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Computer modelling of molten halides using diffraction data

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The aim of this paper is the construction of models of systems with ionic and ionic-covalent bonds (molten salts) using experimental diffraction data and the calculation of their structure and thermodynamic and transport properties. Modelling was performed using algorithm BELION, in which the non-coulomb part of interaction potential between ions in the model was determined by the method of iterative simulation which targeted agreement between calculated and experimental partial pair correlation functions (PPCFs). The ionic charges in salts, which can be fractional, were determined by minimization of internal energy.

In this paper, the algorithm BELION is applied for chlorides of alkaline-earth metals. Pair potentials, PPCFs, atomization energies, self-diffusion coefficients and electric conductivity are calculated. The charge of alkaline-earth metals was in the range of 2.0-2.1, slightly increasing from Mg to Ba. Partial pair correlation functions and atomization energies of models agree well with experimental data for $MgCl_2$, $SrCl_2$ and $BaCl_2$.

Keywords: molten salt, molecular dynamics, partial pair correlation function, ionic charge, atomization energy, diffusion.

Introduction

Partial structure factors and pair correlation functions were established for a number of molten oxides, halides, chlorides, fluorides and others ionic melts by anomalous X-ray scattering, extended X-ray absorption fine structure (EXAFS), neutron diffraction with isotope contrast and other methods[1-5]. These data are used for finding ionic potentials and the construction of atomic models of disordered ionic systems[6].

Omote *et al.*[7] and Waseda *et al.*[8] developed an iterative method for calculation of effective ionic potentials in molten salts on the basis of the hypernetted chain approximation. It was applied for liquid NaCl[8,9], CuBr [9,10], AgBr, CuI and RbBr[10].

An iterative algorithm BELION for modelling melts with ionic and ionic-covalent bonds using molecular dynamics simulation was suggested[11]. This algorithm is similar to the two-component Schommers algorithm[12]. In BELION algorithm, the ionic *i-j* potential is presented as:

$$u_{ij}(r) = \frac{Z_i Z_j e^2}{r} + \varphi_{ij}(r) \qquad [1]$$

where Z_i is a charge of an ion *i*, *r* is a distance between ions *i* and *j*, $\varphi_{ij}(r)$ is a short-range (non-coulomb) part of the ionic potential. $\varphi_{ij}(r)$ is determined using experimental structural characteristics. If the partial pair correlation function (PPCF), determined experimentally, is $g^0_{ij}(r)$, and the model's PPCF calculated with potential $\varphi_{ij}(r)$ is $g_{ij}(r)$, then the relationship between pair potentials $\varphi'_{ij}(r)$ (new approximation) and $\varphi_{ij}(r)$ (previous approximation) can be presented in the form:

$$\varphi'_{ij}(r) = \varphi_{ij}(r) + kT^* \ln \frac{g_{ij}(r)}{g^o_{ij}(r)} \qquad [2]$$

T* in this equation is an effective temperature (generally tenths of the model's temperature) adjusted to provide the good convergence of the results to the asymptotic limit. In the next iteration, the PPCF is calculated using $\varphi'_{ij}(r)$ found in the previous iteration; the iteration procedure is completed when the calculated and experimental PPCFs become practically indistinguishable.

For realization of the BELION algorithm for construction of atomic models of ionic melts, the molecular dynamics method (MD) was used[11]. Coulomb potential was calculated in the Ewald-Hansen approximation with periodic boundary conditions. Non-coulomb part $\varphi_{ij}(r)$ was adjusted in such a way as to provide agreement between calculated and diffraction PPCF histograms. Discrepancy between the calculated and experimental PPCFs was characterized by a discrepancy parameter defined elsewhere[13]; when this parameter was below 0.01, $g^o(r)$ and $g(r)$ were practically indistinguishable. Algorithm BELION was used to model liquid NaCl, FeO, CuBr[11], RbBr, CuCl, CuI, AgBr[13,14], and $ZnCl_2$[15].

The models were validated by comparing calculated atomization energy with experimental data. Usually, the energy of a system in the molecular dynamics simulation is

calculated relative to free motionless ions. Then the atomization energy can be found by the formula:

$$E_{at} = -E_{ion} - U_{trans} + E_{kin} \quad [3]$$

where E_{ion} is the energy of a liquid salt with respect to the system of isolated ions, U_{trans} is the energy of transformation of isolated neutral atoms to ions with charges $\pm z_i$, E_{kin} is the kinetic energy, equal to $3RT$ per mole of a compound MCl_2.

The ion charge can be an integer or fractional number. Experimental ionization energy is given only for integer Z; in this work, the ionization potential for a metallic cation was approximated by the following function of Z:

$$E(M) = Z\left(a + bc^{z}\right) \quad [4]$$

where parameters a, b and c are found using the first three ionization potentials.

The ionic charges were calculated using the variation principle of minimization of energy (maximization of atomization energy) of the system[11,13-15]. For salts examined, the following charges were obtained:

Salt	NaCl	RbBr	CuCl	CuBr	CuI	AgBr	$ZnCl_2$
Cation charge	1.0	1.0	1.20	1.48	1.37	1.15	2.0

Alkalies and zinc in salts have a charge in accordance with the periodic table, while the charge of copper and silver is above +1. This can be explained by the energy of the coulomb interaction, which decreases with increasing charge, and relatively small second ionization potentials of Ag and Cu cations.

This paper focuses on chlorides of alkaline-earth metals. Their structure was studied[2-5,16] by the neutron diffraction with isotope contrast. PPCFs obtained in works[2-5,16] are shown in Figures 1–4 by broken curves.

M–M and Cl–Cl distances in molten MCl_2 are close to those in crystal chloride. Coordination number for pairs M-Cl steadily increases from $MgCl_2$ to $BaCl_2$, and equal to 4.3, 5.3, 6.9 and 6.4 for $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$ respectively[17]. In accordance with work[2], this increase in coordination number can be attributed to the increasing ion size. Interaction between cations of small size and anions in addition to coulomb potential includes energy of polarization of an anion by a cation and other contributions[17,18]. To explain small distances r(M-M) and r(Cl-Cl) in liquid $ZnCl_2$, $MgCl_2$ and $CaCl_2$, authors[2,17,18] suggested to take into account covalent bonds.

This work reports results of computer modelling of chlorides of alkaline-earth metals using the algorithm BELION and experimental diffraction data

In all calculations, a non-coulomb potential was cut at 9.51Å.

Modelling of liquid $MgCl_2$ at 998 K

The structure of liquid magnesium dichloride at 998 K was experimentally studied[2] by the method of neutron diffraction using chlorine isotopes ^{35}Cl and ^{37}Cl. PPCFs of $MgCl_2$ are shown in Figure 1. Mg-Mg and Cl-Cl distances (3.81 п 3.56 Å correspondingly) are quite close, although coulomb repulsion of magnesium cations having a charge +2 is much stronger than repulsion between chlorine anions with a charge -1. Atomization energy for $MgCl_2$ is 988.2 kJ/mol.

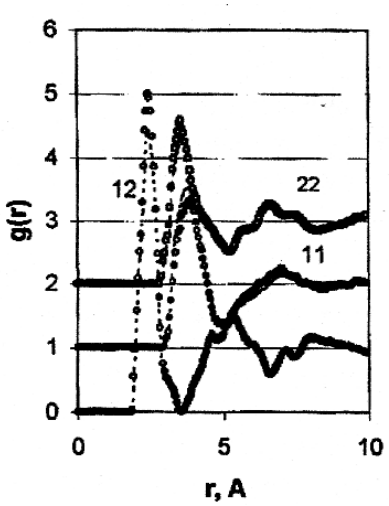

Figure 1. PPCFs of MgC_2 at 998 K; broken lines-experiment, markers-model

PPCFs for molten salts are determined by Fourier transformation of experimental structure factors obtained *in situ* at elevated temperatures. The error in measurement of PPCFs is difficult to estimate. Waseda and Toguri[1] assessed the error in measurement of a distance between closest neighbours 0.001 nm, and the error in measurement of coordination number calculated from PPCFs of 0.2. An accuracy of PPCFs can be assessed by the Reverse Monte-Carlo method. The calculated PPCF for the Cl-Cl pair agreed well with the experimental curve at about all Cl-Cl distances but the vicinity of the first minimum. Deviations from experimental data were observed for the Mg-Mg PPCF in the area of the first peak, and for Mg-Cl PPCF in the area of the first minimum and second maximum. The discrepancy parameters were 0.069, 0.048 and 0.024 for pairs Mg-Mg, Mg-Cl and Cl-Cl respectively (in the radius of 9.51 Å). This means that diffraction PPCFs for Mg-Mg and Mg-Cl cannot be reproduced with high accuracy.

MD models containing 747 or 1968 ions in the basic cube were constructed at 998 K and constant volume using the algorithm BELION[11]. The length of the basic cube edge at this temperature was 28.647 Å for N = 747 and 39.565 Å for N = 1968, calculated from the salt density of 0.0197 at/Å^3[16]. The Verlet algorithm was used to calculate particle

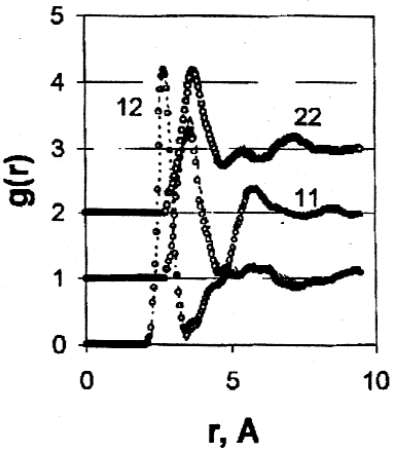

Figure 2. PPCFs of $CaC1_2$ at 1093 K; broken lines-experiment, markers-model

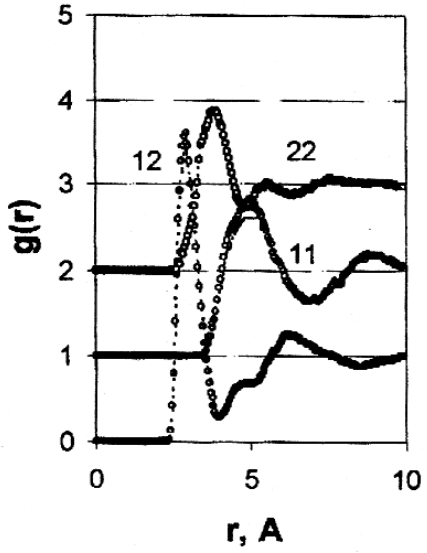

Figure 3. PPCFs of $SrC1_2$ at 1198 K; broken lines-experiment, markers-model

positions at each step of the simulation. Each iteration of the algorithm BELION included 1 000 steps with a time increment of $8.144 \cdot 10^{-16}$s. The first MD model was constructed for the charge of magnesium cation equal to +2. In this case, 70 iterations of the algorithm BELION were needed for the construction of the model.

The MD models were also constructed for the magnesium charge varied between +1.5 and +2.2. These models contained 747 ions. The atomization energy, calculated by Equation [3] for magnesium charge between +1.9 and +2.2 was as follows:

Z_{Mg}	1.9	2.0	2.1	2.2
E_{at}, kJ/mol	961.0	977.3	979.2	930.4

The maximum of the atomization energy and, therefore, minimum of the internal energy correspond to the magnesium charge near +2.05. Taking into account an error in calculation of ionization potential for magnesium and electron affinity for Cl, the magnesium charge can be assumed to be +2.0.

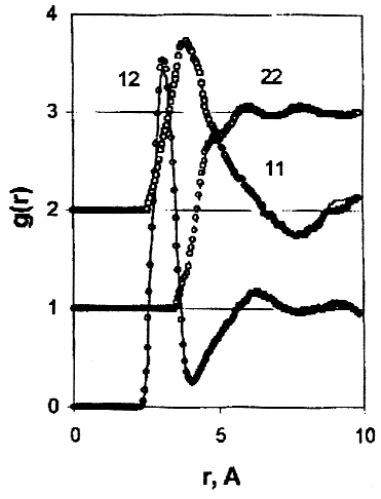

Figure 4. PPCF's of $BaCI_2$ at 1298 K; broken lines-experiment, markers-model

After this, the model containing 1 968 ions was constructed with the magnesium charge of +2.0. PPCFs of the MD model with Z_{Mg}=+2.0 are shown in Figure 1. In general, they agree well with experimental PPCFs, although, as expected, the discrepancy parameters for the model's PPCFs were higher than for the PPCFs obtained by the Reverse Monte-Carlo method. Obviously, the MD simulation with the algorithm BELION cannot provide better agreement with experimental data than the Reverse Monte-Carlo method.

From positions of the first PPCFs' peaks Mg-Mg, Mg-Cl and Cl-Cl, a topological parameter ρ_1 can be found by the following Formula[19]:

$$p_1 = \sum X_i X_j r_1(ij) / d_0 \qquad [5]$$

where X_i = an ionic fraction of an ion i; $r_1(ij)$ = position of the first PPCFs peak for the pair i-j; $d_0 = (V/N)^{1/3}$; N = a number of ions in volume V. The topological parameter defined by Formula [5] characterizes a packing density of disordered systems; for densely packed systems $\rho_1 = 1.08 \pm 0.02$[19]. Thus ρ_1 for $ZnCl_2$ with a near tetrahedral configuration of cations was found to be 0.991[15]. Calculated value of ρ_1 for $MgCl_2$ was even lower, 0.974. However, the coordination number z(Mg-Cl) for Mg-Cl pairs was 5.2 ± 0.9 (here 0.9 is a standard deviation of the coordination number from its average value), and only 19.5% of magnesium cations had coordination number 4.

Non-coulomb parts of ionic potentials for liquid $MgCl_2$ are shown in Figure 5. Mg-Cl and Mg-Mg potentials are of an unusual form. The Mg-Cl potential has a deep minimum near 3.55Å. Possibly, this minimum is due to inaccurate diffraction data. The Mg-Mg potential has a sharp minimum of -1.62 eV at 2.95Å and a maximum of 0.95 eV at 5.05Å. Namely, this minimum is behind a relatively short distance of 3.81Å between magnesium cations (Figure 1). At a distance of about 10Å, non-coulomb interactions between ions are negligible.

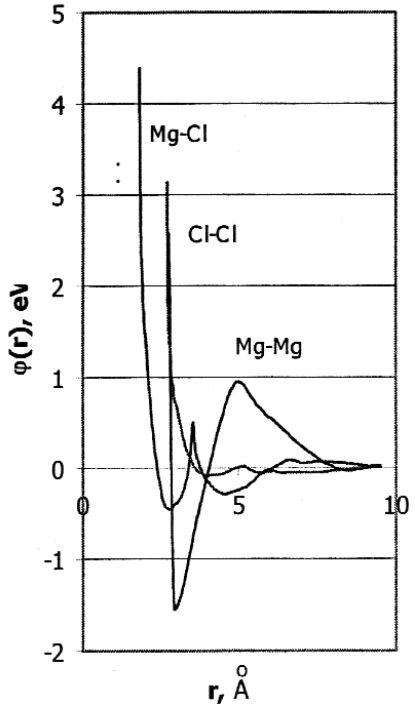

Figure 5. Non-coulomb pair potentials for liquid $MgCI_2$

In the MD simulation, self-diffusion coefficients can be calculated using MD data on the mean square displacement of ions as a function of time. However, results of calculation of diffusion coefficients in liquid $MgCl_2$ at 998 K were inconsistent and inaccurate. Because of this, diffusion coefficients were calculated at the higher temperature of 1300ºC; they were found $1.3.10^{-7}$ and $1.9.10^{-7}$ cm^2/s for Mg^{2+} $_{II}$ Cl^- respectively. Self-diffusion coefficients of the same order were obtained for $ZnCl_2$[15]. Low mobility of ions in magnesium and zinc dichlorides can be attributed to strong correlation in displacement of small cations and large anions surrounded these cations[18], or, in other words, to formation of complexes, such as MCl_4^{2-}.

Modelling of liquid $CaCl_2$ at 1093 K

PPCFs for liquid $CaCl_2$ at 1093 K presented in Figure 2 were obtained[3] by the neutron diffraction method using chlorine isotopes ^{35}Cl and ^{37}Cl. As it follows from Figure 2, the first peak of PPCF for the Ca-Ca pair is located at a closer distance than the first peak of the PPCF for the Cl-Cl pair, although coulomb repulsion between Mg cations with charge +2 is stronger than between chlorine anions with charge -1. It can also be noticed that although the Ca-Cl distance (2.78Å) is larger than the Mg-Cl distance (2.42Å) because the size of the calcium cation is larger, and Cl-Cl ions in $CaCl_2$ are further apart (3.73Å) than in $MgCl_2$ (3.56 Å), the distance between calcium cations (3.6Å) is *shorter* than the Mg-Mg distance (3.81Å).

Simulation of the $CaCl_2$ by the Reverse Monte-Carlo method showed that the parameters characterizing discrepancy between calculated and experimental[3] PPCFs for pairs Ca-Ca, Ca-Cl and Cl-Cl were 0.081, 0.063 and 0.091 respectively (at a distance of up to 9.51Å). This means that experimental PPCFs are not accurate enough, and cannot be reconstructed with high accuracy. This was confirmed by the MD simulation.

MD models containing 747 ions in the basic cube were constructed at 1093 K using the algorithm BELION[11]. The density of liquid calcium chloride at 1093 K is 2.064 g/cm^3 [20], therefore, the length of the basic cube edge in the model of 747 ions was 28.119Å. A discrepancy parameter was high, in the range 0.10–0.12 for the Ca-Ca and Ca-Cl pairs and 0.06 for the Cl-Cl pair. The pressure in the system was between 15–20 GPa, therefore the models were strongly compressed. This indicates the necessity of having more accurate diffraction data for the MD simulation with the algorithm BELION.

Modelling of liquid $SrCl_2$ at 1198 K

The structure of liquid $SrCl_2$ at 1198 K was studied[4]. Diffraction PPCFs are shown in Figure 3. The length of the basic cube edge was 28.966 Å in the model of 747 ions and 40.006Å in the model of 1968 ions (density 2.697 g/cm^3). Atomization energy of liquid $SrCl_2$ was found to be 1218.9 kJ/mol.

Liquid $SrCl_2$ was modelled by the Monte-Carlo method[21] and by the MD method with Born-Mayer potential[4]. In all cases, calculated PPCF for the Sr-Sr pair was visibly different from the experimental data; the first PPCFs peak of the model was of about doubled height of the experimental PPCF.

Analysis of PPCFs by the Reverse Monte-Carlo method gave good results showing a high quality of diffraction data; the discrepancy parameters for Sr-Sr, Sr-Cl and Cl-Cl pairs were 0.050, 0.016 and 0.012 respectively.

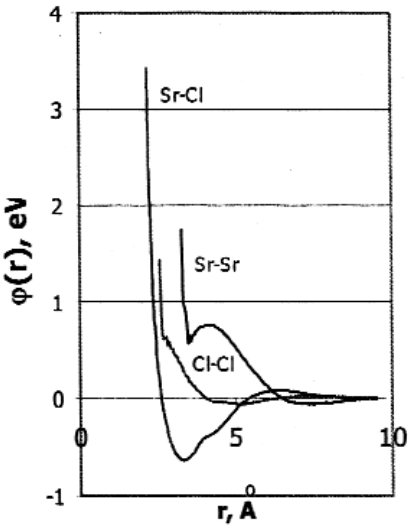

Figure 6: Non-Coulomb pair potentials for liquid $SrCl_2$.

In the MD modeling of the $SrCl_2$ system with 747 ions using the BELION algorithm, the charge of strontium cation was varied in the range 1.8–2.3. Atomization energies for models with different Sr charge were obtained as follows:

Z_{Sr}	1.8	1.9	2.0	2.1	2.2	2.3
E_{at}, kJ/mol	1199.1	1220.4	1225.5	1252.5	1186.7	1151.9

The maximum of the atomization energy and minimum of the internal energy are at the Sr charge of +2.08. The atomization energy of the MD model containing 1 968 ions, constructed with the algorithm BELION at Z_{Sr} = 2.1 was very close to the experimental value. Pressure in the system was low.

PPCFs of the model, shown in Figure 3, are in a good agreement with experimental data[4]. Some discrepancy is observed only in the vicinity of first peaks for Sr-Sr and Sr-Cl pairs. The discrepancy parameters are also small (0.060, 0.045, 0.020 for Sr-Sr, Sr-Cl and Cl-Cl pairs respectively). Good agreement was also obtained for coordination numbers for different pairs. Calculated topological parameter ρ_1 found to be 1.12, is an indication of a dense structure of $SrCl_2$.

Non-coulomb potentials are shown in Figure 6. They have no anomalies.

At 1198 K, coefficients of self-diffusion were determined to be $2.35.10^{-5}$ cm^2/s for strontium and $3.33.10^{-5}$ cm^2/s for chlorine. In measurements of the diffusion coefficients in MD modelling, the average square displacement of ions changed linearly with time.

Modelling of liquid $BaCl_2$ at 1298 K

The structure of liquid $BaCl_2$ was studied at 1298 K by the neutron diffraction method[5]. PPCFs obtained in this work are shown in Figure 4. Atomization energy of $BaCl_2$ was estimated to be equal to 1278.3 kJ/mol. The length of the basic cube edge is 30.184 Å for the model with N = 747 and 41.688 Å when N = 1 968[20].

Analysis of diffraction data obtained[5] by the Reverse Monte-Carlo method gave low values of a discrepancy parameter equal to 0.034, 0.033 and 0.027 for Ba-Ba, Ba-Cl and Cl-Cl pairs respectively, indicating high accuracy of experimental data.

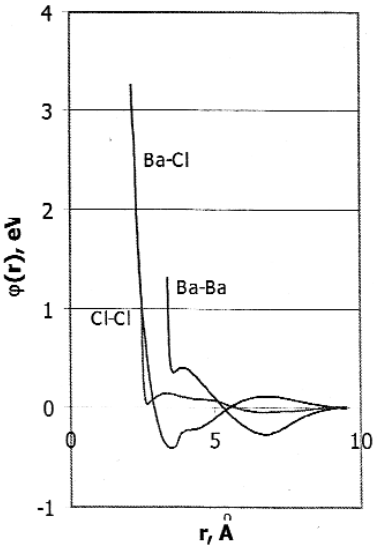

Figure 7: Non-coulomb pair potentials for liquid $BaCl_2$

The MD model containing 747 ions was constructed using the BELION algorithm at 1298 K for the charge of barium cation in the range of 2.0–2.3. The following atomization energies were obtained:

Z_{Ba}	2.0	2.1	2.2	2.3
E_{at}, kJ/mol	1292.9	1325.3	1308.8	1281.5

The atomization energy of liquid $BaCl_2$ is at maximum and, correspondingly, the internal energy is at minimum at Z_{Ba}=+2.12. Assuming Z_{Ba}=+2.10, MD model with the algorithm BELION was constructed for 1 968 ions. The model's atomization energy agreed well with experimental value. The difference between calculated and experimental atomization energy was 4.2%.

The model's PPCFs are presented in Figure 4. They agree very well with diffraction PPCFs. The $BaCl_2$ structure is close to the $SrCl_2$ structure. Non-coulomb potentials, shown in Figure 7, have no anomalies.

In MD measurements of diffusion coefficients, the average square displacements of ions changed linearly with time. Self-diffusion coefficients at 1298 K were determined ash $0.97.10^{-5}$ cm^2/s for the Ba cation and $2.52.10^{-5}$ cm^2/s for the chlorine anion, which seems to be too low for this salt.

Discussion

Enderby and Barnes in review[16] came to the conclusion that a 'simple' ionic model gives good results for salts with cations of a large size, like strontium and barium, and is not appropriate for salts of magnesium, zinc, nickel and others, having a relatively small size. In salts with small cations, M-M distances are too small to describe M-M interactions by Born-Mayer-Huggins type potentials. The BELION algorithm reflects the features in interactions in salts with small cations in non-coulomb potentials. The algorithm BELION gives good results when accurate diffraction PPCFs are available ($MgCl_2$, $SrCl_2$ and $BaCl_2$), and failed to produce a 'good' MD model for calcium chloride, for which diffraction PPCFs are not accurate enough.

Biggin *et al.*[2] suggested that polarization of large anions by small cations plays an important role in inter-ionic interaction. However, a direct correlation between the depth of the M-Cl potential and cationic radius is not detected. Non-coulomb Cl-Cl potentials are quite different in different salts and cannot be represented by a universal Cl-Cl potential. In all salts studied in this work, the cationic charge is close to +2, increasing slightly from $MgCl_2$ (Z_{Mg}=2.05) to $BaCl_2$ (Z_{Ba}=2.12) and, correspondingly, the charge of chlorine anion is close to -1. On the other hand, charges of copper and silver cations in chlorides are well above +1 [13,14]. The ions' charge is established by the balance of coulomb energy of the ionic system, which decreases with increasing the charge value, and the ionization energy, which changes with charge in the opposite direction.

In the MD models of $MgCl_2$ and $ZnCl_2$[15], the mobility of ions is quite low to obtain reliable diffusion coefficients by the MD simulation. However, MD modelling can be used for measurement of diffusion coefficients in liquid $SrCl_2$ and $BaCl_2$. Self-diffusion coefficients in these salts were used to estimate coefficients of specific electro-conductivity by the Nernst-Einstein equation. Calculated coefficients of electrical conductivity in strontium and barium chlorides were 255 and 116 Cm/m respectively, while experimental values are 206 and 212 Cm/m. Keeping in mind quite a distance between structural data and electro-conductivity, the agreement between calculated and experimental data looks reasonable.

References

1. WASEDA, Y. and TOGURI, J. *The Structure and Properties of Oxide Melts*. World Scientific, 1998.
2. BIGGIN, S., GAY, M., and ENDERBY, J.E. The Structures of Molten Magnesium and Manganese (II) Chlorides. *J. Phys. C.: Solid State Phys*., vol. 17, no. 6. 1984. pp. 977–985.
3. BIGGIN, S. and ENDERBY, J.E. The Structure of Molten Calcium Chloride. *J. Phys. C.: Solid State Phys*., vol. 14, no. 25. 1981. pp. 3577-3583.
4. McGREEWY, R.L. and MITCHELL, E.W. The Determination of The Partial Pair Distribution Functions for Molten Strontium Chloride. *J. Phys. C.: Solid State Phys*., vol. 15, no. 27. 1982. pp. 5537–5550.
5. EDWARDS, F.G., HOWE, R.A., ENDERBY, J.E., and PAGE, D.I. The Structure of Molten Barium Chloride. *J. Phys. C.: Solid State Phys*., vol. 11, no. 6. 1978. pp. 1053–1057.
6. BELASHCHENKO, D.K. and GINZBURG, A.S. Computer Simulation of Noncrystalline Systems Using Structural Diffraction Data. *High Temperatures*, vol. 40. no. 1. 2002. pp. 120–138.
7. OMOTE, K. and WASEDA, Y. A Method for Estimating the Effective Pair Potentials of Molten Salts from Measured Structure Data. *J. Phys. Soc. Japan.* , vol. 66, no. 4. 1997. pp. 1024–1028.
8. WASEDA, Y., OMOTE, K., and TAMAKI, S. Effective Pair Potentials of a Binary Fluid Mixture and their Application to Molten Salts. *High Temp. Mater. & Processes*, vol. 16, no. 2. 1997. pp. 109-122.
9. OMOTE, K., SAITO, M. and WASEDA, Y. Effective Pair Potentials of Liquid CuBr Estimated from the Anomalous X-Ray Scattering Data. *J. Phys. Soc. Japan*., vol. 66, no. 10. 1997. pp. 3097–3101.

10. MITEV, P.D., SAITO, M. and WASEDA, Y. Effective Pair Potentials of Molten AgBr, CuBr, CuI and RbBr Estimated from the Experimental Partial Structure Factors. *Int. Conf. on Liquid and Amorphous Metals (LAM-11)*. Yokohama. 9-14 Sept. 2001. Abstracts. p. 100.
11. BELASHCHENKO, D.K. Constructing Models of Ionic Liquids from Diffraction Data. *Russ. J. Phys. Chem*., vol. 76. no. 9. 2002. pp. 1461–1471.
12. BELASHCHENKO, D.K. and MOMCHEV, M.P. Pair Interactions in Liquid Eutectic Ag-Ge Alloy. Izv. Vuzov. *Chernaya Metallurgiya*, no. 7. 1992. p. 72 (in Russian).
13. BELASHCHENKO, D.K. and OSTROVSKI, O.I. Computer Modeling of Liquid Salts RbBr, CuCl, CuBr, CuI and AgBr. *Calphad*, vol. 28, no. 4. 2002. pp. 523–538.
14. BELASHCHENKO, D.K. and OSTROVSKI, O.I. Computer Simulation of the Structure of Liquid Metal Halides RbBr, CuCl, CuBr, CuI and AgBr. *Russ. J. Phys. Chem*., vol. 77, no. 4. 2003. pp. 627–635.
15. BELASHCHENKO, D.K. and OSTROVSKI, O.I . Computer Simulation of Liquid $ZnCl_2$ Using Diffraction Data. *Russ. J. Phys. Chem*., vol. 77. no. 7. 2003. pp. 1111–1117.
16. ENDERBY, J.E. and BARNES, A.C. Liquid Semiconductors. *Rep. Prog. Phys*., vol. 53, no. 1. 1990. pp. 85–179.
17. ENDERBY, J.E. The Structure of Molten Salts. *Molten Salt Chemistry*. Mamantov, G. and Marassy, D. (eds). Reidel Publ. Company. NATO SAD, v 202. 1987. pp. 1–15.
18. ENDERBY, J.E. Liquid State Physics. *J. Phys. C.: Solid State Phys*., vol. 15. no. 22. 1982. pp. 4609–4625.
19. BELASHCHENKO, D.K. Computer Simulation of the Structure and Properties of Non-Crystalline Oxides. *Russ. Chemical Reviews*, vol. 66, no. 9. 1997. pp. 733–762.
20. *Molten Salts Handbook*. V.1. Chimiya (Publisher), Leningrad, 1971 (in Russian).
21. DE LEEUW S. *Mol. Phys*, vol. 36. 1978. p. 765.