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Freezing of Ionic Melts into Normal and Superionic Phases

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The freezing mechanisms of molten alkali halides typified by RbCl and NaCl on the one hand, and molten fluorite-type materials BaCl₂ and SrCl₂ on the other, are compared and contrasted. Experimentally, the volume change across the solid-liquid transition is large for the alkali halides (~20%) and almost an order of magnitude smaller for the fluorites, where the freezing transition is to a superionic phase.

For RbCl and NaCl therefore, the free energy gain associated with the large volume change is one major feature in freezing, the other being the strong charge ordering. This is made quantitative and structural predictions for molten RbCl are in excellent agreement with neutron data. The agreement for NaCl is of poorer quality, but still semiquantitative.

In the case of freezing into the superionic phase, it turns out instead that the major features are the strong ordering of the divalent cation component and the difference in the partial molar volumes of anion and cation. The pronounced cation ordering is reminiscent of a tendency of strong repulsive Coulomb interactions inducing a classical Wigner transition, which in this case corresponds to the cation sub-lattice freezing. The microscopic theory presented then indicates that the disordered chlorine ions behave as a lattice liquid, the periodic external potential being created by the largely rigid cation lattice.

1 INTRODUCTION

In spite of the crucial importance of long-range Coulomb interactions, a variety of structural features are to be found in classical ionic assemblies. For example, alkali halides on the one hand, and fluorite-type materials on the other, have strikingly different melting behaviour, the former class showing

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very substantial volume changes $\Delta V/V \equiv \eta$, of the order of 15–25% and a discontinuous increase in the ionic conductivity by some orders of magnitude across the melting transition. In contrast, several fluorites show a continuous increase of the conductivity with temperature, to values typical of molten salts, in the solid before melting and a volume change of $\sim 3\text{--}5\%$ on melting. Though these are the classes of material dealt with in the present paper it is of interest to add that noble metal halides exhibit high ionic conductivity in the solid before melting, with volume changes which are known to be $\sim 8\%$ for AgCl and AgBr.

The purpose of the present paper is to discuss the freezing process in RbCl (see Rovere *et al.*¹) and NaCl on the one hand, and BaCl₂ and SrCl₂ on the other, using the microscopic theory given earlier.^{2,3} The basic difference between the two types of material is that the molten alkali halides freeze into a normal face-centred-cubic phase, whereas in BaCl₂ and SrCl₂ the cation sub-lattice provides a periodic potential in which still relatively disordered anions move. Appropriate language to describe this latter system seems to be a lattice liquid. In our earlier work on freezing into a superionic phase, linear response theory was used to estimate the ratio of a particular Fourier component of the anion density to that of the corresponding component for the cation sub-lattice for the case of BaCl₂. The present paper presents a fully non-linear solution, which, as we shall see, validates the above linear response assumption.

The basic input information required to develop the microscopic theory is the knowledge of the partial direct correlation functions $\tilde{c}_{ij}(k)$, or, more conveniently for present purposes, the charge-number ($Q-N$) counterparts. We shall see that in the freezing process for molten alkali halides the two ionic components play essentially equal roles, and the most important structural parameters are $\tilde{c}_{NN}(k=0)$ (namely the compressibility) and $\tilde{c}_{QQ}(\mathbf{G}_1)$ at the first set of reciprocal lattice vectors $\{\mathbf{G}_1\}$. In contrast, for freezing into the fluorite superionic phase, the dominant structural parameters are $\tilde{c}_{NQ}(k=0)$ (namely the difference in molar volumes of the components) and $\tilde{c}_{++}(\mathbf{G}_1)$.

2 FREEZING THEORY OF RbCl AND NaCl

We turn first to the molten alkali halides. Structural data for liquid RbCl have been reported by Mitchell *et al.*,⁴ and for liquid NaCl by Edwards *et al.*⁵ (see also Biggin and Enderby⁶). For these materials, it was assumed that inclusion of the first two sets of reciprocal lattice vectors, $\{\mathbf{G}_1\}$ and $\{\mathbf{G}_2\}$, would be adequate. The set $\{\mathbf{G}_1\}$ are reciprocal lattice vectors of the type (111) and correspond to the principal peak in the charge-charge structure factor $S_{QQ}(k)$ in the liquid. The second set $\{\mathbf{G}_2\}$ are of the type (200) and (220) corresponding to the principal peak in $S_{NN}(\mathbf{k})$.

The statistical mechanical equations given earlier² for the freezing transition are solved with the input of $\tilde{c}_{OQ}(G_1)$ and $\tilde{c}_{NN}(k=0)$ to determine the volume change η , the value of $\tilde{c}_{NN}(G_2)$, and the Fourier components of the single particle densities at $\{\mathbf{G}_1\}$ and $\{\mathbf{G}_2\}$. In our earlier calculations for RbCl,¹ while $\tilde{c}_{OQ}(G_1)$ was taken from the experiment, $\tilde{c}_{NN}(k=0)$ was varied in order to reproduce the observed volume change. The value of $\tilde{c}_{NN}(G_2)$ thus obtained was in reasonably good agreement with the measured value, but $\tilde{c}_{NN}(k=0)$ was appreciably more negative than the experimental value for the liquid. This we take to herald the presence of non-linear effects, these being directly related to the large value of the volume change η .

Early work on the monatomic liquid argon by Ramakrishnan and Yussouff⁷ has encountered a similar problem, and they included non-linear effects via a three-body direct correlation function at long wavelengths. The appropriate generalization to the present case, as discussed below, is the correlation function \tilde{c}_{NNN} at long wavelengths, which describes the dependence of compressibility on volume.

Experimental information on three-body correlation functions is lacking for ionic liquids. In the present calculations \tilde{c}_{NNN} at long wavelengths is therefore treated as a parameter, after fixing $\tilde{c}_{NN}(k=0)$ from the experimental value of the compressibility of the liquid.

3 EQUATIONS TO INCLUDE NON-LINEAR EFFECTS VIA THREE-BODY PARTIAL DIRECT CORRELATION FUNCTIONS

We recall that the theory can be formulated in terms of the thermodynamic potential Ω which is a functional of the single particle densities $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r})$. A set of coupled equilibrium equations for these densities is obtained by requiring that Ω be a minimum. For coexistence between liquid (*l*) and solid (*s*) phases, the difference $\Delta\Omega = \Omega_s - \Omega_l$ must vanish. The appropriate equations given earlier² in a linear response approximation are easily modified to include non-linear terms by analogy with the treatment given by Haymet and Oxtoby⁸ for a monatomic fluid.

The equilibrium equations for the single particle densities in the two-component ionic system then are

$$\ln \left[\frac{\rho_{is}(\mathbf{r}_1)}{\rho_{il}} \right] = \sum_j \int d\mathbf{r}_2 c_{ij}(\mathbf{r}_1, \mathbf{r}_2) [\rho_{js}(\mathbf{r}_2) - \rho_{jl}] + \frac{1}{2} \sum_{j,k} \iint d\mathbf{r}_2 d\mathbf{r}_3 c_{ijk}^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) [\rho_{js}(\mathbf{r}_2) - \rho_{jl}] [\rho_{ks}(\mathbf{r}_3) - \rho_{kl}] \quad (3.1)$$

for $i = 1, 2$. The first term on the right-hand side contains the direct correlation functions $c_{ij}(\mathbf{r}_1, \mathbf{r}_2) = c_{ij}(|\mathbf{r}_1 - \mathbf{r}_2|)$ of the liquid and represents the first-order response to the change in densities. The three-body correlation functions $c_{ijk}^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = c_{ijk}^{(3)}(\mathbf{r}_1 - \mathbf{r}_2, \mathbf{r}_1 - \mathbf{r}_3)$ of the liquid which enter the second term are defined by the functional derivatives

$$c_{ijk}^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \frac{\delta c_{ij}(\mathbf{r}_1, \mathbf{r}_2)}{\delta \rho_k(\mathbf{r}_3)} \quad (3.2)$$

For the difference in thermodynamic potentials we similarly have

$$\begin{aligned} \Delta\Omega/k_B T = & - \sum_i \int d\mathbf{r}_1 [\rho_{is}(\mathbf{r}_1) - \rho_{il}] \\ & + \frac{1}{2} \sum_{i,j} \iint d\mathbf{r}_1 d\mathbf{r}_2 [\rho_{is}(\mathbf{r}_1) + \rho_{il}] c_{ij}(\mathbf{r}_1, \mathbf{r}_2) [\rho_{js}(\mathbf{r}_2) - \rho_{jl}] \\ & + \frac{1}{6} \sum_{i,j,k} \iiint d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 [2\rho_{is}(\mathbf{r}_1) + \rho_{il}] c_{ijk}^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) [\rho_{js}(\mathbf{r}_2) - \rho_{jl}] \\ & \quad [\rho_{ks}(\mathbf{r}_3) - \rho_{kl}] \end{aligned} \quad (3.3)$$

We introduce next the Fourier expansions²

$$\rho_{is}(\mathbf{r}) = \frac{1}{2} \rho_l \left[1 + \eta + \sum_{\mathbf{G}}' \rho_{\mathbf{G}} \exp(i\mathbf{G} \cdot \mathbf{r}) \right] \quad (3.4)$$

and

$$\rho_{2s}(\mathbf{r}) = \frac{1}{2} \rho_l \left\{ 1 + \eta + \sum_{\mathbf{G}}' \rho_{\mathbf{G}} \exp[i\mathbf{G} \cdot (\mathbf{r} + \mathbf{h})] \right\} \quad (3.5)$$

where ρ_l is the liquid density and \mathbf{h} is the vector joining the two ions in the unit cell of the crystal. With the further definitions

$$c_{ij}(r) = \left(\frac{2}{N} \right) \sum_{\mathbf{k}} \tilde{c}_{ij}(k) \exp(i\mathbf{k} \cdot \mathbf{r}) \quad (3.6)$$

and

$$c_{ijk}^{(3)}(\mathbf{r}, \mathbf{r}') = \left(\frac{4}{N^2} \right) \sum_{\mathbf{k}, \mathbf{k}'} \tilde{c}_{ijk}^{(3)}(\mathbf{k}, \mathbf{k}') \exp(i\mathbf{k} \cdot \mathbf{r} + i\mathbf{k}' \cdot \mathbf{r}'), \quad (3.7)$$

eqs. (3.1) and (3.3) can be rewritten in terms of Fourier transforms. We assume that the only important contribution of the non-linear terms arises from the change of compressibility with volume, which is expressed by the double Fourier transform of the quantity

$$c_{NNN}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \frac{1}{4} \sum_{i,j,k} \frac{\delta c_{ij}(\mathbf{r}_1, \mathbf{r}_2)}{\delta \rho_k(\mathbf{r}_3)} \quad (3.8)$$

in the limit of long wavelengths. Denoting this quantity by $\tilde{c}_{NNN}(0, 0)$, the equilibrium equations for the Fourier components of the single particle density, in a form which is most convenient for their numerical solution, are

$$1 + \eta = \exp[\eta\tilde{c}_{NN}(0) + \eta^2\tilde{c}_{NNN}(0, 0)] \cdot V^{-1} \int d\mathbf{r} \exp[F_1(\mathbf{r}) + F_2(\mathbf{r})] \quad (3.9)$$

and

$$2\rho_{\mathbf{G}} = \exp[\eta\tilde{c}_{NN}(0) + \eta^2\tilde{c}_{NNN}(0, 0)] \cdot V^{-1} \int d\mathbf{r} \exp[-i\mathbf{G} \cdot \mathbf{r} + F_1(\mathbf{r}) + F_2(\mathbf{r})]. \quad (3.10)$$

Here,

$$F_1(\mathbf{r}) = \sum_{\mathbf{G}} \rho_{\mathbf{G}} \tilde{c}_{NN}(\mathbf{G}) \exp(i\mathbf{G} \cdot \mathbf{r}) [1 + \exp(i\mathbf{G} \cdot \mathbf{h})] \quad (3.11)$$

and

$$F_2(\mathbf{r}) = \sum_{\mathbf{G}} \rho_{\mathbf{G}} \tilde{c}_{QQ}(\mathbf{G}) \exp(i\mathbf{G} \cdot \mathbf{r}) [1 - \exp(i\mathbf{G} \cdot \mathbf{h})]. \quad (3.12)$$

Finally, the expression for $\Delta\Omega$ is

$$\frac{\Delta\Omega}{Nk_B T} = -\eta + \tilde{c}_{NN}(0)(\eta + \frac{1}{2}\eta^2) + 2\tilde{c}_{NNN}(0, 0)(\frac{1}{2}\eta^2 + \frac{1}{3}\eta^3) + 2 \sum_{\mathbf{G}} [\tilde{c}_{NN}(\mathbf{G})\rho_{\mathbf{G}}^2 \cos^2(\frac{1}{2}\mathbf{G} \cdot \mathbf{h}) + \tilde{c}_{QQ}(\mathbf{G})\rho_{\mathbf{G}}^2 \sin^2(\frac{1}{2}\mathbf{G} \cdot \mathbf{h})], \quad (3.13)$$

$\Delta\Omega$ being equal to zero at coexistence.

4 NUMERICAL PREDICTIONS OF MICROSCOPIC THEORY FOR RbCl AND NaCl

Using the equations set out in Section 3 above, plus input from experiment already referred to, the numerical results obtained are shown for RbCl and NaCl in Table I below.

TABLE I
Detailed numerical predictions on $\tilde{c}_{NN}(G_2)$, $\rho_{\mathbf{G}_1}$, $\rho_{\mathbf{G}_2}$ and $\tilde{c}_{NNN}(0, 0)$.

	$\tilde{c}_{NN}(0)$	$\tilde{c}_{QQ}(G_1)$	$\tilde{c}_{NN}(G_2)$	$\tilde{c}_{NNN}(0, 0)$	ρ	$\rho_{\mathbf{G}_1}$	$\rho_{\mathbf{G}_2}$	
RbCl	Th.	- 7.33	0.75	0.29	- 105	0.14	0.46	0.36
	Exp.	- 7.33	0.75	0.29	—	0.142	—	—
NaCl	Th.	- 6.3	0.72	0.28	- 31	0.25	0.53	0.42
	Exp.	- 6.3	0.72	0.15	—	0.25	—	—

For RbCl, it is gratifying that the theory predicts $\tilde{c}_{NN}(G_2)$ in agreement with experiment. The value of $\tilde{c}_{NNN}(0, 0)$ of -105 is of the same order of magnitude as that found for the corresponding three-body function for liquid argon by Ramakrishnan and Yussouff.⁷ We reiterate that this choice of $\tilde{c}_{NNN}(0, 0)$, when combined with the measured volume change, accounts for the shift in compressibility from the measured liquid value that was found necessary in previous work.¹

In the case of NaCl, the prediction of $\tilde{c}_{NN}(G_2)$ is only semiquantitative, while the value of $\tilde{c}_{NNN}(0, 0)$ is only about 1/3 of that for RbCl. It is seen that the Fourier components of the density are quite similar in magnitude and behaviour in the two cases. We feel it would be of considerable interest if these predictions could be confronted with the results of diffraction experiments on the hot solid.

5 MICROSCOPIC THEORY OF FREEZING OF BaCl₂ AND SrCl₂ INTO A SUPERIONIC PHASE

We are now working³ in these systems in terms of the species i -species j partial direct correlation functions $\tilde{c}_{ij}(k)$, using the linear response form of Eqs. (3.1). Fourier analyzing the densities, we write

$$\rho_{is}(\mathbf{r}) = \rho_{is} + V^{-1} \sum_{\mathbf{G}} \rho_{i\mathbf{G}} \exp(i\mathbf{G} \cdot \mathbf{r}) \quad (5.1)$$

for $i = 1, 2$. In particular, the component with $\mathbf{G} = 0$ of Eqn. (3.1) leads to

$$\ln \left(\frac{\rho_{is}}{\rho_{il}} \right) + \frac{1}{V} \int d\mathbf{r} \ln \left[1 + \frac{1}{V\rho_{is}} \sum_{\mathbf{G}} \rho_{i\mathbf{G}} \exp(i\mathbf{G} \cdot \mathbf{r}) \right] + \frac{1}{\rho_l} \sum_j (\rho_{js} - \rho_{jl}) \tilde{c}_{ij}(0) \quad (5.2)$$

where the Fourier transform $\tilde{c}_{ij}(k)$ is defined by writing

$$c_{ij}(r) = (V\rho_l)^{-1} \sum_{\mathbf{k}} \tilde{c}_{ij}(k) \exp(i\mathbf{k} \cdot \mathbf{r}). \quad (5.3)$$

The quantity appearing on the right-hand side of Eq. (5.2) can be related to N - Q direct correlation functions using

$$\sum_j \left(\frac{\rho_{jl}}{\rho_l} \right) \tilde{c}_{ij}(0) = \tilde{c}_{NN}(0) + \tilde{c}_{NQ}(0). \quad (5.4)$$

The discussion of the behaviour at small k of the partial structure factors and partial direct correlation functions for 2:1 liquids follows closely that given

by Rovere *et al.*⁹ for molten alkali halides, the main results we need below being

$$\tilde{c}_{NN}(0) = 1 - \frac{1}{S_{NN}(0)} = 1 - (\rho_1 k_B T K_T)^{-1} \quad (5.5)$$

and

$$\tilde{c}_{NQ}(0) = \frac{2\rho_{11}(v_2 - v_1)}{(\rho_1 k_B T K_T)}, \quad (5.6)$$

where K_T is the isothermal compressibility, while v_1 and v_2 are the partial volumes of the two species, 1 now being the cation. The thermodynamic definition of v_i is

$$v_i = (\partial\mu_i/\partial p)_{T,N}. \quad (5.7)$$

It is therefore clear that the difference in partial molar volumes of anion and cation enters, via Eq. (5.2), the calculation of the volume change on freezing.

The other equations entering the theory are the equilibrium conditions for the $\mathbf{G} \neq 0$ components of the densities,

$$\int d\mathbf{r} \ln \left[1 + \frac{1}{V\rho_{is}} \sum_{\mathbf{G}'} \rho_{i\mathbf{G}'} \exp(i\mathbf{G}' \cdot \mathbf{r}) \right] \exp(-i\mathbf{G} \cdot \mathbf{r}) = \frac{1}{\rho_i} \sum_j \rho_{j\mathbf{G}} \tilde{c}_{ij}(\mathbf{G}), \quad (5.8)$$

and the condition of coexistence of the two phases, which means equating to zero the difference $\Delta\Omega$ in their thermodynamic potentials. This difference is given on account of the equilibrium equations by

$$\begin{aligned} \Delta\Omega/k_B T = & -(\rho_s - \rho_l)V + \frac{1}{2} V(\rho_s^2/\rho_l^2 - 1)\tilde{c}_{NN}(0) \\ & + (2V\rho_l)^{-1} \sum_{i,j} \sum_{\mathbf{G}} \tilde{c}_{ij}(\mathbf{G})\rho_{i\mathbf{G}}\rho_{j\mathbf{G}} \end{aligned} \quad (5.9)$$

Clearly this calculation involves the compressibility through $\tilde{c}_{NN}(0)$.

6 NUMERICAL PREDICTIONS FOR BaCl_2 AND SrCl_2

Here, only the first set $\{\mathbf{G}_1\}$ of reciprocal lattice vectors have been included, corresponding to the first peak in the cation-cation structure factor $S_{11}(\mathbf{G}_1)$. For each value of $\tilde{c}_{NQ}(0)$ chosen and taking $\tilde{c}_{11}(\mathbf{G}_1)$ from experiment, the values of the volume change η and of the compressibility ($\tilde{c}_{NN}(0)$) were varied in determining the solution of the set of coupled equations for $\tilde{c}_{12}(\mathbf{G}_1)$, $\tilde{c}_{22}(\mathbf{G}_1)$, $\rho_{1\mathbf{G}_1}$ and $\rho_{2\mathbf{G}_1}$, agreement between the first two quantities and experiment being a test of the accuracy of the results. Starting with $\tilde{c}_{NQ}(0) = 0$,

TABLE II
 Numerical predictions of microscopic theory for BaCl₂ and SrCl₂.

		$\tilde{c}_{NQ}(0)$	$S_{NN}(0)$	η	$\tilde{c}_{++}(G_1)$	$\tilde{c}_{+-}(G_1)$	$\tilde{c}_{--}(G_1)$	ρ_{1G}^+	ρ_{2G}^+
BaCl ₂	Th.	-16	0.073	0.035	0.150	-3.1	-2.2	0.53	0.22
	Exp.	—	0.073	0.035	0.150	-2.3	-3.0	—	—
SrCl ₂	Th.	-12	0.066	0.024	-0.46	-2.9	-1.2	0.42	0.24
	Exp.	—	0.066	0.024	-0.46	-2.5	-1.8	—	—

* In units of ρ_{11}/ρ_1 and ρ_{21}/ρ_1 , respectively.

the solution was in strong disagreement with experiment and insensitive to changes in η and $\tilde{c}_{NN}(0)$. Therefore $\tilde{c}_{NQ}(0)$ was varied and the results in Table II give an illustration of the quality of the agreement with experiment that can be reached by keeping this quantity as a free parameter.

Agreement with experiment for \tilde{c}_{12} and \tilde{c}_{22} at the first reciprocal lattice vector is fair, especially considering the neglect of all the higher reciprocal lattice vectors in the application of the theory.

The value of $\tilde{c}_{NQ}(0)$ predicted as -16 for BaCl₂ and -12 for SrCl₂ in Table II clearly implies from Eq. (5.6) that the cation volume is greater than that of the anion, an opposite situation to that one would predict from ionic radii. The reason for this is believed to be the large charge +2e on the cations, which tends to lead to a 'classical Wigner lattice.' The hole thereby created around a chosen cation has essentially to do with Coulomb repulsion rather than ionic core radius. Some independent evidence relating to this point is to be found in the work of Abramo *et al.*¹⁰ who have fitted to the measured structure factors the mean spherical approximation to a model of charged hard spheres. This leads to hard sphere diameters which are in accord with the sign of the above prediction for $\tilde{c}_{NQ}(0)$, though much smaller in magnitude.

Although the determination of ρ_{2G} in Table 2 was derived from the non-linearized theory recorded in the previous section, the numerical result agrees closely with those obtained by linearizing in ρ_{2G} , namely

$$\rho_{2G} = \frac{\tilde{c}_{12}(G)\rho_{1G}}{[(\rho_1/\rho_{2s}) - \tilde{c}_{22}(G)]} \quad (6.1)$$

It is of interest that this procedure is, of course, a direct calculation on a lattice liquid, the Fourier component ρ_{2G} being a consequence of the disordered chlorine component experiencing the periodic lattice potential imposed by the rigid cation sublattice. Of course, to work out corresponding results at a finite temperature below the freezing point would require knowledge of the anisotropy of the partial direct correlation functions at the temperature in question.

7 CONCLUSIONS

A consistent pattern emerges from the microscopic theory of freezing into both normal (RbCl and NaCl) and superionic (BaCl_2 and SrCl_2) phases. In particular, for the alkali halide RbCl, excellent structural predictions result, as well as numerical estimates of the Fourier components of the density at the first two reciprocal lattice vectors. To our knowledge, no experimental values have yet been determined for these Fourier components in the hot solid. For NaCl, the agreement is less good, but still semiquantitative.

For the superionic cases, only a single set of reciprocal lattice vectors has been included, and the need to transcend this approximation may well arise later. The most interesting prediction here is the difference in the partial molar volumes in BaCl_2 and SrCl_2 , the interpretation we propose being that a classical Coulomb hole exists because of strong Coulomb repulsion between the divalent ions. Though these partial molar volumes are precisely defined by thermodynamics, we know of no way by purely thermodynamic measurements in which they can be separately extracted. A small angle scattering experiment could allow a measurement of the difference in partial molar volumes, which would settle the matter under discussion. Finally, a diffraction experiment to test our predictions would be of obvious interest; we only know presently of data for PbF_2 , and here the experiments have only been carried out appreciably below the melting temperature. Nevertheless, we would expect the ratio of the lattice liquid Fourier components to the rigid sub-lattice values to decrease with increasing temperature, so even low temperature data would be useful for comparison.

While it is not surprising that as we go from monovalent alkali halides to fluorite materials with divalent cations there are major changes in behaviour, it is less easy to see why that should be so when alkali metal cations are replaced by Cu^+ or Ag^+ ions. Structural data using neutrons with the method of isotopic substitution have been obtained by Page and Mika¹¹ (see also Eisenberg *et al.*¹²) on molten CuCl and the structural correlations are very different from those found in molten alkali halides. The Cu structure factor is rather featureless, which is somewhat analogous to the Cl structure factor in BaCl_2 and SrCl_2 .

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