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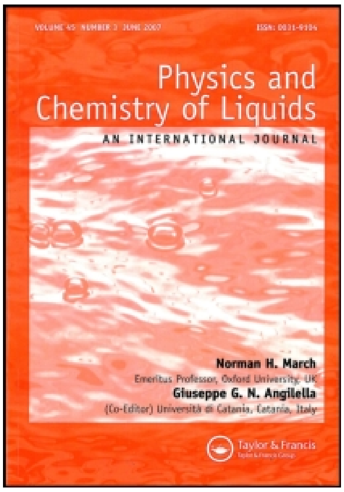

Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:
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To cite this Article Day, S. E. and McGreevy, R. L.(1985) 'Structure Factors of Molten $CaCI_2$ and $MgCI_2$ at Low Q', Physics and Chemistry of Liquids, 15: 2, 129 — 136
To link to this Article: DOI: 10.1080/00319108508078474
URL: http://dx.doi.org/10.1080/00319108508078474

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Phys. Chem. Liq., 1985, Vol. 15, pp. 129–136
0031-9104/85/1502-0129$18.50/0

Printed in the United Kingdom

Structure Factors of Molten $CaCl_2$ and $MgCl_2$ at Low Q

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(*Received June 12, 1985*)

We have measured the total structure factors $S(Q)$ of molten $CaCl_2$ and $MgCl_2$ over the range $0.174 < Q < 3.37$ Å^{-1} as a function of temperature using the D1B diffractometer at the Institut Laue Langevin in Grenoble. Changes in $S(Q)$ for molten $CaCl_2$ are consistent with the hypothesis that the anomalously close cation grouping observed just above the melting point breaks up with increasing temperature. $S(Q)$ for molten $MgCl_2$ increases rapidly at low Q to values above the compressibility limit for $Q \to 0$. It is suggested that this is directly related to the observation of a propagating transverse charge density fluctuation in this melt, and may be indirect evidence of many body interactions.

1 INTRODUCTION

Neutron diffraction studies of molten alkaline earth chlorides using the technique of isotopic substitution have shown that the structures of $BaCl_2$ and $SrCl_2$ are approximately isomorphous.[1,2] Molten $CaCl_2$ has a similar anion structure ($g_{--}(r)$) but a different cation structure ($g_{++}(r)$) with the ions more closely grouped.[3] In the case of molten $MgCl_2$, however, $g_{--}(r)$ is different and its first peak is at about the same distance as that in $g_{++}(r)$; $g_{+-}(r)$ is well defined and has a coordination number of $\simeq 4$ which, together with the relative spacing of ions, indicates that molten $MgCl_2$ has a layer structure[4] similar to that in the crystalline state. Molten $ZnCl_2$ has a similar cation size to $MgCl_2$ and also has a coordination number of $\simeq 4$; in this case, however, the coordination is not planar but tetrahedral.[5]

Light scattering studies of molten salts[6] show no change in the shape of the spectrum as the temperature is increased except in the case of $CaCl_2$. It was suggested that this change may be due to the break up of the close cation grouping giving a structure similar to that of $SrCl_2$ and $BaCl_2$. To investigate this we have measured the total structure factor $S(Q)$ of molten

$CaCl_2$ by neutron diffraction at 1083 K and 1223 K (covering the same temperature range as the light scattering experiments) over the range $0.17 < Q < 3.3$ Å^{-1}. We have also measured, at 1023 K and 1223 K, $S(Q)$ for molten $MgCl_2$, for which there is no change in the shape of the light scattering spectra with temperature.

2 EXPERIMENTAL AND DATA ANALYSIS

^{37}Cl would be the optimum Cl isotope to use in this experiment because its low cross-section means that the neutron scattering from the cations forms a relatively larger part of the intensity and hence changes in the partial structure factor for cations, $S_{++}(Q)$, would be more easily observed. It is necessary, however, to avoid oxygen impurity which can be present in large quantities, so to minimize the oxygen content we have prepared our samples as described by Bunten *et al.*[6] This requires relatively large amounts of starting material and hence of ^{37}Cl. For this reason we have used the naturally occurring isotope mixture. Measurements were made using the D1B diffractometer at the Institut Laue Langevin in Grenoble with an incident neutron wavelength of 2.52 Å. Figure 1 shows examples of the spectra obtained.

As well as measurements of the spectra of molten $CaCl_2$ and $MgCl_2$ at two temperatures, spectra were measured for an empty sample container,

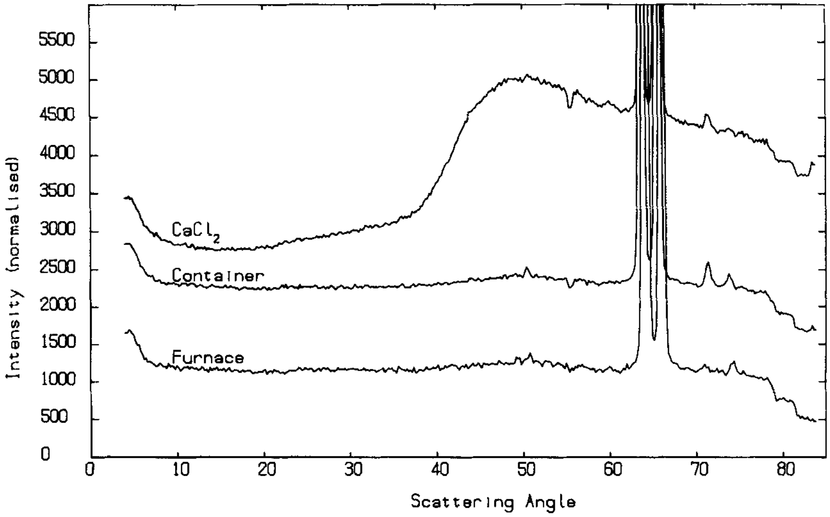

FIGURE 1 Monitor normalised scattered intensities from molten $CaCl_2$ (1083 K), container and furnace.

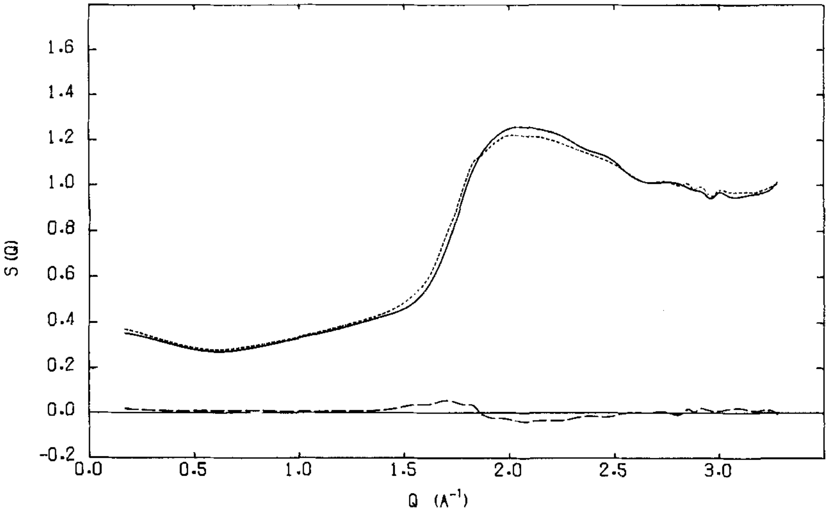

FIGURE 2 Total structure factors $S(Q)$ for $CaCl_2$ at 1083 (solid line), 1223 K (dotted line) and the difference (broken line).

the empty furnace and a sample container filled with boron carbide (a good neutron absorber). These were used to correct the sample spectra for absorption and scattering by the furnace and container. Corrections were also made for self absorption and for inelastic and multiple scattering, as outlined by McGreevy and Mitchell.[2] The results were normalised using the intensity from the vanadium sample container, which had been smoothed by fitting cubic splines. The structure factors obtained were also smoothed and are displayed in Figures 2 and 3, together with the difference in structure factors at the two temperatures. Only for $Q > 2.6$ Å^{-1} are problems with the smoothing observed, in the form of small oscillations caused by smoothing though the large Bragg peaks from the niobium heater and the smaller Bragg peaks from the vanadium containers (see Figure 1).

3 RESULTS AND DISCUSSION

3.1 Temperature dependence

The plot of the difference in structure factors between two temperatures for $CaCl_2$ (Figure 2) reveals an increase in intensity at $Q \simeq 1.7$ Å^{-1} at the higher temperature. $MgCl_2$ (Figure 3) does not show a similar increase, but both salts show a lowering of the first main peak around $Q \simeq 2.0$–2.1 Å^{-1}, as would be expected for a general decrease in structural order.

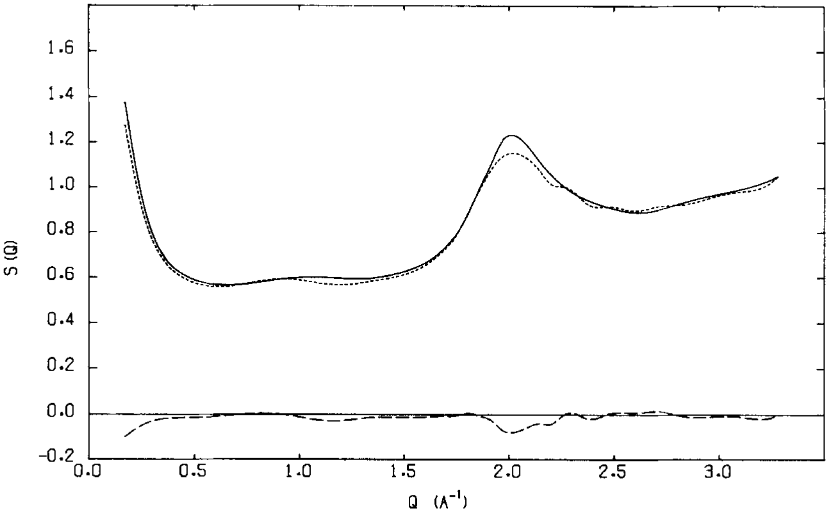

FIGURE 3 Total structure factors $S(Q)$ for $MgCl_2$ at 1023 K (solid line), 1223 K (dotted line) and the difference (broken line).

The total structure factors $S(Q)$ may be written as

$$MgCl_2\colon S(Q) = 0.213 + 0.302\,S_{++}(Q) + 1.030\,S_{--}(Q) + 1.120\,S_{+-}(Q) \quad (1)$$

$$CaCl_2\colon S(Q) = 0.220 + 0.250\,S_{++}(Q) + 1.040\,S_{--}(Q) + 1.020\,S_{+-}(Q) \quad (2)$$

(the coefficients being determined by the relevant neutron scattering cross sections). The partial structure factors $S_{ij}(Q)$ are related to the partial radial distribution functions $g_{ij}(r)$ by

$$S_{ij}(Q) = c_i\delta_{ij} + c_ic_j\rho \int 4\pi r^2(g_{ij}(r) - 1)\frac{\sin Qr}{Qr}\,\mathrm{d}r \quad (3)$$

where ρ is the number density and c_i the ionic concentration. The coefficient of $S_{++}(Q)$ is much smaller than that of $S_{--}(Q)$ and $S_{+-}(Q)$, so any change in $S_{++}(Q)$ will produce a correspondingly small change in $S(Q)$. The first peak in $S_{++}(Q)$ for $CaCl_2$ occurs[3] at $Q \simeq 2.4$ Å^{-1}. If the close cation grouping breaks up then the peak in $S_{++}(Q)$ will move to lower Q, corresponding to a shift in the peak in $g_{++}(r)$ to larger r. If the structure becomes isomorphous with $SrCl_2$, for which the first peak in $S_{++}(Q)$ occurs[2] at $Q = 1.59$ Å^{-1} then, taking account of the different cation sizes, the peak in $S_{++}(Q)$ will be at 1.67 Å^{-1}. This is consistent with the increase in intensity observed in $S(Q)$ for $CaCl_2$ in this region. The increase is also of the expected magnitude if the structure becomes isomorphous with $SrCl_2$. Unfortunately the partial structure factors available for $CaCl_2$ are not sufficiently accurate to enable a more detailed calculation.

A feature observed in the structure factor of $MgCl_2$ at 1023 K is the small broad peak at around 1.1 $Å^{-1}$. This is related to the correlation between the planes of coordinated Mg^{2+} ions; the corresponding Bragg peak from crystalline $MgCl_2$ occurs at 1.07 $Å^{-1}$. The peak obtained from the melt shifts to slightly lower Q at the higher temperature, indicating that the spacing between planes increases. This feature is small because the intensity depends on the cation scattering which, from Eq. (1), is small relative to the anion scattering.

3.2 Low Q behaviour

The lowest Q values measured in this experiment are below those previously measured for molten salts, for example the diffraction measurements of Biggin and Enderby[3] on $CaCl_2$ and Biggin *et al.*[4] on $MgCl_2$ reached $Q \simeq 0.5$ $Å^{-1}$. We find that below this value $S(Q)$ increases. The expected value of $S(Q)$ as $Q \to 0$ for an ideal system may be derived from

$$S_{ij}(Q = 0) = 4\rho k_B T K_T \qquad (4)$$

where k_B is Boltzmann's constant, T is the temperature and K_T is the isothermal compressibility. Together with Eqs (1, 2) this gives

$CaCl_2$: $S(Q = 0) = 0.270$ at 1083 K
$S(Q = 0) = 0.284$ at 1223 K
$MgCl_2$: $S(Q = 0) = 0.443$ at 1023 K
$S(Q = 0) = 0.492$ at 1223 K

For $CaCl_2$ $S(Q)$ is slightly above this value at the lowest Q measured (0.174 $Å^{-1}$) while for $MgCl_2$ it is considerably above. The structure factors at low Q ($Q < 0.5$ $Å^{-1}$) are of the form[13]

$$S(Q) = S_0 + A\kappa^{(2-\eta)}/(Q^2 + \kappa^2)^{(1-\eta/2)} \qquad (5)$$

with coefficients

$CaCl_2$ at 1083 K: $S_0 = 0.270$ $A = 0.137$ $\kappa^{-1} = 4.2$ Å
$CaCl_2$ at 1223 K: $S_0 = 0.284$ $A = 0.176$ $\kappa^{-1} = 5.4$ Å
$MgCl_2$ at 1023 K: $S_0 = 0.443$ $A = 5.33$ $\kappa^{-1} = 12$ Å
$MgCl_2$ at 1223 K: $S_0 = 0.443$ $A = 4.02$ $\kappa^{-1} = 11$ Å

η is found to be effectively zero when the data is fitted to Eq. (5). The values of S_0 are satisfactorily given by the theoretical $Q = 0$ limits except in the case of $MgCl_2$ at 1223 K. The temperature dependence of the isothermal compressibility is not known for either salt, but has been assumed to be proportional to the adiabatic compressibility.[7]

A rise in the structure factor at low Q is well known for liquids approaching the liquid/vapour critical point, where K_T diverges. Although the critical temperature and pressure for $MgCl_2$ are not known they are unlikely to be close to values reached in this experiment, indeed the observed value of $S(Q \to 0)$ does not change significantly with temperature and no evidence of critical opalescence is observed in the light scattering results at similar temperatures. Although molten $MgCl_2$ has a high compressibility compared to other molten salts,[7] probably because of the planar nature of the structure, it would need to be another order of magnitude larger to explain these results.

An increase in $S(Q)$ at low Q is also well known in binary liquids such as molten alloys. In this case the extra scattering is due to concentration fluctuations and is proportional to

$$S_{cc}(Q = 0) = Nk_B T \Big/ \left(\frac{\partial^2 G}{\partial c^2}\right)_{T,P,N} \tag{6}$$

where G is the Gibbs free energy and

$$S_{cc} = c_2^2 S_{11} + c_1^2 S_{22} - 2c_1 c_2 S_{12} \tag{7}$$

In an ionic system concentration fluctuations are equivalent to charge fluctuations. The light scattering results of Bunten *et al.*[6] show evidence of a propagating transverse optic mode (charge density fluctuation) in molten $MgCl_2$. In molten $CaCl_2$ a similar mode is overdamped. We suggest, therefore, that the large rise in $S(Q)$ at low Q for $MgCl_2$ may be related to the existence of such a propagating mode, and is "dynamic" in origin rather than "structural".

The structures of molten $MgCl_2$ and $CaCl_2$ just above the melting point, with the close grouping of Ca^{2+} ions and the planar Mg^{2+} coordination, are evidence of anisotropic forces. These are probably many body forces between the small cations via the highly polarisable anions. Pastore *et al.*[8] have suggested that such forces are necessary to describe $g_{++}(r)$ in molten $SrCl_2$. The strength of the interaction is less in $CaCl_2$ than in $MgCl_2$, allowing the break up of the Ca–Ca grouping as the temperature increases. The correlation length κ^{-1} (see above), derived from the rise in $S(Q)$ at low Q, may represent the range of the many body interaction. In $CaCl_2$ this is of the order of the sum of the ionic diameters (5.6 Å) while in $MgCl_2$ it is more than twice the sum of the ionic diameters (4.8 Å), sufficiently long to allow charge density fluctuations to propagate; the distinction between propagating and overdamped modes may then be reflected in the size of the constant

A (Eq. (5)). It is also interesting to speculate on whether these phenomena are related to the direct observation of acoustic mode softening in molten $MgCl_2$ by McGreevy and Mitchell.[9]

The cation size in molten $ZnCl_2$, as noted earlier, is approximately equal to that in $MgCl_2$, and the cation–anion coordination is four fold, but tetrahedral rather than planar. Evidence of propagating modes has been observed in the light scattering spectra from molten $ZnCl_2$ by Aliotta *et al.*[10] However the available structure factors from neutron diffraction[4] only reach a minimum Q of 0.5 $Å^{-1}$, and from X-ray diffraction[11] of 0.3 $Å^{-1}$, not sufficiently low to observe if there is a rise in $S(Q)$ similar to that in $MgCl_2$. A similar propagating mode has also been observed in light scattering[12] from molten $MgBr_2$ but no diffraction data are available for this melt. In order to test the relation between structure and dynamics suggested here the structure factors of molten $ZnCl_2$ and $MgBr_2$ should be measured at low Q.

4 CONCLUSIONS

The changes in $S(Q)$ with temperature measured for molten $CaCl_2$ are consistent with the hypothesis that the anomalously close cation grouping observed just above the melting point breaks up with increasing temperature to give a structure isomorphous with $SrCl_2$ and $BaCl_2$. This should be confirmed by a further experiment using isotopic substitution. The large rise in $S(Q)$ at low Q for $MgCl_2$ is not understood, but we suggest that it may be related to the propagating transverse charge density fluctuations that have been observed in light scattering experiments and may give an indication of the range of many body interactions.

Acknowledgements

We should like to thank Professor E. W. J. Mitchell for useful discussions and the staff of the I.L.L., Grenoble, for assistance with these experiments. We also wish to thank the S.E.R.C. for continued financial support for this work.

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