

## Brief Reports

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### Continuous pressure-induced structural transition in the noble-metal halide melts

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The reduction of the charge of the species in molten salts, including the complete removal of the Coulomb interaction, appears to have the same effect as an increase in the pressure on these systems. This observation leads to the prediction that a continuous pressure-induced structural change is to be found in the noble-metal halide melts at much lower pressures than those used to induce a similar transition in the alkali halide melts.

Some years ago, Marvin Ross and co-workers<sup>1-3</sup> examined the evidence for a continuous pressure-induced transition in the alkali halide melts, namely, a transition from the structure of a simple molten salt to that of a rare gas-like equimolar atomic liquid binary mixture. Their work followed extensive experimental, and a few theoretical, studies of these melts when subjected to high pressures.<sup>4</sup> In particular, Ross and Rogers<sup>2</sup> carried out extensive calculations for molten CsI, for which the melting curve was estimated by exploiting the fact that CsI is isoelectronic with Xe. These calculations clearly establish how the structural reordering of this melt takes place. In spite of differences of detail between the structure of molten CsI and other alkali halide melts,<sup>5</sup> the study of Ross and Rogers incorporated all the important features that characterize the changes experienced by all the alkali halide melts along the melting curve.

More recently, we presented the results of computer simulations for molten "NaCl" and "CuCl".<sup>6</sup> The quotation marks indicate that, besides the simulation of the actual systems, we also considered the structural and dynamical changes produced by varying the degree of charge transfer  $|Z|$ . Our work addressed the question of the interplay between charge ordering and size effects of two classes of molten salts of which the above may be regarded as archetypes: NaCl of the alkali halides, CuCl of the noble-metal halides. The molecular dynamics (MD) simulations studied the effects on the structure and ionic transport properties of the two systems resulting from reducing the charge on the species, including the complete removal of the Coulomb interaction. CuCl melts from

what may be regarded as a superionic phase, and it is long known that it exhibits some homopolar binding<sup>7</sup> which we model by taking a partial charge  $|Z|=0.501$ . Moreover, there is a larger size difference between the ionic radii,  $\sigma_{\omega}$ , in CuCl than in NaCl ( $\sigma_M/\sigma_X=0.36$  in CuCl and  $\sigma_M/\sigma_X=0.74$  in NaCl;  $M=Na, Cu, X=Cl$ ). Our results show that there are marked differences in the structure and ionic transport properties not only between the actual systems but also when the Coulomb interaction is removed (the case  $|Z|=0$ ). We noted that there appear to be two competing lengths, the ionic radii and the mean ion sphere radius  $a=(3/4\pi\rho)^{1/3}$ , with  $\rho$  denoting the ionic density. In the case of CuCl,  $\sigma_{Cl}>a$  and, as a result, its structure is largely insensitive to the Coulomb interaction; it appears as if the Cl ions are always affected by the repulsive wall rather than the Coulomb repulsion in determining their partial structure factor. Hence the changes resulting from reducing the charges in CuCl are noted in the partial structure factor of the Cu ions and in the cross correlation. In NaCl,  $\sigma_{Cl}, \sigma_{Na}<a$ , and all three partials change significantly as the charge is reduced to zero.

In a private communication Ross brought to our attention the possible connection between their study,<sup>2</sup> on the effect of compression on the alkali halide melts, and ours,<sup>6</sup> on the effects of reducing the ion charge. Although our work was carried out at constant density, the similarity between their results for the partial pair distribution functions  $g_{ij}(r)$  for molten CsI under compression, and ours, with partial or no charge for molten NaCl, appears to indicate that the increase in pressure along the

TABLE I. Results obtained for “NaCl”, “CuCl”, “CuBr”, and “AgI” systems.

System	$E( Z )/E_0$	$P( Z )/P_0$	$n_{++}$ ( $R_{++}$ ) (Å)	$n_{--}$ ( $R_{--}$ ) (Å)	$n_{+-}$ ( $R_{+-}$ ) (Å)	
	$ Z_0 1$	1	1	14.1 (6.3)	14.1 (6.3)	4.8 (4.2)
NaCl	0.32	0.012	30	3.8 (4.4)	6.6 (5.0)	7 (4.8)
	$ Z $ 0.	-0.12	40	5.3 (4.4)	7.2 (5.0)	5.8 (4.7)
CuCl	$ Z_0 0.501$	1	1	13.4 (5.5)	13.5 (5.5)	4.3 (3.6)
	$ Z $ 0.	-0.44	8	43.5 (7.7)	12. (5.2)	6.1 (4.4)
CuBr	$ Z_0 0.483$	1	1	13.5 (5.8)	13.5 (5.8)	4 (4.5)
	$ Z $ 0.	-0.5	7.5	40. (7.9)	12. (5.5)	6.3 (4.6)
AgI	$ Z_0 0.6$	1	1	14.8 (6.4)	13.7 (6.2)	5 (4.3)
	$ Z $ 0.	-0.66	1.5	53. (8.8)	12.8 (6.1)	2.3 (4.1)

melting line has the effect of reducing the ion charge.

The purpose of this paper is to report the results of calculations for the pressure  $P$ , obtained from our MD simulations, which show that indeed the change from a fully to a partially ionized “NaCl” melt results in an increase of  $P$  in the system. Moreover, and assuming the above connection holds for the noble-metal halides as well, we suggest that a similar pressure-induced structural transition in the noble-metal halides should be expected to be found at lower pressures than in the alkali halides.

For reasons discussed below, the results presented in this paper have meaning only in a qualitative sense. However, we submit that they establish the correct trends to be expected from more exacting calculations.

We have calculated the equation of state for “NaCl” and the noble-metal halides “CuCl”, “CuBr”, and “AgI” using the relation

$$\frac{P}{\rho K_B T} = 1 - \frac{4\pi\rho}{6} \sum_{ij} \int_0^\infty r^3 \frac{\delta\phi_{ij}(r)}{\delta r} g_{ij}(r) dr, \quad (1)$$

where the potentials  $\phi_{ij}(r)$  used in the calculations are as discussed in Refs. 6 and 8.

The calculation of Eq. (1) is, in all cases, very sensitive to errors, given that it sums over areas of similar magnitude and opposite signs. The difficulty in our case is compounded by both the long-range Coulomb interaction, and that the information we have of the  $g_{ij}(r)$  is restricted to the size of the simulation box. We have estimated the pressure by taking  $g_{ij}(r)$  within the simulation box in such a way that the oscillation completes a full loop. Beyond this, we have assumed  $g_{ij}(r)=1$ . This assumption introduces significant systematic errors in our calculations for which we cannot give a precise estimate. However, as a guide, it yields pressures near the triple point of the actual systems of a few kbars instead of a few bars. Therefore, the results are presented in the form of the ratio  $P(|Z|)/P_0$ , where  $P_0$  is the pressure of the actual system near the triple point, and  $P(|Z|)$  the value of the pressure for a given choice of the ion charge  $|Z|$ . For the same reasons, we are not including the values of the configurational contribution to the free energies (typically  $-60$  kcal/mol for the “superionic” melts, and  $+30$  kcal/mol for the  $|Z|=0$  cases). We include the results

for the energies as the ratio  $E(|Z|)/E_0$ , where  $E_0$  is the configurational free energy of the actual system near the triple point.

In the case of the partially ionized “NaCl” melt, we report the results for  $|Z|=0.32$  instead of the value  $|Z|=0.5$  used in Ref. 6. The reason is that for  $|Z|=0.5$ , we could not take a full oscillatory loop within the simulation box for all three  $g_{ij}(r)$ , whereas the unpublished results for  $|Z|=0.32$  made this possible. The results obtained are summarized in Table I.

We note that the changes in pressure for CuCl and CuBr are about the same, but much smaller than in NaCl. This is to be expected as both the structure and ionic transport properties for CuCl and CuBr are very similar.<sup>8</sup> The results for molten AgI contain the largest errors but, if its structure and ionic transport properties are a useful guide, we suggest it reflects the correct trend.

The configurational free energy in “NaCl” goes down as the charge is reduced to  $|Z|=0.32$ , as a result of shallower minima in the cation-anion interaction. In all cases, the energies change sign for the  $|Z|=0$  because the “neutral” systems are only probing the repulsive walls.

In Table I, we have also included the coordination numbers  $n_{ij}$  ( $ij=+, -$ ). These were evaluated by estimating the area underneath the first peak of  $g_{ij}(r)$ , from the point where  $g_{ij}(r=R_0)=0$  to the estimated position of the first minimum, i.e.,  $g_{ij}(r=R_{ij})$ . The values of  $R_{ij}$  are listed in brackets next to the coordination numbers.

The values of  $n_{ij}$  for the actual NaCl system are in good agreement with other computer simulations and experimental results.<sup>9</sup> As the charge is reduced, the coordination numbers in “NaCl” go down in value. This is a consequence of working at constant density, namely, the thermodynamic state of the system is unlikely to be along the melting line.

The results for the noble-metal halide melts are very different. The anion-anion coordination numbers,  $n_{--}$ , do not change significantly on withdrawing the charges, because the anions are not affected by the Coulomb repulsion.<sup>4</sup> On the other hand, the cation-cation coordination numbers,  $n_{++}$ , increase dramatically, as a consequence of the size effect.<sup>4</sup> Actually, the first peak of  $g_{++}(r)$  samples the average size of the cluster enclosed in the cage formed by the anions. The  $n_{+-}$  coordination number in

“CuCl” and “CuBr” increases to about 6 for  $|Z|=0$ . We believe that the decrease of  $n_{+-}$  “AgI” is a consequence of the large errors involved in its estimation, and we expect that a computer simulation with a large number of particles will bring this value up in line with those obtained for the other superionic melts.

To our knowledge, experimental results for the noble-metal halide melts under pressure have not been reported in the literature. This paper suggests that the pressure-induced structural transition in these systems is likely to take place at pressures that are more easily accessible

than those needed for the alkali halide melts.

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