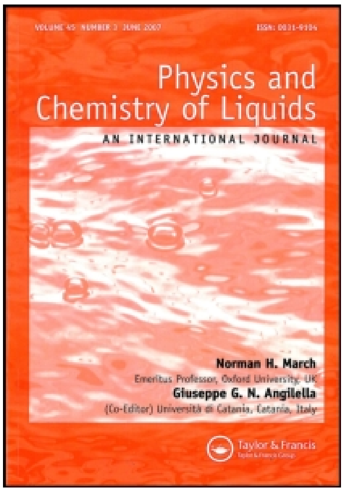

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Structure of Molten Silver Chloride

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From neutron elastic scattering measurements using the technique of isotopic enrichment, the partial structure factors of silver chloride are obtained.

These show important differences from CsCl, and in particular the behaviour at large momentum transfer suggest that chemical bonding plays an important role. A tentative model is thereby proposed for the structure, based on sp^3 hybridization.

1 INTRODUCTION

In the molten state, silver chloride shows some specific differences from ionic melts like KCl. For example, associated with the melting process at a lower temperature, the volume expansion on melting is small (8.9%[1]). The enthalpies of mixing[2a,b] with alkali halides can be described by the ionic conformal solution along lines given by Davis and Rice,[3] if the nearest-neighbour dispersion interactions are taken into account.

Furthermore, transport properties such as the thermoélectric power[4] show striking differences from these of the alkali halides. All these properties seem to the connected with a mixture of covalent and ionic interactions. A similar situation exists for the thallium and the copper halides. The increase in the degree of covalency on melting and with temperature in the liquid state is supported by N M R measurements.[5]

It seems plausible to introduce a covalency contribution in the liquid also from solid state results on AgCl. Recently, the dispersion curves for the

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lattice vibrations were measured by neutron inelastic scattering.[6] The authors obtained good agreement with theoretical predictions based on a shell model with deformable ions and covalent coupling between the neighbours.[7a,b] The deformability of the Ag^+ ion-d shell and the covalent coupling with the neighbours have been taken into account by introducing two new degrees of freedom in the electronic shell of the Ag^+ ion, compared to the alkali ion. They have a quadrupolar and a rotational symmetry character. It seems an interesting matter to study how these particular characteristics will influence the behaviour in the liquid state compared with that for the alkali halides.

Simulation data requires some hypothesis about the ionic pair potentials and this problem has not yet been tackled. Therefore, the microscopic information to date is due to elastic neutron scattering experiments.

2 EXPERIMENTAL DATA

Our experiments were performed on the D4 spectrometer of the Institut Laue-Langevin high flux reactor at Grenoble. The neutron scattering length used is $\lambda = 0.696$ Å and more technical details on the spectrometer itself can be found in reference 8.

Molten AgCl is contained in a quartz tube of 7 mm diameter and 0.5 mm thickness. The useful part of the sample is delimited by two pieces of boron nitride (a high neutron absorber) and the irradiated height is 3 cm. The whole system is placed in a furnace made of a thin vanadium tube of 2.5 cm diameter and kept under a vacuum of about 10^{-5} mm of mercury. The AgCl structure was investigated at two temperatures: near the melting point (510° C) and higher (850° C). The 3 enriched compounds, used for each temperature, were chosen because they have suitable neutron characteristics. AgCl neutronic constants are reported in Table I. To obtain the coherent part of the measured scattered intensity, numerous corrections for background, container diffusion absorption, multiple and inelastic scattering, were necessary. All these corrections are described in references 8 and 9. The accuracy of the corrected intensities is about 3% and the error made on the scattering angle is 0.01 degree. Thus in the static approximation the total structure factor is related to the corrected coherent intensity by the following expression.

$$S_T(9) = \frac{\mathrm{Icoh}\ (9)}{\mathrm{Icoh}\ (\infty)}$$

where $9 = \frac{4\pi \sin\theta}{\lambda}$ (2θ scattering angle) is the momentum transfer.

TABLE I

Scattering data for the isotopes of chlorine and for silver

Compound	Enrichment %	M	σ coh metal (barn) (d)	σ coh chlore (barn) (d)	σ incoh metal (barn) (b)	σ incoh chlore (barn) (a)	b coh chlore (10^{-12}) cm	b coh chlore (10^{-12}) cm	σ coh/mol (barn)	Total abs μ 0.7 A cm^{-1} (a) (b)	melting point °C (c)
Ag_NCl_{35}	Cl_{35}: 99.32 Cl_{37}: 0.68	142.88	4.6	17.30	1.9	2	0.61	1.172	21.90	1.46	455
Ag_NCl_n	Cl_{35}: 75.53 Cl_{37}: 24.47	143.33	4.6	11.45	1.9	3.4	0.61	0.955	16.05	1.25	455
Ag_NCl_{37}	Cl_{35}: 24.42 Cl_{37}: 75.58	144.40	4.6	2.95	1.9	2	0.61	0.485	17.55	0.83	455

$d_g/cm^3 = 5{,}267 - 0{,}0092\,t$ (e)

(a) D. J. Page, K. Mika *J. Phys.* (1971) C4, 18, 3034

(b) G. E. Bacon *Neutron Diffraction* Oxford University Press.

(c) *Handbook of Chemistry and Physics* (1967) Chemical Ruber CO F 124

(d) Neutron diffraction Commission *Act. cryst.* (1969) A 25 391

(e) D. Yaffee, E. R. Van Artsdal *J. Phys. Chem.* (1956) 60, 1125

The relation between $S_T(9)$ and the partial structure factors is given by:

$$c_1^2b_1^2(S_{11} - 1) + c_2^2b_2^2(S_{22} - 1) + 2c_1c_2b_1b_2(S_{12} - 1) = (c_1b_1^2 + c_2b_2^2)(S_T - 1) \quad (1)$$

in which Sij is the partial structure factor, (c_i), (b_i) are the concentration and the scattering length of the species i. Using isotopic substitution on the same compound we can obtain three different total structure factors and consequently three different equations of the form of Eq. (1). The resolution of this linear system gives the values of the partial structure factors. This resolution is not generally as easy as appears at a first glance because of the very small values of the determinant.

Table II gives the coefficients of the linear system and, as can be seen in our case, they are well enough defined. However, because of small errors on each $S_T(q)$ the vertical accuracy of the partial structures factors is not very good but the relative height of each peak and its position are correctly determined.

3 INTENSITY DATA AND PARTIAL STRUCTURE FACTORS

The corrected intensity data obtained at the investigated temperatures, 510°C and 850°C, are shown on Figures 1 and 2. The flatness of these curves at small momentum transfer permits an easy extrapolation for $q \to 0$. An accurate value of the intensity I(0), which is an important quantity to calulate $I_{coh}(q)$ (9), is then obtained.

The most interesting property of those intensity curves is their oscillating character at high momentum transfer compared to the ionic liquid behaviour. This observation leads us to conclude, by comparison with the intensity scattered by molecular liquids, that the local structure of AgCl would be more "molecular" that the KCl or CsCl ones.

The partial structure factors obtained by solving the linear system (1) are plotted in Figures 3 and 4. From these curves several features must be pointed out:

a) *The thermodynamical limit* $\underset{q\to 0}{A_{ij}(q)} = nK_BT\beta_T$ *is verified for KCl as for CsCl*

TABLE II

Coefficients of the linear system (Equation 1)

Compound	Abundance	b_1	b_2	b_1^2	b_2^2	$2b_1b_2$	$2(b_1^2 + b_2^2)$
$AgCl^{35}$	99.32%	0.61	1.172	0.372	1.372	1.43	3.488
AgCl	(nat)	0.61	0.955	0.372	0.912	1.16	2.568
$AgCl^{37}$	(75.53%)	0.61	0.485	0.372	0.235	0.59	1.214

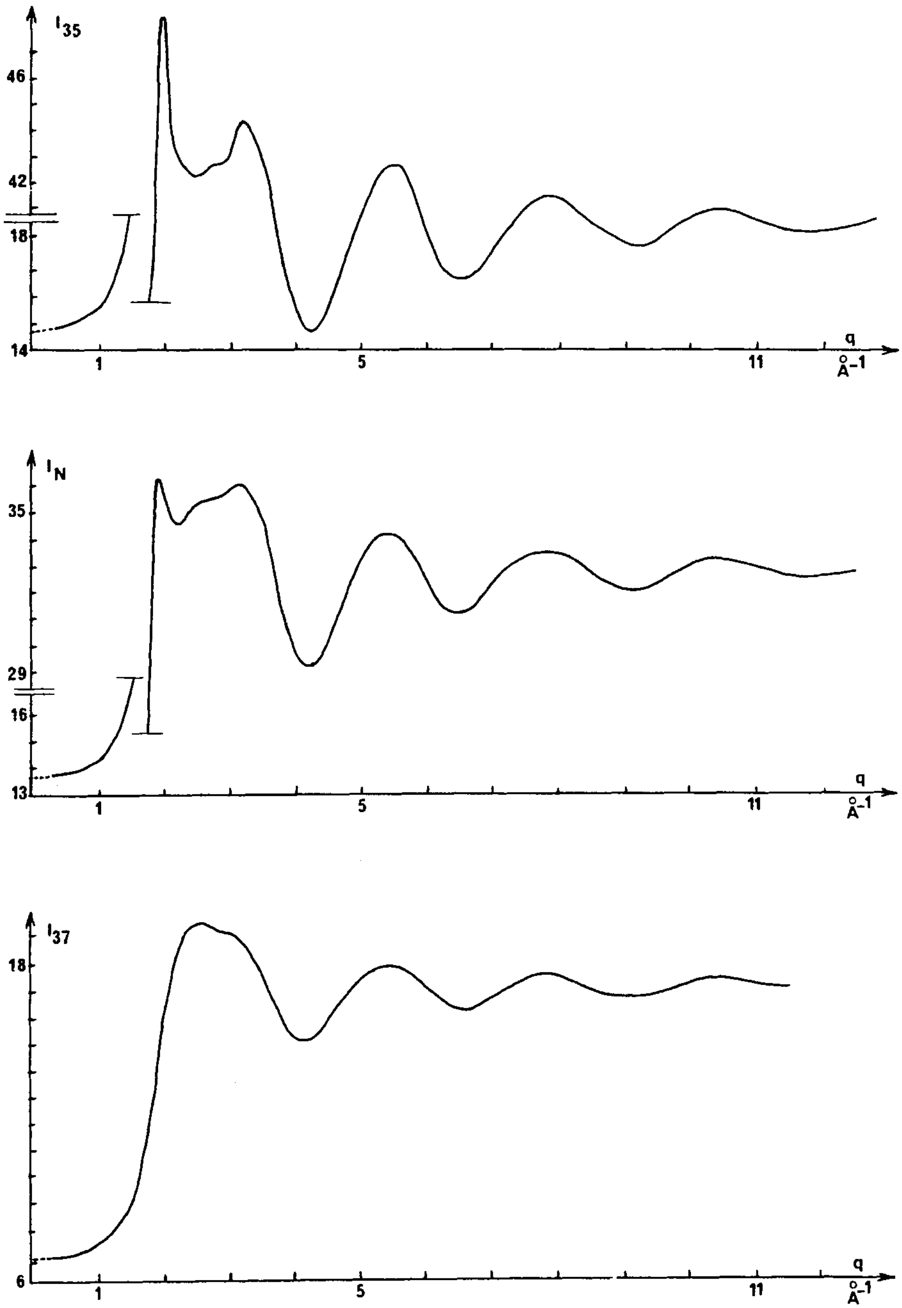

FIGURE 1 Angular variation in coherent intensity of neutrons scattered by liquid ${}^{x}Ag^{x}Cl$ sample (x = 35, N, 37) at 510°C.

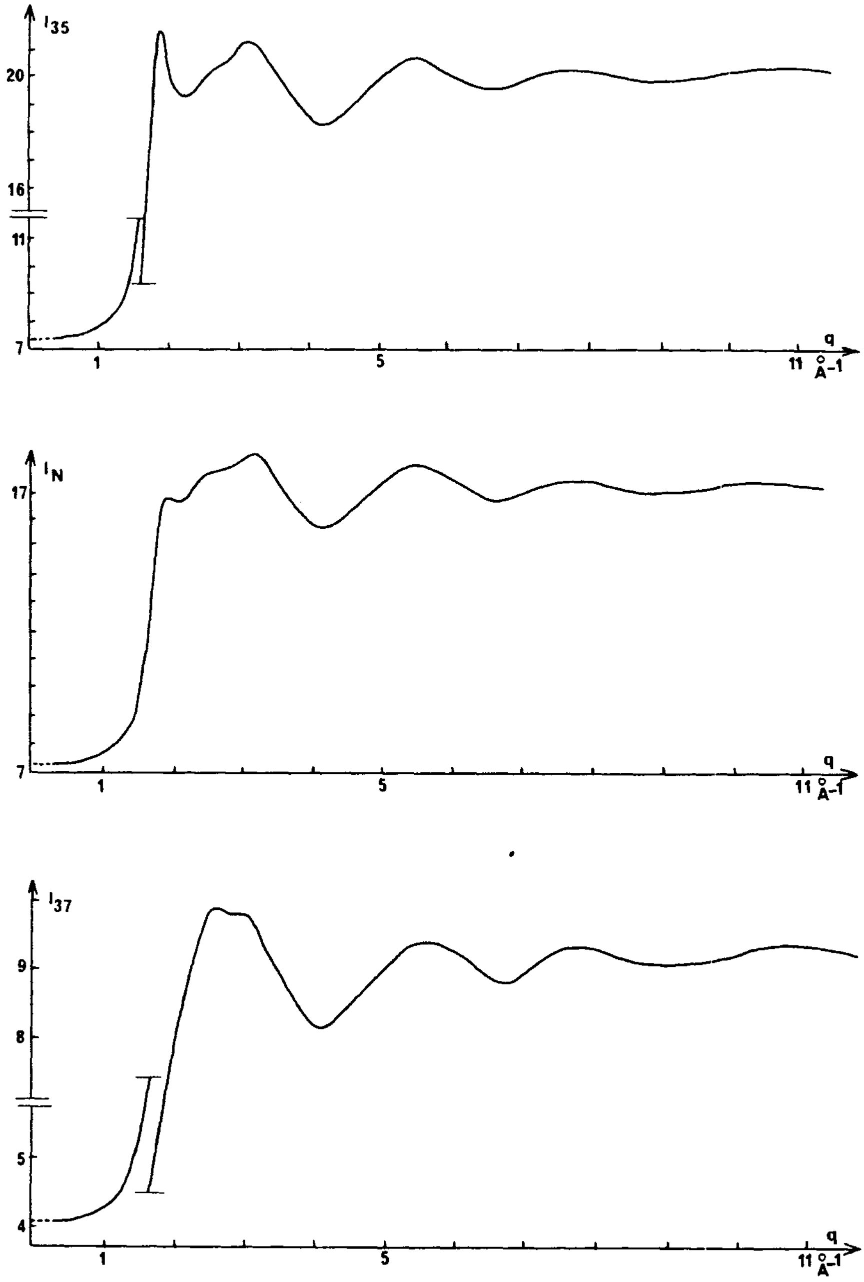

FIGURE 2 Angular variation in coherent intensity of neutrons scattered by liquid ${}^{x}Ag{}^{x}Cl$ sample (x = 35, N, 37) at 850° C.

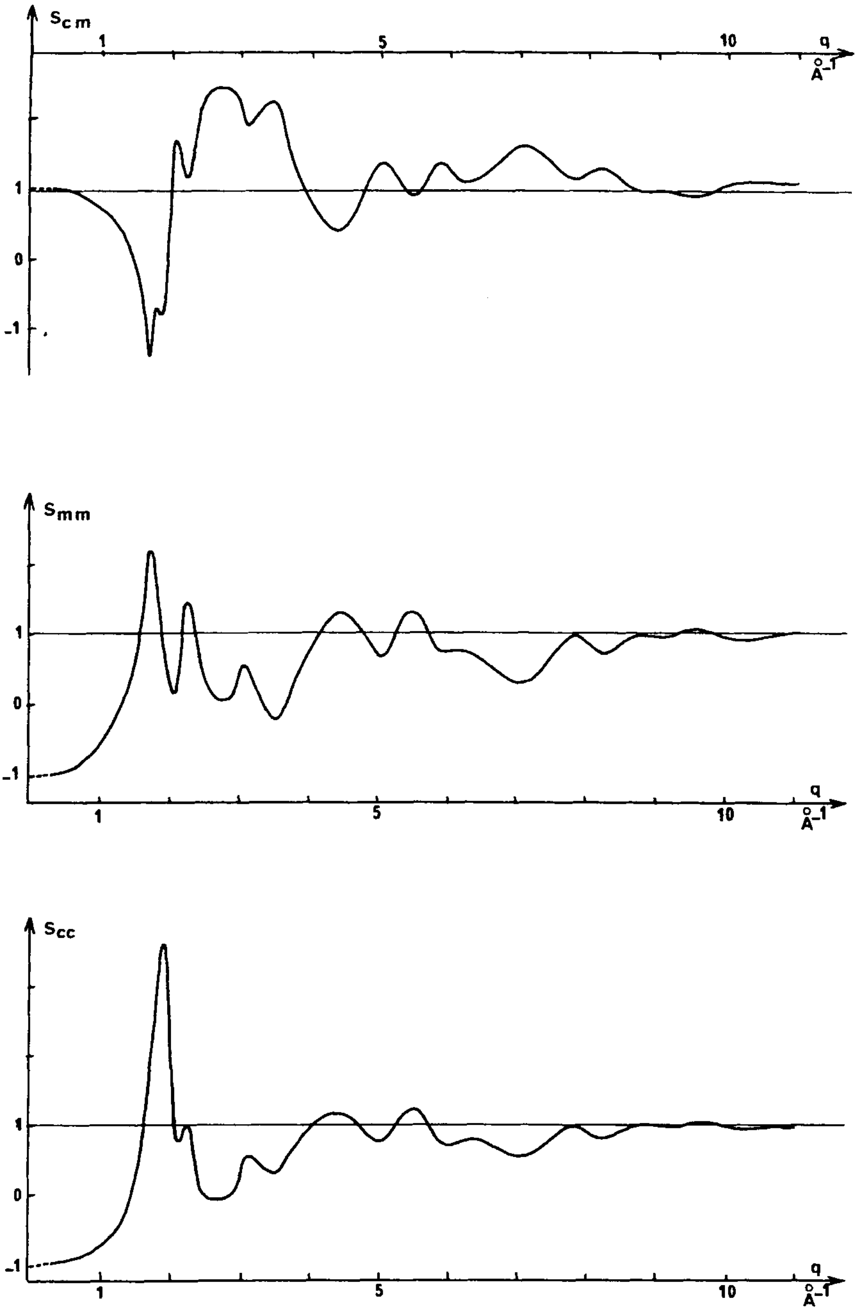

FIGURE 3 The smoothed partial structure factors for AgCl at 510°C.

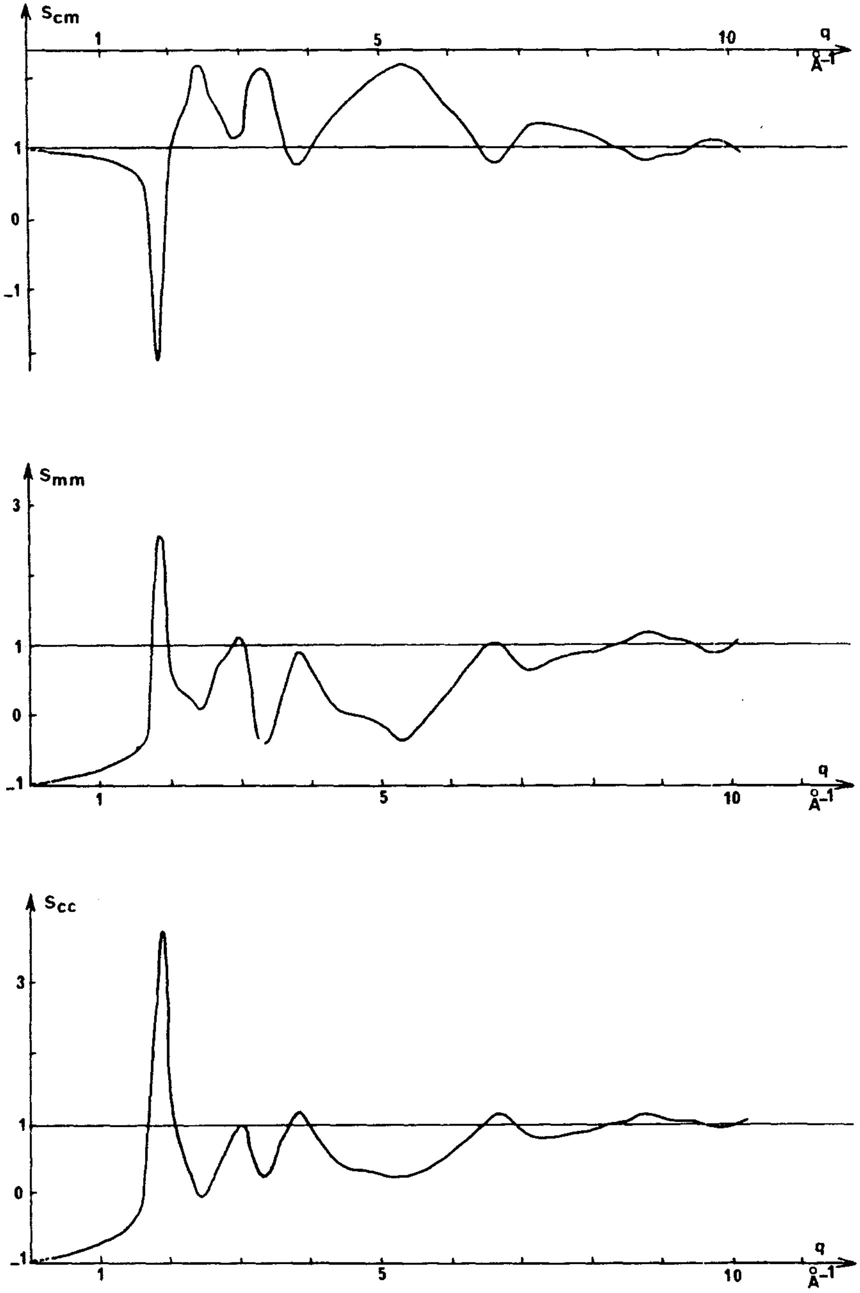

FIGURE 4 The smoothed partial structure factors for AgCl at 850° C.

n is the ionic pair density
K_B the Boltzman constant
T the temperature
β_T the isothermal compressibility
$A_{ij}(q)$ is related to the partial structure factors $S_{ij}(q)$ by
$A_{ii}(q) = c_i[S_{ii} - 1] + 1$
$A_{ij}(q) = (c_i c_j)^{1/2}(S_{ij} - 1)$
$i \neq j$

b) If we plot $A_{ij}(q)$ versus q^2, the slope of the curves at small q has the same characteristics as the KCl or CsCl one. We have in fact

$$\underset{q\to 0}{\frac{\partial A_{11}}{\partial(q^2)}} > 0 \; \underset{q\to 0}{\frac{\partial A_{22}}{\partial(q^2)}} > 0 \text{ and } \underset{q\to 0}{\frac{\partial A_{12}}{\partial(q^2)}} < 0$$

in agreement with the calculations of Abramo *et al.*[10]

c) Contrarily to our results on ionic compounds *we note a great difference between the two partial structure factors of like ions:* the position, the number and the intensity of the main peaks are different. We can thus conclude that the cations and the anions have not the same behaviour. The increase in temperature is characterised by a symmetrisation of the part played by the cations and the anions. This is clearly shown, by the values of the partial structure factors S_{mm} and S_{cc} at 850° C which become nearly the same.

d) The strongly oscillating character of these three partial structure factor contrasts with the generally observed behaviour in the case of liquid metals or rare gases. However it is of some interest from these scattering factors *to calculate the mass and charge correlation functions.* Indeed these new functions can be related by a linear combination of the $S_{ij}(q)$ according to the analysis proposed by Bathia and Thornton[11] on binary metallic mixtures and by Abramo *et al.*,[10] for ionic liquids. The definitions of mass and charge correlation function are:

$$\begin{aligned} \text{mass–mass: } S_{NN}(q) &= C_1^2 S_{11} + C_2^2 S_{22} + 2C_1C_2S_{12} \\ \text{charge–charge: } S_{qq}(q) &= C_1C_2(1 + C_1C_2(S_{11} + S_{22} - 2S_{12})) \\ \text{mass–charge: } S_{NQ}(q) &= C_1C_2(C_1(S_{11} - S_{12}) - C_2(S_{22} - S_{12})) \end{aligned}$$

These correlation factors are represented on Figures 5 and 6. We have also reported on Figure 7 the corresponding functions for molten CsCl.[9]

Using Fourier transform, the mass-mass correlation function $S_{NN}(q)$ gives the mean distribution $g_m(r)$, and no more informations can be deduced from these three curves *but it is striking to notice that* $S_{NQ}(q)$ *is not equal to zero as for CsCl.* In fact, a little peak appears around 1,90 Å^{-1} and is due to the difference between S_{11} and S_{22} *showing clearly the unsymmetrical behaviour of the two ions.*

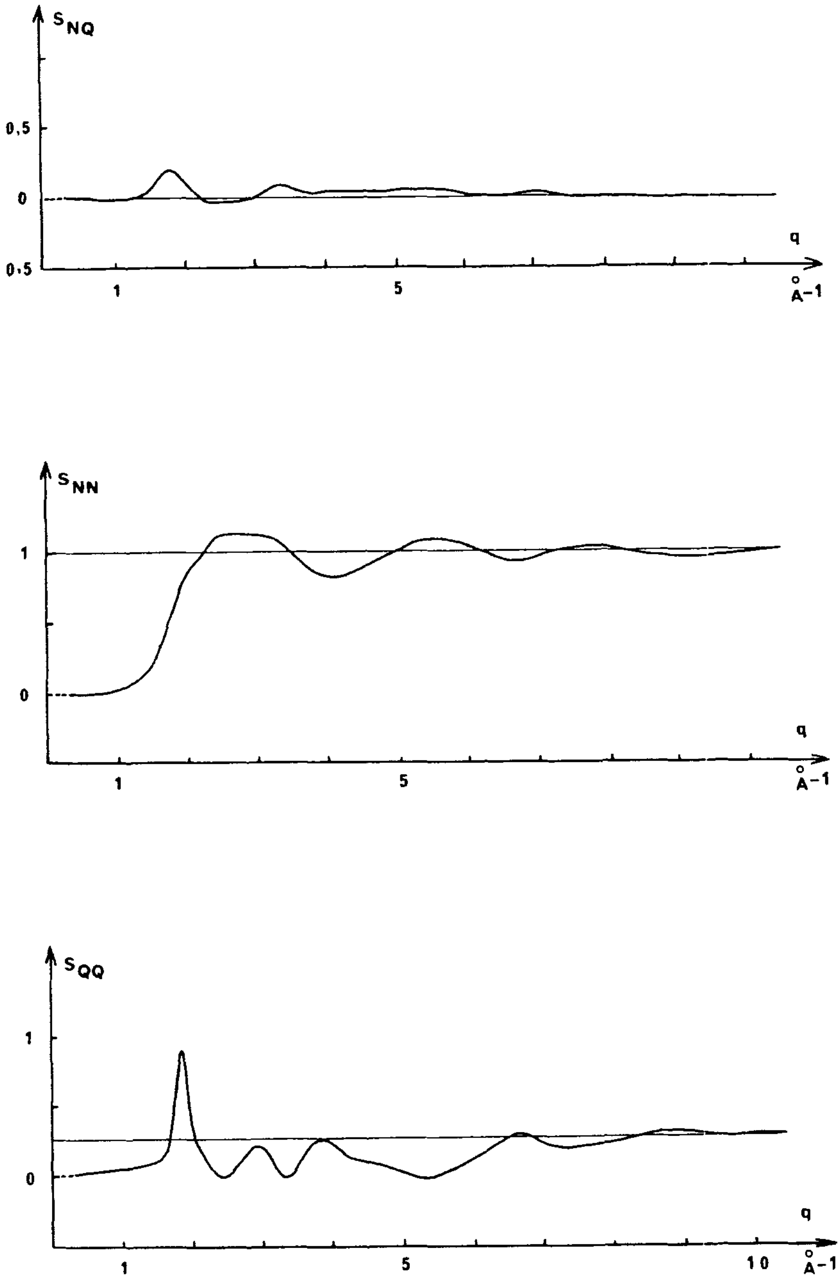

FIGURE 5 The mass-charge, mass-mass and charge-charge correlation functions for AgCl at 510° C.

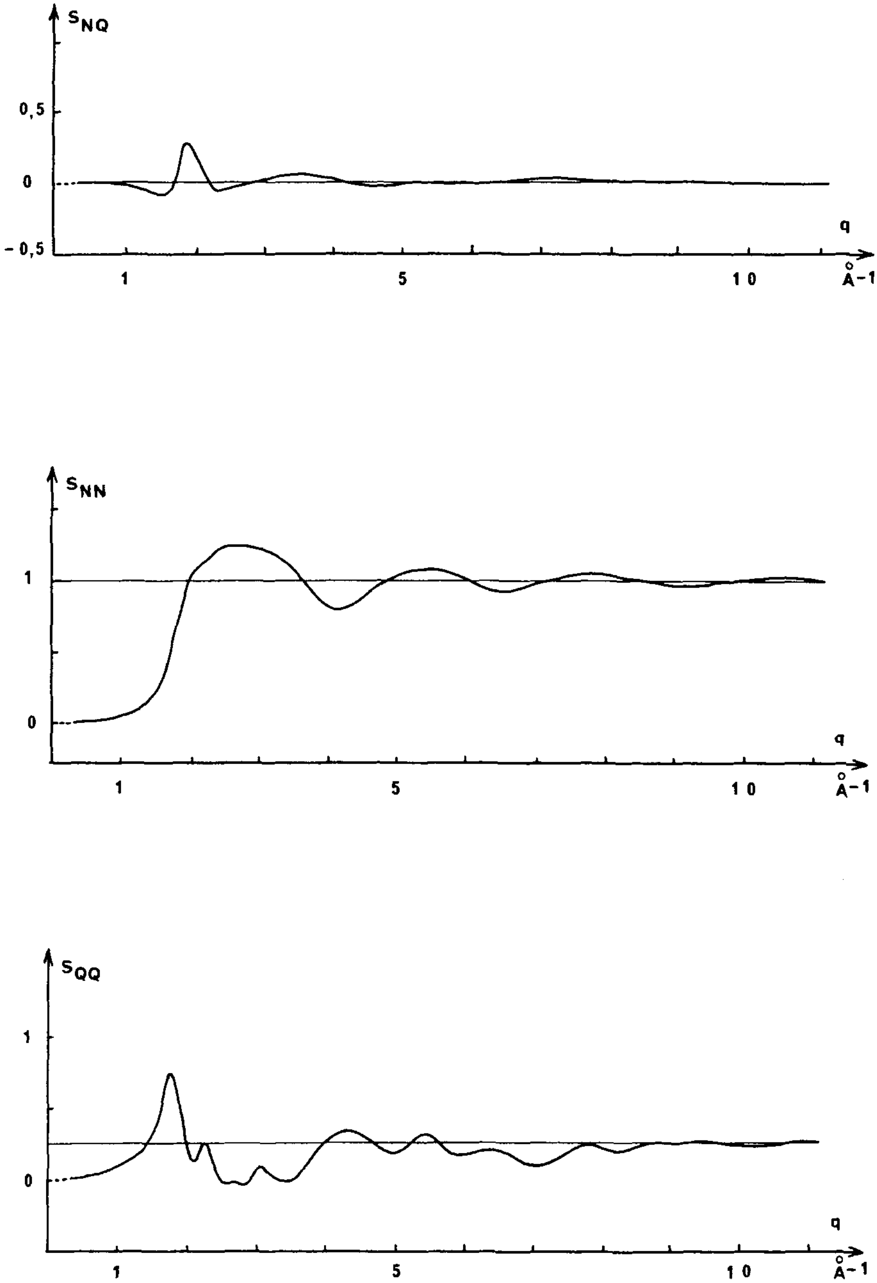

FIGURE 6 The mass-charge, mass-mass and charge-charge correlation functions for AgCl at 850° C.

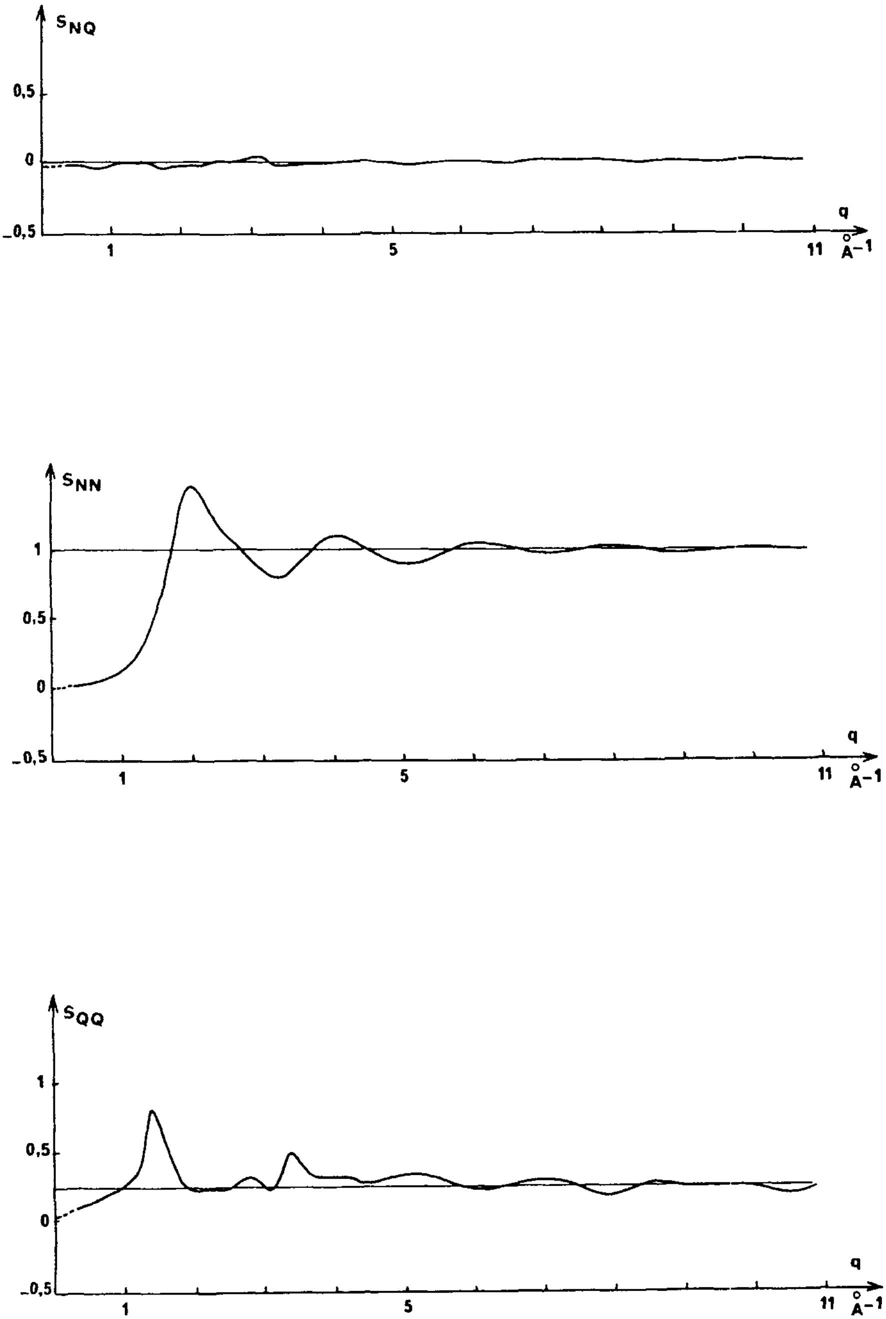

FIGURE 7 The mass-charge, mass-mass and charge-charge correlation functions for CsCl at 720° C.

4 DISTRIBUTION FUNCTIONS

The three pair distribution functions $g_{ij}(r)$ are calculated from the partial structure factors, by the relation

$$g_{ij}(r) = 1 + \frac{1}{2\pi^2 r g_0} \int_0^\infty q[S_{ij}(q) - 1] \sin qr dq \qquad (2)$$

where g_0 is the atomic density r the interatomic distance.

a The mean and total distribution functions

The mean distribution function $g_m(r)$ is related to the partial distribution functions by the equation

$$g_m(r) = 0.5(0.5g_{cc} + 0.5g_{mm} + g_{cm})$$

It is then interesting to compare it to the total distribution function $G_T^X(r)$ obtained by Fourier transform of the total scattering factors $S_T^X(q)$ (X is the isotopic enrichment X = 35, N, 37). G_T^N (from the natural compound) is the only information we can get if only one diffraction data is available on the ionic compound (RX or neutron).[12,13] We have drawn on Figures 8–9 the curves $G_T^N(r)$ and $g_m(r)$ obtained on molten AgCl at 510° C.

The total distribution functions are characterised *by a main peak at 2.60 Å which corresponds to the first equilibrium distance of unlike ions. The second peak of* $G_T^N(r)$ *or* $g_m(r)$ *at 3.85 Å which would be attributed to the first equilibrium distance of like ions does not correspond to this distance but is the second anion-cation equilibrium distance, as shown below.*

The shortest approach distance can also be evaluated from G_T^N *or* $g_m(r)$. This value is given either by the crossing of G_T^N with the line $1 - \frac{(c_1b_1 + c_2b_2)^2}{c_1b_1^2 + c_2b_2^2}$ or when $g_m(r)$ becomes equal to zero. We find that the minimum cation-anion distance is 1.80 Å at 510°C and 1.65 Å at 850° C.

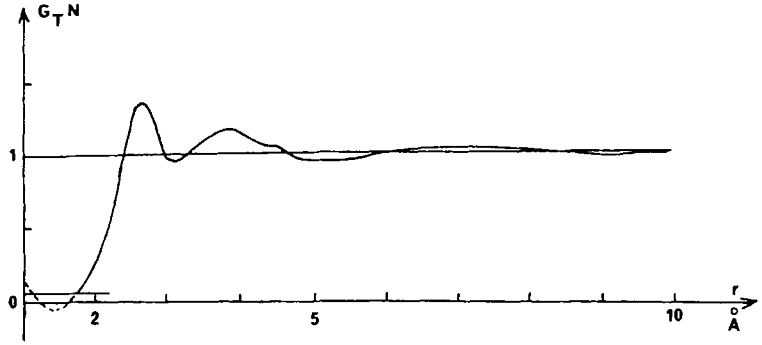

FIGURE 8 Total distribution function for natural AgCl.

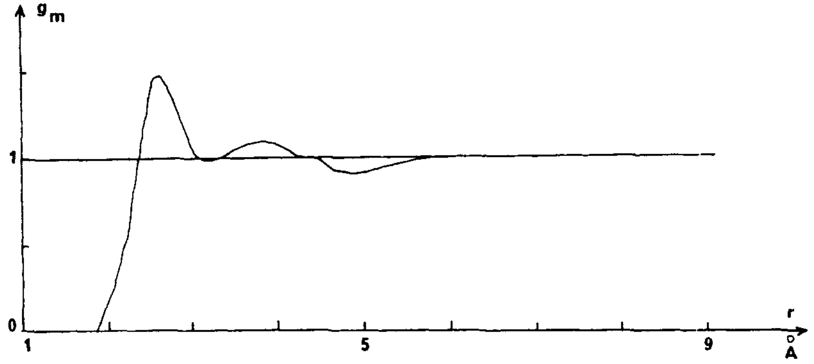

FIGURE 9 Mean distribution function for AgCl.

The plot of the mean radial distribution function $4\pi r^2 g_m g_0$ shows a second peak around 3.90 Å.

Although this peak does not correspond at all to the + + or – – equilibrium distance, it is interesting to notice that its value (3.90 Å) is the most suitable so that this liquid verify the extension of the Lindemann law for hard sphères to molten salt, recently proposed by J. J. Van Loef[15,16]. The Lindemann law for hard spheres gives the hard core diameter deduced from viscosity measurements versus density.[14,15] As an another illustration of this law, J. L. Van Loef proposes a relation ship between the hard core value and the nearest neighbour distance in monoatomic liquids.

We report on the following table the value of the ratio $\frac{\sigma}{r\,\mathrm{max}}$ where r_{max} is given either by the position of the main distances between like ions (first peak of $g_{++}(r)$ or $g_{--}(r)$), or by the position of the second maximum of the mean radial distribution function.

TABLE III

Extension of the Lindemann law to molten salts

Salt	σ(Å)	$\sigma^3/\mathrm{Vm}(10^{-24})$	r_{max} (from g^{++}) (Å)	$\frac{\sigma}{r_{max}}$	r_{max} (from $4\pi r^2 g_0 g_m(r)$) (Å)	$\frac{\sigma}{r_{max}}$
KCl	4.21	1.52	4.90	0.86	4.7	0.895
CsCl	4.51		3.85	1.17	5.0	0.905
AgCl	3.58	1.55	3.40	1.05	3.90	0.92

$\overline{\frac{\sigma^3}{V_m}} = 1.54$ $\overline{\frac{\sigma}{r_{max}}} = 0.907$

$\frac{\sigma^3}{V_m}$ is a direct measure of the packing fraction of the molten salt near T_m; the value of the second maximum of the mean radial distribution function corresponds roughly to the mean largest structured entity we can find in the liquid beyond this distance the behaviour of $g_m(r)$ being almost flat. It appears of interest to point out that it is this distance which can verify the extension of the Lindemann law to molten salts.

b Partial distribution functions

The aim of this study is to analyse the partial distribution functions which give a picture of the microscopic local structure of the compound under investigation. These functions are shown on Figures 10 and 11 for AgCl at 510° C and 850° C. Three kinds of information can be deduced: the shortest approach distance, the interatomic distance and the coordination number. These data are reported on Table IV with the corresponding ones for solid AgCl near melting point

TABLE IV

Distribution functions characteristics for AgCl at 510° C and 850° C

	g_{cm}				g_{mm}				g_{cc}			
Compound	d_{cm}	r_{max}	r_{min}	n_{cm}	d_{mm}	r_{max}	r_{min}	r_{mm}	d_{cc}	r_{max}	r_{min}	n_{cc}
AgCl 510° C	1.80	2.60	3.40	4.3	2.50	3.40	3.85	3.1	2.60			
AgCl 850° C	1.65	2.55	3.10	2.7	2.65	3.15	3.85	4.1	2.70	3.15	3.70	2.7
AgCl solide p.f.		2.97		6		4.07		12		4.07		12

d_{cm}, d_{mm}, d_{cc}: closest approach distance
r_{max}: position of the first maximum
r_{min}: position of the first minimum
n_{mm}, n_{cc}, n_{cm}: coordinance number for metal-metal, chlorine-chlorine and metal-chlorine distributions They are calculated with: $d_{ij} < r < r_{min}$ i,j = m,c

The most important characteristics of these results are:

1 *At* 510° C

A strong reduction of the first anion-cation equilibrium distance, compared to the solid one and to liquid KCl and CsCl.

A decrease of the coordination number from 6 in the solid to 4 in the liquid.

A strong structural characteristic of the Ag^+ *distribution which leads to a silver* coordination number of about 3.

A flat distribution (but not equal to 1) *for the anions between 3.40 Å and 4.80 Å.*

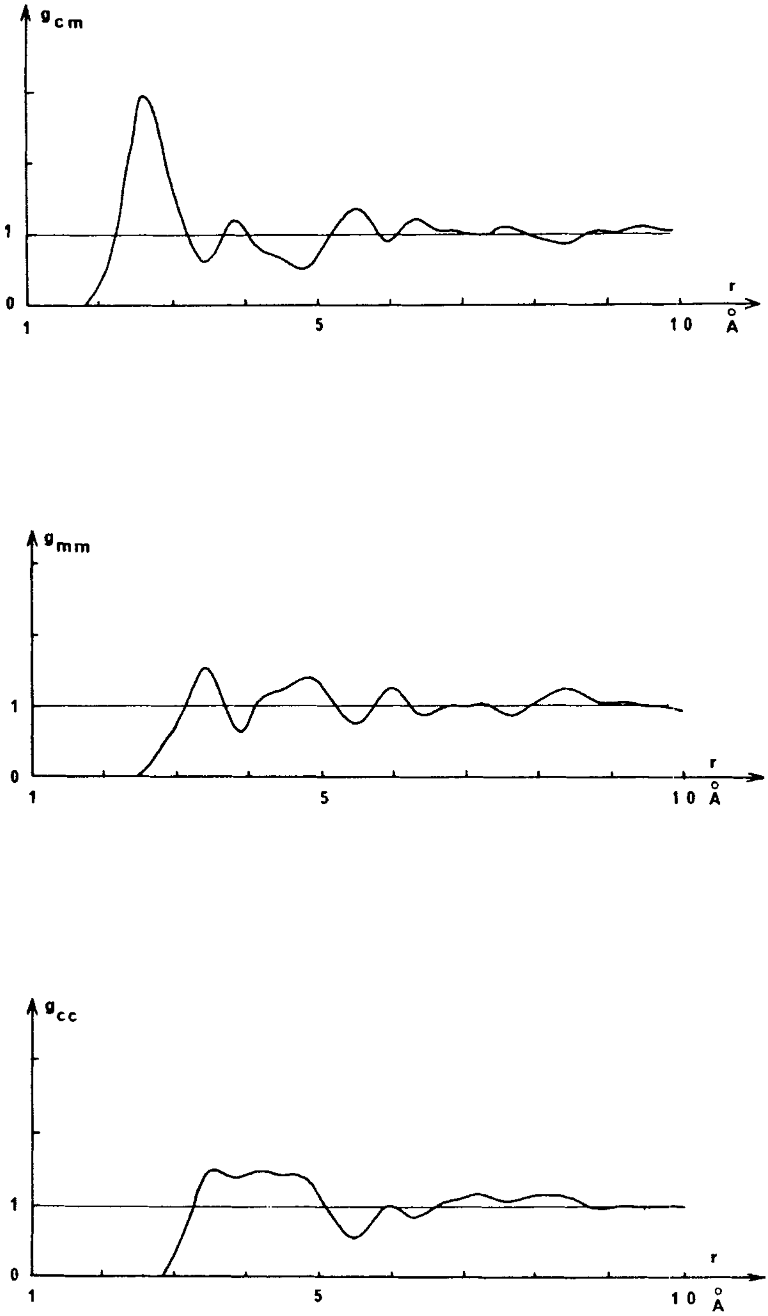

FIGURE 10 The partial radial distribution functions for liquid AgCl at 510°C.

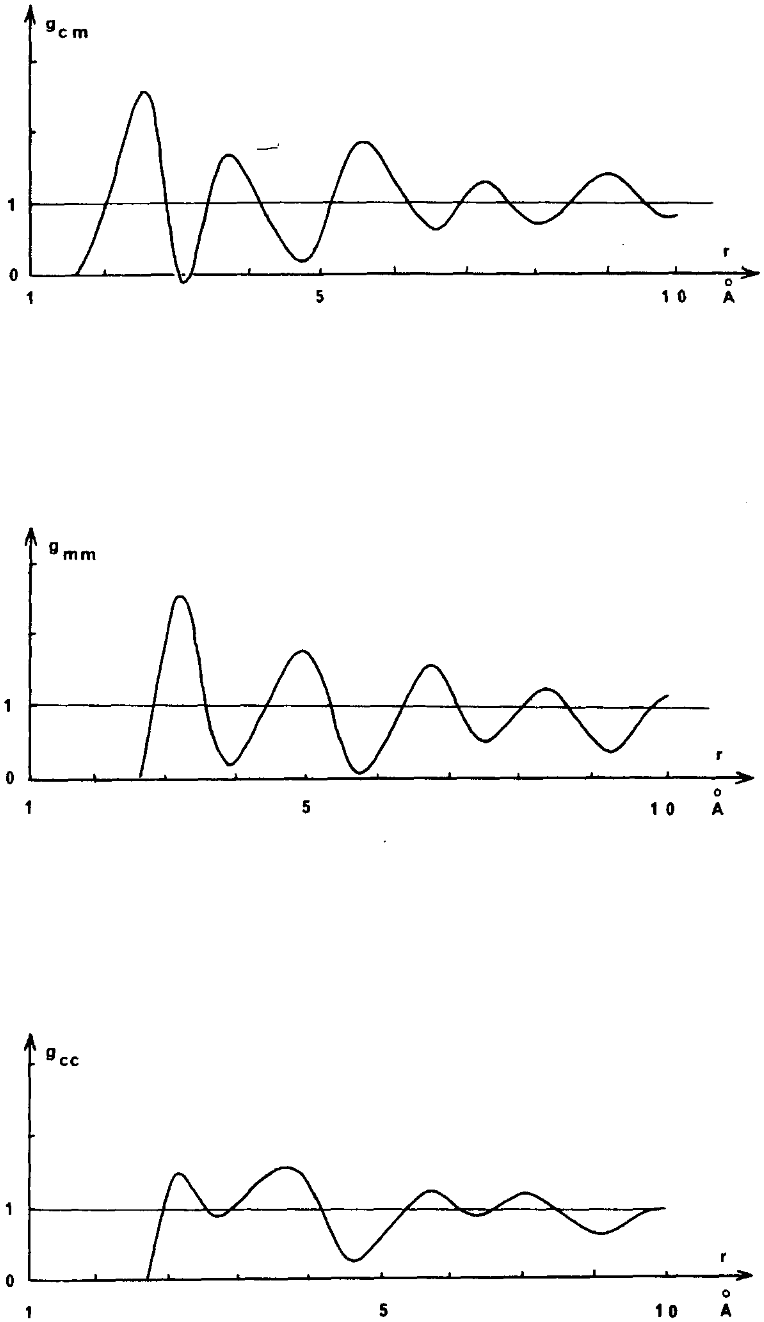

FIGURE 11 The partial radial distribution functions for liquid AgCl at 850° C.

It is of some interest to remark that the coordination number corresponding to the two first peaks of g_{mm} and to the wide peak of g_{cc} is 12 as for the solid.

2 *At* 850° C

The decrease of the main equilibrium distances and of the first coordination number which becomes about 2.7.

A symmetrisation of the distribution of like ions but an increase of the Ag^+ structuration.

5 RESULTS, ANALYSIS, DISCUSSION

Our results concerning the partial structure (which are not influenced by a Fourier transform), the pair distribution functions and the modification with temperature lead us to the conclusion that *the covalent bond in AgCl is strongly increased by melting. This "quasi-molecular like" structure of liquid AgCl is clearly illustrated by*:

The persistent oscillatory character of the intensity curves at large momentum transfer.

The great reduction of the shortest approach distance and the cation-anion distance by melting.

The decrease of the coordination number in the first coordination shell.

The important Ag^+ structural features at 850° C.

The structural evolution we have observed when the temperature is increased is in agreement with mass spectrometry measurements[17] which show the existence in the vapor of a trimer species.

Considering the analogy between the properties of molten AgCl and CuCl it is then interesting to take into account the mass spectrometry and electronic diffraction results published on CuCl[18,19] vapor. These authors point out that the CuCl vapor structure consists essentially in a trimer, the structure of which can be described by a six-ring of equal sides. The tops of the ring are occupied by Cu or Cl and the angles Cl–Cu–Cl and Cu–Cl–Cu are respectively about 150° and 90°.

Our results showing the decrease of the coordination numbers from the melting point to high temperature can be correlated with the coordination number 2 in the vapor.

At 510° C, our results indicate: for the first coordination number about 4 chlorine ions around a central silver ion at a mean distance of 2.60 Å, for the second coordination numbers 3 silver at 3.40 Å and about 9 (delocalised) at a mean position of 4.80 Å. It is thus possible built a local structure model which can give a six-ring structure in the vapor phase.

In this structure (Figure 12), the tetradral arrangement for 4 chlorine

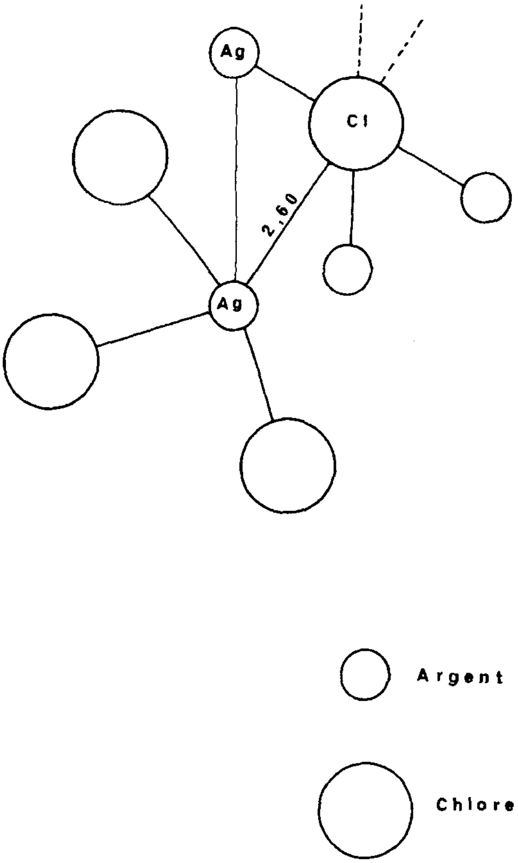

FIGURE 12 Structural model proposed for AgCl at 510° C.

around a central silver is the one defined by a sp^3 silver hybridation. A chlorine has then 3 free orbitals each of them having the possibility of being twice bonded. It would be therefore possible to surround this chlorine by 6 silver, the Ag–Cl–Ag angle being 90°; we shall assume that only 4 bonds are effective.

The coordination of chlorine is 4: the Ag^+ central, and three other Ag^+ placed in the plane perpendicular to the bond between the central ion and one chlorine.

According to this local model, the central ion is surrounded by 12 Ag^+ at the distance $2.60\sqrt{2} = 3.64$ Å. Our measurements show that these 12 silvers are shared into two groups: one with 3 Ag^+ situated at a mean distance of 3.40 Å; and the second with 9 silver distributed between 3.85

and 5.50 Å. This can be explained if we suppose that the tetrahedra are not regular but slightly stretched out. Then it presents three identical faces bigger than the fourth and which are in a privileged position for 3 silvers.

CONCLUSION

The structural results we have just described allow a better understanding of the local structure of molten silver chloride. We have particularly pointed out that melting induces a strong increase of the AgCl covalent bond. This feature is illustrated by:

A reduction from 2.97 Å in the solid to 2.60 Å in the liquid of the mean anion-cation distance.

A reduction from 6 to 4 of the first nearer neighbours of molten AgCl at 510°C.

At higher temperatures this covalent bond is increased and the reduction to about 2.7 of the first coordination number is an illustration.

Our experiments, however, lead to different results from those of Page and Mika[20] on a compound having similar physical properties: CuCl. In contrast to the results obtained by these authors, the structure factor and the Ag–Ag distribution function that we propose are strongly structured whereas the Cu–Cu ones are almost featureless. (The authors have assumed the possibility of the formation of partially covalent compounds which they write as $(Cu^+Cl_n^-)^{(n-1)-}$, which could give a resultant excess of Cu^+ ions approaching the idea of a plasma.)

In a recent publication, Powles[21] reinterpretes the partial structure factors and the partial distribution function, data obtained by Page and Mika in term of a liquid consisting of CuCl molecules. So, the existence of free Cu^+ is not necessary although not excluded.

Our experimental structure factors on AgCl present differences with CuCl ones. The anlysis along a molecular model looks inconsistent with the data on vapor phase and may be less likely as the proposed model in which the regular local arrangement for anions and cations still expresses the strong effect of ionicity.

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