicted compressibility limit as $Q \rightarrow 0$. Isotopic substitution should also be used to confirm that the low Q scattering is inherent to the sample, and to determine whether fluctuations occur in number density, mass density etc. However it should be noted that it may be difficult to prepare isotopic samples of the required purity. Small angle scattering measurements on other molten salts are required to see if the existence of LRO is a more general phenomenon in systems that show IRO. MgBr$_2$ and MgI$_2$ would be of particular interest since in these the compressibility is even higher than in MgCl$_2$.

Acknowledgements

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