

This article was downloaded by:

On: 28 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713646857>

Structure Factors of Molten CsCl at Low Q

M. C. Fairbanks^a; R. L. McGreevy^a

^a Clarendon Laboratory, Oxford, UK

To cite this Article Fairbanks, M. C. and McGreevy, R. L.(1989) 'Structure Factors of Molten CsCl at Low Q ', *Physics and Chemistry of Liquids*, 19: 2, 81 – 90

To link to this Article: DOI: 10.1080/00319108908028438

URL: <http://dx.doi.org/10.1080/00319108908028438>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

STRUCTURE FACTORS OF MOLTEN CsCl AT LOW Q

M. C. FAIRBANKS and R. L. MCGREEVY

Clarendon Laboratory, Parks Road, Oxford, OX1 3PU, UK.

(Received 7 September 1988)

The structure factors for three samples of molten CsCl with different isotopic chlorine compositions have been measured accurately in the region $0.2 < Q < 3.0 \text{ \AA}^{-1}$ using the D1B diffractometer at the Institut Laue Langevin. A rise in the measured structure factors for $Q < 0.5 \text{ \AA}^{-1}$ is explained as being due to inelastic scattering from overdamped acoustic modes.

KEY WORDS: Isotopic substitution, inelastic scattering, acoustic modes.

INTRODUCTION

Recent measurements of the low Q structure factor of molten $\text{MgCl}_2^{1,2}$ show features that are not expected from molten salt systems. The total structure factor, $S_T(Q)$, of molten MgCl_2 shows a large rise for $Q < 0.2 \text{ \AA}^{-1}$. It has been proposed that this feature is evidence of long range ordering in the melt, over a correlation length of approximately 60 \AA , since the results are inconsistent with the possible presence of impurities in the sample. Molten CaCl_2^1 also has a rise in $S_T(Q)$ for $Q < 0.5 \text{ \AA}^{-1}$, although in this melt the feature is very much smaller than in MgCl_2 .

In addition to providing evidence of long range ordering, the structure factors at low Q can be used to derive other properties of a molten salt. It is possible to expand the low Q partial structure factors of a molten alkali halide as simple polynomials^{3,4} in Q . The coefficients obtained in this asymptotic expansion can be related to long range terms in the interionic potential. For example the van der Waals term in the potential, which decreases as $1/r^6$, determines the coefficient of Q^3 . Other coefficients are related to thermodynamic variables of the system. It is therefore, in principle, possible to test stringently the longer range parts of the interionic potentials used in theory and computer simulation by performing accurate neutron scattering measurements of structure factors at low Q .

Low Q structure factors may also give some indication as to the dynamics of the liquid under investigation. Models of the dynamical structure factor, $S_T(Q, \omega)$, attempt to relate dynamical properties of the system to the experimentally measured structure factor. For example, under the assumptions of a model which contends that the dynamical structure factor may be described in terms of 3 Lorentzians⁵, the

minimum observed at $Q \simeq 0.3 \text{ \AA}^{-1}$ in the static structure factor of liquid Ar⁶ may be associated with the anomalous dispersion of longitudinal acoustic modes in that region.

In order to investigate these aspects of the structure factor we have performed accurate neutron diffraction experiments on 3 isotopically (Cl) enriched samples of molten CsCl at lower Q values than previously achieved for this salt. Use of different isotopic compositions makes it possible to separate some of the numerous contributions to $S_T(Q)$ in such a binary system.

EXPERIMENTAL

Details of the compositions and scattering lengths of the samples are given in Table 1. These samples are identical to those used in previous measurements of the static and dynamical structure factors^{7,8}. The structure factors have been measured using the D1B diffractometer at the Institut Laue Langevin, Grenoble, with an incident neutron wavelength of 2.5 Å. A range of scattering angles from 5 to 80° gives a momentum transfer range $0.2 < Q < 3.0 \text{ \AA}^{-1}$. This Q range provides a sizeable overlap with the previously measured structure factors⁷ thus allowing a quantitative comparison to be made.

During each experimental run the samples, contained in cylindrical vanadium cans, were held at a steady temperature of 1023 K (melting point 918 K). In order to obtain the required statistical accuracy it was necessary for each run to last approximately 20 hours. In addition shorter runs were performed on the empty furnace and an empty sample container.

The experimental data was analysed in the standard way. Background and container scattering were subtracted and corrections for absorption in the container and self-absorption in the sample were performed using the method of Poncet⁹. Corrections for multiple scattering and for the contribution from single particle inelastic scattering (Plazcek corrections) were made following the methods of Blech and Averbach¹⁰ and Yarnell *et al.*¹¹ respectively. Finally an absolute normalisation was made using the incoherent scattering from the vanadium container.

Table 1 Compositions and scattering parameters of the three samples.

	Cs ³⁷ Cl	CsCl	Cs ³⁵ Cl
% ³⁵ Cl	1.8	75.53	99.4
% ³⁷ Cl	98.2	24.47	0.6
$c_+^2 \bar{b}_+^2$	0.076	0.076	0.076
$c^2 \bar{b}^2$	0.026	0.228	0.339
$2c_+ \bar{c}_- \bar{b}_+ \bar{b}_-$	0.089	0.262	0.320
a_m^2	0.191	0.569	0.735
a_q^2	0.018	0.402	0.627
$2a_m a_q$	0.117	0.957	-1.358

CROSS SECTIONS

The cross-section measured in a neutron diffraction experiment on a multi-component system may be written in terms of various sets of inter-related partial structure factors, $A_{ij}(Q)$. In a study that is primarily concerned with measuring the structure of a molten alkali halide we write the cross-section in terms of those related to the correlation between the positions of the different species of particles in the melt. In this case

$$\frac{1}{N} \frac{d\sigma}{d\Omega} = (c_+ \bar{b}_+^2 + c_- \bar{b}_-^2) S_T(Q) = c_+ \bar{b}_+^2 + c_- \bar{b}_-^2 + F(Q) \quad (1)$$

where

$$F(Q) = c_+^2 \bar{b}_+^2 (A_{++} - 1) + c_-^2 \bar{b}_-^2 (A_{--} - 1) + 2c_+ c_- \bar{b}_+ \bar{b}_- (A_{+-} - 1) \quad (2)$$

c_i are the concentrations, \bar{b}_i the coherent scattering lengths and $4\pi\bar{b}_i^2$ the total scattering cross sections of species i . It is possible, by performing scattering experiments on 3 samples with different isotopic compositions of one or both of the atomic species present, to solve the set of simultaneous equations thus obtained and hence calculate the partial structure factors.

RESULTS

The structure factors, $F(Q)$, of the 3 molten CsCl samples are shown in Figure 1. It is immediately obvious that they are not featureless for $Q < 0.8 \text{ \AA}^{-1}$ but exhibit a broad minimum in the region of 0.7 \AA^{-1} . It will prove to be advantageous to think of this minimum being caused by the fact that the structure factors rise at low Q . The rise has the greatest relative strength in $F(Q)$ for molten Cs^{37}Cl .

This feature makes fitting to polynomial expansions of the structure factors^{3,4} extremely difficult as the coefficients obtained depend strongly on the Q range of the fit. It has therefore not been possible to follow the asymptotic approach and derive parameters in the potential. It is, however, illuminating to compare the structure factors measured in this experiment (hereafter referred to as D1B data) with those measured previously⁷ using the D4 diffractometer at the Institut Laue Langevin with an incident neutron wavelength of 0.7 \AA (D4 data). In Figure 2 such a comparison has been made for both $F(Q)$ and $A_{ij}(Q)$. It should be noted that the partials have been obtained by a direct separation. It was not necessary to employ complex iterative smoothing procedures⁷ as no attempt has been made to transform structure factors to radial distribution functions. In the figure it can be seen that the two sets of $E(Q)$ differ markedly in the range $0.2 < Q < 1.4 \text{ \AA}^{-1}$. There is also a large discrepancy between the A_{++} partials, whereas the other 2 partials agree more closely.

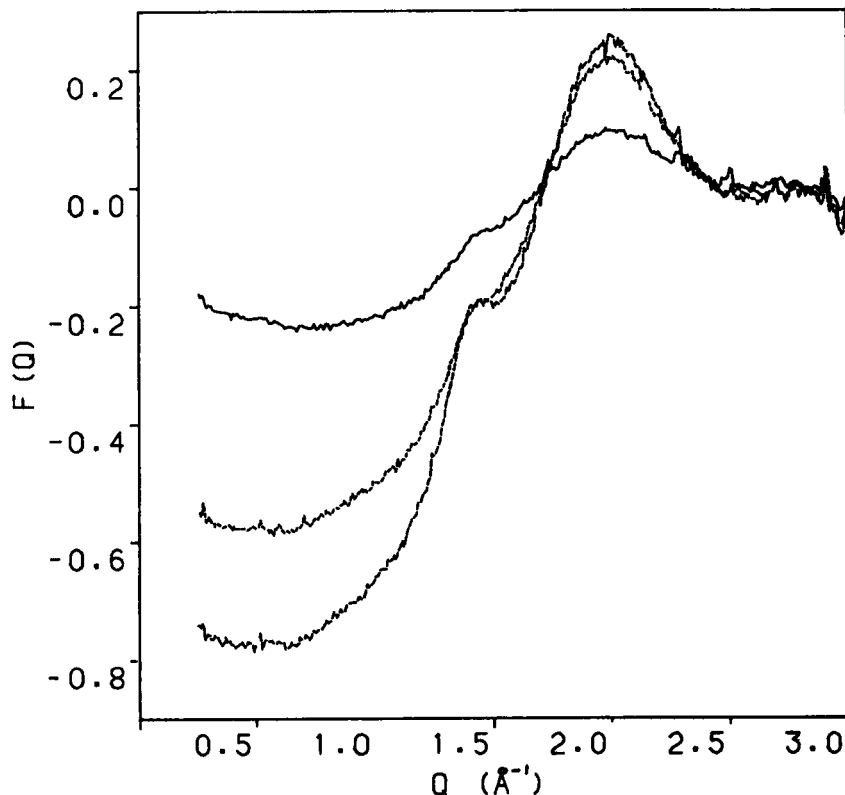


Figure 1 Structure factor $F(Q)$ for molten Cs^{37}Cl (solid curve), CsCl (short dash) and Cs^{35}Cl (long dash): DIB data normalised to the compressibility limit.

NORMALISATION OF STRUCTURE FACTORS

It is well known¹² that the partial structure factors of an ionic liquid must tend to a limit governed by the isothermal compressibility (K_T) as $Q \rightarrow 0$

$$A_{ij}(Q \rightarrow 0) - 1 = \rho k_B T K_T - \delta_{ij}/c_i \quad (3)$$

and at high Q

$$A_{ij}(Q \rightarrow \infty) - 1 = 0 \quad (4)$$

It is common in diffraction experiments that the absolute normalisation of structure factors produces high and low Q limits for $F(Q)$ that are a few per cent different from those expected. This is due to an inexact knowledge of factors such as sample and vanadium dimensions and densities. Since in isotopic substitution experiments the structure factors for the different samples must be consistent the experimentally

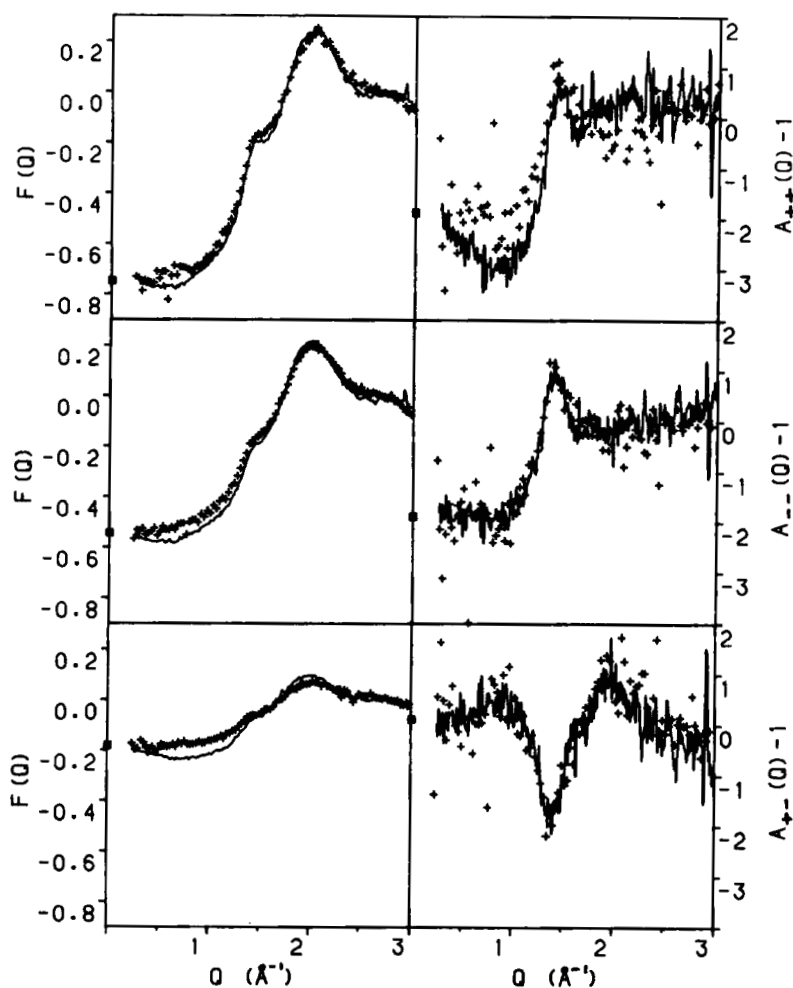


Figure 2 A comparison of $F(Q)$ and $A_{ij}(Q)$ as measured on D1B (solid curve) and D4 (+): compressibility limit (■) normalisation.

measured data are often normalised to the compressibility limit by extrapolation to $Q = 0$. This has been done for both D1B and D4 data in Figure 2. However, as the D1B data show a rise as Q decreases, whereas the D4 data do not, there must be some inconsistency in the procedure.

We have therefore renormalised the D1B structure factors to their respective D4 counterparts by minimising the differences in the range $0.5 < Q < 1.5 \text{ \AA}^{-1}$. The new structure factors were then separated into a new set of partials. We should emphasise that the new D1B structure factors will not now extrapolate to the correct compressibility limits. The results of this procedure are shown in Figure 3, where it can be seen that there is good agreement between both sets of structure factors for $Q > 0.5 \text{ \AA}^{-1}$.

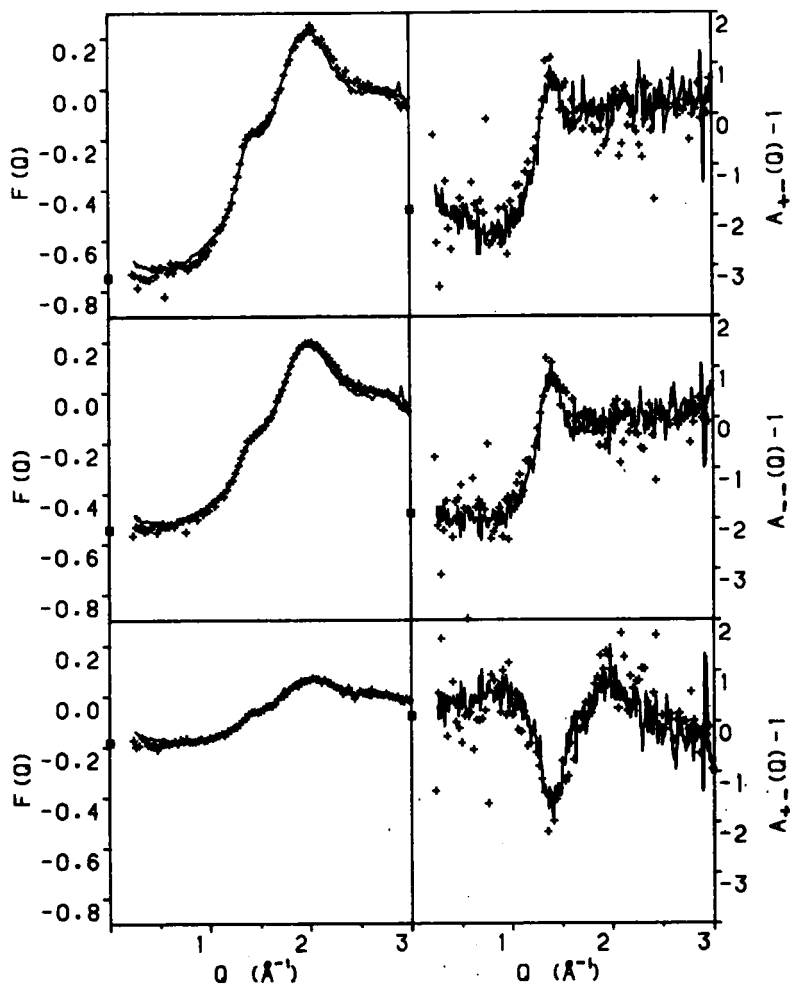


Figure 3 A comparison of $F(Q)$ and $A_{ij}(Q)$ as measured on D1B (solid curve) and D4 (+): $0.5 < Q < 1.5 \text{ \AA}^{-1}$ normalisation—see text for details.

We conclude that the differences observed in the D1B and D4 structure factors at higher Q were caused by the low Q normalisation procedure.

DISCUSSION

In order to ascribe an origin to the rise observed in the low Q structure factors measured on D1B, and the absence of this feature in the corresponding spectra measured on D4, it is necessary to consider precisely how static structure factors are measured experimentally. In a neutron diffraction experiment the detectors do not simply count elastically scattered neutrons at a given Q , as is required in principle, but

rather add all elastically and inelastically scattered neutrons at a given scattering angle θ , with the efficiency varying as a function of the scattered neutron energy. The static structure factor $S_T(Q)$ is the zeroth moment of the dynamical structure factor, $S_T(Q, \omega)$,

$$S_T(Q) = \int_{\text{constant } Q} S_T(Q, \omega) d\omega \quad (5)$$

whereas the experimentally measured structure factor $S_T(\theta)$ is given by

$$S_T(\theta) = \int_{\text{constant } \theta} (k_f/k_i)\varepsilon(k_f)/\varepsilon(k_i)S_T(Q, \omega) d\omega \quad (6)$$

where k_i and k_f are the incident and scattered neutron wavevectors respectively, and $\varepsilon(k)$ is the detector efficiency. For most detectors $\varepsilon(k)$ is approximately proportional to $1/k$, so

$$S_T(\theta) \simeq \int_{\text{constant } \theta} S_T(Q, \omega) d\omega \quad (7)$$

It is therefore important to consider the (Q, ω) path along which this constant θ integration is carried out. The locus is given by

$$Q^2 = k_i^2(1 + x - 2x^{0.5} \cos(\theta)) \quad (8)$$

where x is the ratio of incident and scattered neutron energies. Figure 4 compares these loci for diffraction instruments using incident wavelengths of 2.5 Å (D1B) and 0.7 Å (D4). It is immediately obvious that the detector loci for D4 are closer to the required constant Q loci than those for D1B.

The structure factor in a diffraction experiment, $S_T(\theta)$, is normally corrected in an attempt to obtain the real structure factor $S_T(Q)$. These are the inelasticity or 'Plazcek' corrections (see e.g. Yarnell *et al.*¹¹). In the absence of a complete knowledge of $S_T(Q, \omega)$ (in which case $S_T(Q)$ would also be known) it is necessary to use a model. For most systems, except those with light atoms such as hydrogen, the corrections are small and a simple free particle model is generally adequate. However in the present case both D1B and D4 data have been corrected using such a model, and yet the results deviate at low Q . The model is therefore inadequate, and we must consider the dynamics of the system more carefully.

If we examine the relation between the velocity of sound in the melt and the two sets of detector integration loci (Figure 3), we can see that at low angles the 0.7 Å loci cut through at two distinct points, whereas the dispersion is roughly parallel to the 2.5 Å loci. Although side peaks in $S_T(Q, \omega)$, corresponding to propagating acoustic modes, have not been observed in molten salts in the (Q, ω) region covered by neutron scattering experiments⁸, overdamped modes will still contribute some intensity. Their dispersion is expected to follow the velocity of sound up to $Q \simeq 1 \text{ \AA}^{-1}$, after which it becomes flat. The 'additional' intensity (relative to a free particle or simple diffusion model) will contribute very little to $S_T(\theta)$ when the integration is along 0.7 Å loci, but will contribute significantly along 2.5 Å loci at low angles. We therefore expect $S_T(\theta)$ for D1B to rise above that for D4, as is observed. At scattering angles below those

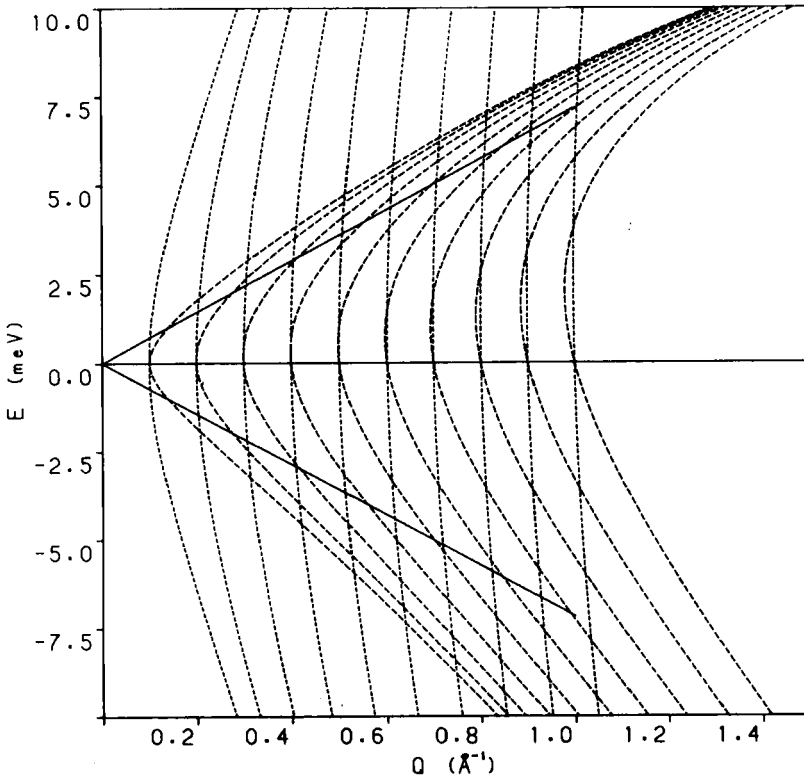


Figure 4 (Q, ω) detector integration loci for incident wavelengths of 2.5 Å (long dash) and 0.7 Å (short dash). The solid line indicates the sound velocity for molten CsCl at 1023 K. The loci correspond to those with elastic Q values that are multiples of 0.1 \AA^{-1} .

measured the D1B loci would no longer coincide with the sound mode dispersion and $S_T(\theta)$ would fall to its expected low Q limit. At higher angles the flattening of the dispersion, together with the decreased contribution of acoustic modes, will also result in agreement of the two measured structure factors.

There are two reasons why the standard inelasticity correction procedures do not account for this contribution. Firstly the free particle model of $S_T(Q, \omega)$ used only considers single particle recoil effects, and not the collective type of motion involved here. Secondly the method of correction, which involves expansion of $S_T(Q, \omega)$ in powers of $(Q_0^2 - Q^2)$, where Q_0 is the elastic momentum transfer at a particular scattering angle, is less accurate as the energy transfer of the relevant inelastic scattering process increases. Even if a suitable model of $S_T(Q, \omega)$ was available this would make them inappropriate.

Support for the proposal that the low Q rise in $F(Q)$ measured on D1B is caused by inelastic contributions from overdamped acoustic modes may be obtained by a comparison of the relative strengths of this feature for the samples of different isotopic

compositions. $F(Q)$ may be written in terms of structure factors associated with mass density (m —acoustic modes) and charge density (q —optic modes) as⁸

$$F(Q) = a_m^2(A_{mm} - 1) + a_q^2(A_{qq} - 1) + 2a_m a_q(A_{mq} - 1) \quad (9)$$

where, for an alkali halide,

$$a_m = (\bar{b}_+ + \bar{b}_-)/2 \quad (10)$$

$$a_q = (\bar{b}_+ m_- - \bar{b}_- m_+)/ (m_+ + m_-) \quad (11)$$

The values of the coefficients are given in Table 1. The rise in $F(Q)$ has the largest relative strength in the Cs³⁷Cl sample, for which a_m^2 proportionately has the largest value.

As noted in the introduction a rise in $S_T(Q)$ at low Q has been observed^{1,2} for both MgCl₂ and CaCl₂. While the explanation given here for CsCl can account for the small rise in CaCl₂, it cannot account for the extremely large rise in MgCl₂. In this case the same result has been obtained using neutrons of different wavelengths.

CONCLUSIONS

We have observed the contribution of overdamped acoustic modes to the measured static structure factor of molten CsCl at low Q . This occurs because of the coincidence of the mode dispersion, given by the sound velocity at low Q , and the (Q, ω) integration paths of the low angle neutron detectors on the instrument used. The low Q rise caused makes it impossible, using this data, to calculate long range terms in the interionic potential via the asymptotic expansion of the structure factors. If such calculations are to be performed it will be necessary to use short wavelength neutrons in a small angle scattering experiment, rather than the long wavelength neutrons conventionally used.

More generally these results illustrate the point that the *measured* structure factor in a diffraction experiment is not the *real* structure factor, but only an approximation. Measured structure factors will therefore differ between different measurements. In conventional neutron diffraction experiments, using reactor sources with short wavelength neutrons, the approximation is good for systems with heavy atoms. When longer wavelengths are used, in an attempt to increase the Q range covered, the approximation becomes worse. In the case of diffraction using pulsed neutron sources, where there is a range of incident wavelengths, the effects of inelastic scattering become more complex. New techniques for inelasticity corrections are required to take account of this. However it may in future be possible to use the differences between structure factors measured at different wavelengths in order to derive information about the dynamical, rather than the static, structure factor.

Acknowledgements

We should like to thank the staff of the Institut Laue Langevin, particularly Dr. G. Kearley, for assistance with experiments.

References

1. S. E. Day and R. L. McGreevy. *Phys. Chem. Liq.*, **15**, 129 (1985).
2. M. C. Fairbanks, M. A. Howe and R. L. McGreevy. *Phys. Chem. Liq.*, **18**, 179 (1988).
3. P. V. Giaquinta, M. Parinello and M. P. Tosi. *Phys. Chem. Liq.*, **5**, 305 (1976).
4. M. Rovere, P. V. Giaquinta, M. Parinello and M. P. Tosi. *Phil. Mag.*, **39**, 167 (1979).
5. A. A. van Well, P. Verkerk, L. A. de Graaf, J-B. Suck and J. R. D. Copley. *Phys. Rev. A*, **32**, 2384 (1985).
6. P. Verkerk. Thesis. Technische Hogeschool Delft (1985).
7. J. Locke, R. L. McGreevy, S. Messoloras, E. W. J. Mitchell and R. L. McGreevy. *Phil. Mag B*, **51**, 301 (1985).
8. R. L. McGreevy, E. W. J. Mitchell, F. M. A. Margaca and M. A. Howe. *J. Phys. C*, **18**, 5235 (1985).
9. P. F. J. Poncet. Thesis. University of Reading (1976).
10. I. A. Blech and B. L. Averbach. *Phys. Rev.*, **137**, 1113 (1965).
11. J. L. Yarnell, M. J. Katz, R. G. Wenzel and S. H. Koenig. *Phys. Rev. A*, **7**, 2130 (1973).
12. J. G. Kirkwood and F. P. Buff. *J. Chem. Phys.*, **19**, 774 (1951).