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Molecular-network–ionic structure transitions in liquid AlCl_3 and ZnCl_2 halogenides under pressure

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Abstract

We present the *in situ* high-pressure–high-temperature x-ray diffraction study of the liquid AlCl_3 and ZnCl_2 halogenides having a quasi-molecular network structure in liquid state at normal pressure. These liquids are intermediate between pure covalent and ionic melts. Structural study of these liquid halogenides is indicative of a rapid and strong breakdown of an intermediate-range order in a tetrahedral network of melts for the initial pressure range, 0–2.5 GPa for AlCl_3 and 0–1.8 GPa for ZnCl_2 , and points to rather sharp transitions in liquids with the formation of a short-range order structure similar to ionic melt structures around 4 GPa for AlCl_3 and 3 GPa for ZnCl_2 . Thus, pseudo-covalent liquid halogenides like AlCl_3 and ZnCl_2 provide testimony to two phenomena under high pressures, namely, a gradual decay of structural correlations in the tetrahedral network of the melt and a sharp transition from molecular-network to ionic structure in liquid on further compression. Such a two-stage structural transformation under pressure is the general feature for a wide class of simple melts, including most of the pseudo-covalent halogenides.

1. Introduction

In contrast to widely known structural phase transitions in crystals, the phase transformations in simple isotropic liquids are quite rare and unexplored. There are very few examples of both smooth and sharp transitions in liquids, including those occurring in a supercooled state (P, Se, S, I_2 , Bi, Te, Si, H_2O , $\text{Y}_2\text{O}_3\text{--Al}_2\text{O}_3$) [1–3]. The origins of different types of transformation in disordered substances are analysed in [4]. It is reasonable to assume that melts exhibit sharp transitions in the cases when their crystalline counterparts undergo transformations with significant coordination changes and, correspondingly, large volume jumps. High-pressure studies of liquid covalent oxides (B_2O_3 , GeO_2) [5, 6] and chalcogenides (GeSe_2) [7], whose

crystals undergo coordination changes, have allowed us to reveal some structural changes in melts but have not provided new unequivocal examples of sharp liquid–liquid transitions.

Liquid halogenides present another interesting class of melts. Depending on the ion size ratio, the condensed phases of halogenides may be both ionic and molecular substances [8–10]. Trihalogenides (LaCl_3 , UCl_3 , TbCl_3 , YCl_3) and dihalogenides (CaCl_2 , SrCl_2 , BaCl_2) with large-sized cations crystallize in the ionic lattice with the coordination number $Z = 6$ – 9 for the ions of metals, and the melts of the given crystals represent ionic liquids (the coordination number $Z \approx 6$ – 7) [8–17]. Halogenides with small-sized cations (CaCl_3 , AlBr_3 , SbCl_3 , ZnCl_2 , BeF_2) display strong pseudo-covalence effects associated with a significant contribution of dipole polarization forces [8, 9]. Crystals and melts of these halogenides have the coordination number $Z \approx 4$ for ions of metals and are molecular (AlBr_3) or pseudo-covalent (ZnCl_2) substances [8–10]. Due to pseudo-covalence effects, crystals of some halogenides (AlCl_3 , FeCl_3 , MgCl_2 , MnCl_2 , CdCl_2) are ordinary ionic substances ($Z \approx 6$), while their melts are low-coordinated ($Z \approx 4$) liquids [8–10, 17, 18], which results in record, for inorganic substances, volume jump values during melting (for AlCl_3 $\Delta V_m/V \approx 88\%$) [9, 10].

The last mentioned class of halogenides is of special interest, since the melts of these halogenides are intermediate between ionic and covalent liquids, and one can expect significant structural changes to occur in these melts under compression. In the present work the AlCl_3 trihalogenide and the ZnCl_2 dihalogenide have been chosen as the subjects of investigation. Both crystalline and liquid ZnCl_2 have pseudo-covalent tetrahedrally ordered structures, while the liquid AlCl_3 has a pseudo-molecular structure in contrast to the ionic structure of its crystalline state. Preliminary results of our study were briefly outlined in [19]. In contrast to [19], where only one preliminary set of experimental data has been used, the present paper is based on three independent sets of experiments. This enables us to make unambiguous conclusions about the nature of the structural changes in the AlCl_3 and ZnCl_2 melts under pressure and to analyse in detail the main aspects of the corresponding phase transformations in these liquids.

In the quasi-molecular AlCl_3 melt, the Al_2Cl_6 dimer molecules can form some disordered clusters of the AlCl_4^- tetrahedral network with a large number of atomic-scale ‘microvoids’ [11, 18]. One should note the existence of a sharp pre-peak of the structure factor of the melt at $k \sim 1 \text{ \AA}^{-1}$ [8, 15, 20]. It is agreed that this pre-peak accounts for the ordering of intermolecular ‘voids’ [21]. Previously, no examinations of the AlCl_3 compound under pressure have been performed. It was reasonable to suppose that the molecular-network structure of the AlCl_3 liquid under compression could undergo modification, and that a transition to an ionic melt with a higher coordination number might occur. From the data on the volume and entropy jumps, accompanying melting of AlCl_3 at normal pressure [9, 10], one can estimate the initial slope of the melting curve as $\sim 600 \text{ K GPa}^{-1}$, which is rather high for inorganic substances and indicative of the low density of the liquid state. Another quasimolecular liquid trihalogenide, namely BiCl_3 , was studied under pressure [22]. A continuous transition from insulator to ionic state was found in BiCl_3 at pressures less than 1 GPa. It is naturally supposed that a similar transformation to the highly ionic liquid should take place in the AlCl_3 melt, although at higher pressures.

The ZnCl_2 compound has been studied in more detail both at normal and high pressures. At ambient pressure in crystalline modifications of ZnCl_2 , the Zn^{2+} ions are in a tetrahedral environment of Cl^- ions. The ZnCl_4^{2-} tetrahedra, as the basic structural element, are retained in the melt. In contrast to such liquid halogenides as MgCl_2 , MnCl_2 and CdCl_2 , the tetrahedral environment in the ZnCl_2 liquid is near ‘ideal’, resulting in the formation of a three-dimensional network of the tetrahedra linked by corner-sharing, which is similar to the network of covalent melts [8, 9, 14]. There is a certain degree of short-range order structural similarity between

the ZnCl_2 network melt and AlCl_3 molecular-network melt [8, 11, 13]. In particular, there is a pre-peak of considerable intensity in the structure factor of both liquids at small wavevectors $k \sim 1 \text{ \AA}^{-1}$ [21, 23]. Yet, in distinction to very high viscosity values for ZnCl_2 ($\sim 10 \text{ Pa s}$), the viscosity of the AlCl_3 liquid is extremely low ($\sim 10^{-3} \text{ Pa s}$); it is even below the values for the ionic melts of trihalogenides ($\sim 10^{-2}$ – 10^{-1} Pa s) [9, 10]. It is assumed that the low viscosity of the AlCl_3 melt is due to a large number of ‘microvoids’ in the tetrahedral network [8, 11, 18]. High viscosity values of the ZnCl_2 melt lead to the glass formation at cooling with rates $|\dot{T}| < 1 \text{ K s}^{-1}$, that allows us to regard this halogenide as a ‘fragile’ analogue of covalent oxides [8, 24]. Studies of the structure and properties of ZnCl_2 at ambient pressure have revealed an anomalous behaviour for many of its physical characteristics [9, 15, 16, 20, 25]. Compression at room temperature of both crystalline and glassy forms of ZnCl_2 results in their transformation at $P \sim 2.5$ – 3 GPa to a high-pressure crystalline δ -phase (the coordination number $Z = 6$) [24, 26]. The structure of the compressed ZnCl_2 melt has been explored only at low pressures (up to 0.3 – 0.4 GPa) by x-ray and neutron diffraction methods [27, 28]. It was concluded that the tetrahedral short-range order is retained in the melt, and that the intermediate order undergoes slight modification at compression. The short-range order structure of the ZnCl_2 melt was studied by EXAFS at pressures up to 0.2 GPa [29], while the viscosity of the liquid ZnCl_2 was studied at $P < 0.1 \text{ GPa}$ [30]. An increase of the coordination number from four to six at a phase transition under compression in the solid ZnCl_2 gave promise that the corresponding structural anomalies and phase transformations exist in the melt in an accessible range of pressures.

2. Experimental details

We have studied the structure of the liquid and crystalline AlCl_3 and ZnCl_2 by *in situ* x-ray diffraction. *In situ* structural investigations of the solid and liquid AlCl_3 and ZnCl_2 phases were carried out by the energy-dispersive x-ray diffraction method in the MAX-80 installation at the SPring-8 synchrotron radiation facility (the BL14B1 beamline). A cubic press was used for generating high pressures up to 6.5 GPa . Pressed cylindrical tablets of 1 – 1.5 mm in diameter and 0.6 – 1.2 mm in height were produced from AlCl_3 and ZnCl_2 powders (99%, MERC, Germany) and placed into a high-pressure cell in a dry argon box. In the initial state, the AlCl_3 compound had a monoclinic structure ($C2/m$ space group, $a = 5.93 \text{ \AA}$, $b = 10.24 \text{ \AA}$, $c = 6.17 \text{ \AA}$, $\beta = 108^\circ$). Due to a water admixture ($\sim 1\%$), the low-pressure phase of ZnCl_2 was not the most stable orthorhombic modification, and it had a low-temperature γ -phase structure (HgI_2 structure type, $P4_2/nmc$ space group, $a = 3.70 \text{ \AA}$, $c = 10.67 \text{ \AA}$). The outer part of the cell presented a cube from amorphous boron; the sample was placed in a container from graphite or hexagonal boron nitride. The heating was produced by passing the alternating current through a graphite heater; the temperature was measured by a chromel–alumel or platinum–platinum–rhodium thermocouple. The pressure was determined from the equation of state of the reference substances (NaCl and BN). The cell was exposed to air for about 1 min (from taking it out of the argon box to the generation of the minimum blocking pressure of 0.2 – 0.3 GPa). The x-ray phase analysis of the samples under pressure showed that the volume fraction of hydroxide for both substances did not exceed 5% .

3. Results and discussion

The pressure–temperature phase diagrams of the substances are shown in figures 1 and 2. The events of melting were justified by the disappearance of the narrow sharp Bragg peaks of the crystalline phases. We can observe the multiple reversible melting–crystallization processes for

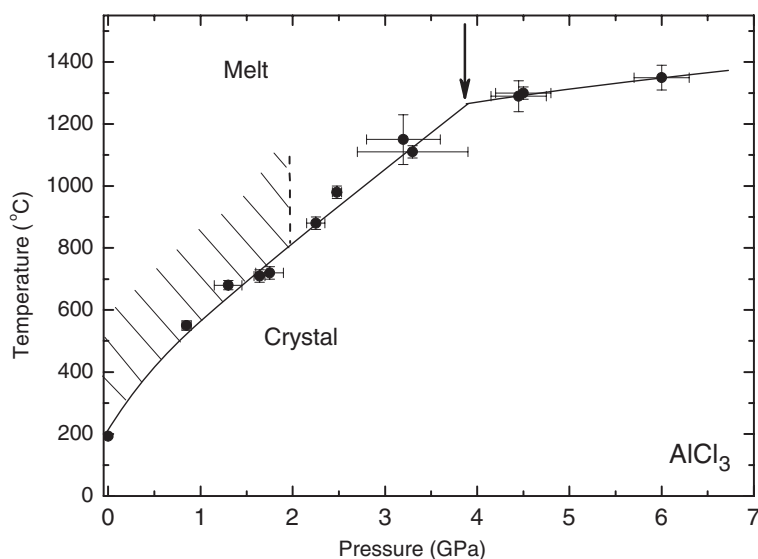


Figure 1. Pressure–temperature phase diagram of AlCl_3 developed from the present *in situ* x-ray diffraction experiments. The experimental melting curve (black symbols and lines), the approximate region with respect to pressure of the continuous decay of intermediate structural correlations (shaded area), and the pressure point of the abrupt liquid–liquid transition near the melting curve (vertical arrow) are shown.

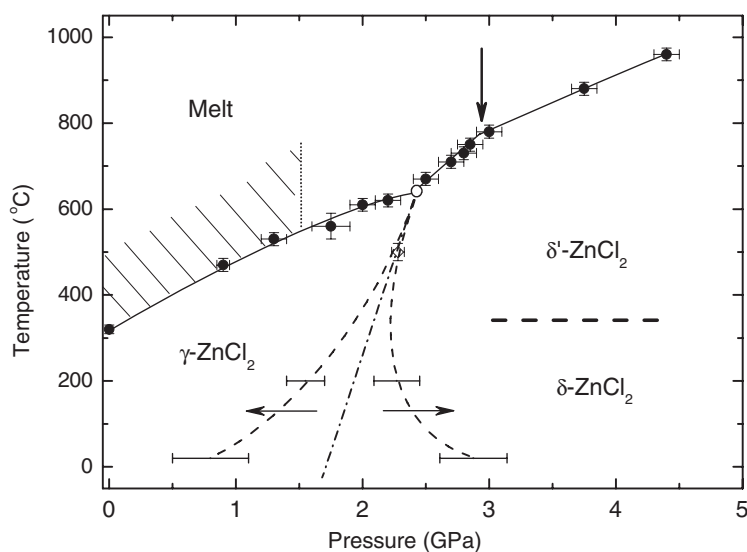


Figure 2. Pressure–temperature phase diagram of ZnCl_2 developed from the present *in situ* x-ray diffraction experiments. The experimental melting curve (black symbols and lines), the kinetic lines of direct and reverse phase transitions between γ and δ phases (thin dashed lines), where the horizontal bars correspond to experimental intervals of transitions, the approximation of the equilibrium line for γ and δ phases (dash–dotted line), the γ – δ –liquid triple point (open circle), the approximate transition line from δ to distorted high–pressure δ' phase (thick dashed line), the approximate region (with respect to pressure) of the continuous decay of intermediate structural correlations (shaded area), and the pressure point of the abrupt liquid–liquid transition near the melting curve (vertical arrow) are shown.

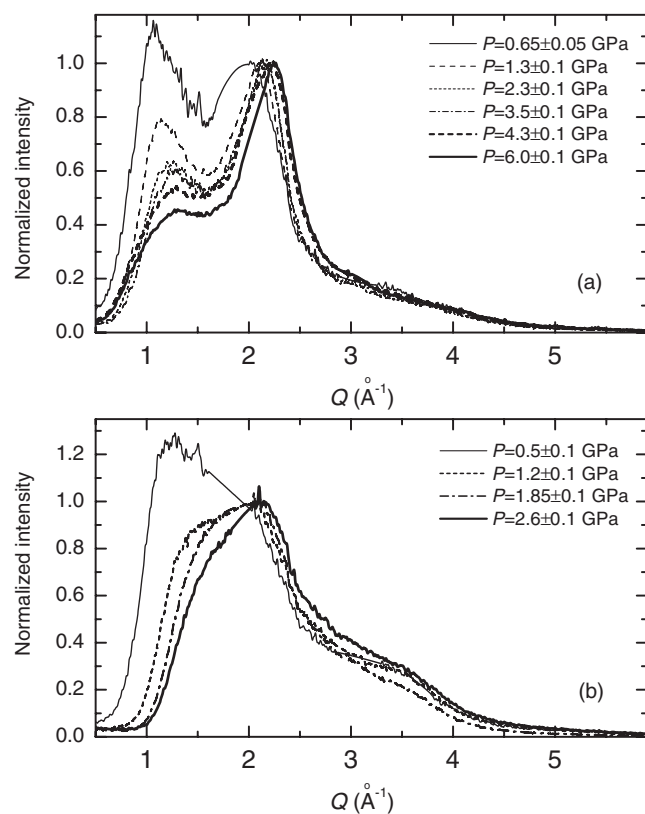


Figure 3. X-ray diffraction data for AlCl_3 (a) and ZnCl_2 (b) melts, recorded at different pressures near the melting curve at the angle of the detector $2\theta = 4^\circ$ (smoothed by the Fourier transformation filter).

both substances at all pressures exceeding ≈ 0.5 GPa for the experimental heating/cooling rates $\sim 1\text{--}10$ K s^{-1} .

When investigating the AlCl_3 melting curve, we found a significant decrease of the melting curve slope at compression to 3 GPa and an additional bend of the melting curve (with change of the melting curve slope from 250 down to 50 K GPa^{-1}) at $P \approx 4$ GPa. The change of the melting curve slope accompanied by the monotonic compression of the crystalline phase means a rapid densification of the melts according to the Clapeyron–Clausius equation. At room temperature the structure of the AlCl_3 crystal remains unchanged up to 6.5 GPa; at high temperatures, an insignificant distortion of the structure takes place.

The ZnCl_2 melting curve slope at compression is visibly reduced to 80 K GPa^{-1} near the triple point (figure 2). At pressures above the triple point, an additional decrease in the slope at $P \approx 3$ GPa from 200 to 120 K GPa^{-1} is also observed. It again means a rapid densification of the melts. The structure of the ZnCl_2 high-pressure δ -phase is defined as a distorted CdI_2 -type (WTe_2 -type, $Pmn2_1$ space group; the lattice parameters at $P = 4.68$ GPa are $a = 3.213$ Å, $b = 5.813$ Å, and $c = 11.868$ Å). Thus, an earlier identification of the high-pressure phase structure [26] was incorrect. The volume jump at the γ – δ transition is about 15%. When heating the high-pressure phase to over 300 °C, an additional distortion of the structure occurs (distorted HgCl_2 -type orthorhombic, $Pmmm$ space group; the lattice parameters at 4.53 GPa and 530 °C are $a = 5.290$ Å, $b = 10.727$ Å, and $c = 3.921$ Å). Detailed data on the structure of the AlCl_3 and ZnCl_2 crystalline modifications will be presented elsewhere.

Structural data for liquid AlCl_3 and ZnCl_2 under pressure are presented in figures 3–6. The structure of the liquids was studied at temperatures higher by 30–150 K than the

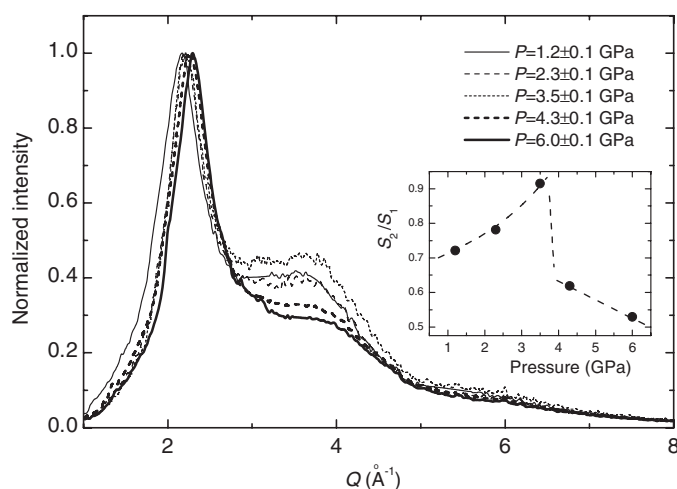


Figure 4. X-ray diffraction data for AlCl_3 melt, recorded near the melting curve for the angle of the detector $2\theta = 8^\circ$ (smoothed by the Fourier transformation filter). The thin and thick lines correspond to the liquid before and after the transition, respectively. The pressure dependence of the amplitude ratio between the second and first diffraction peaks from the current picture is shown in the inset (dashed lines are guides for the eyes).

melting temperature. At small diffraction angles $2\theta = 3^\circ\text{--}4^\circ$ of this particular detector, the energy-dispersive x-ray diffraction method adequately represents the basic features of the structure factor (including the positions and the intensities of peaks) only for small wavevectors ($k \sim 1\text{--}2 \text{ \AA}^{-1}$), while large diffraction angles $2\theta = 8^\circ\text{--}14^\circ$ are required for examining the structure factor in the region $3\text{--}7 \text{ \AA}^{-1}$ of the wavevectors. Intermediate values of the wavevectors ($k \sim 2\text{--}3 \text{ \AA}^{-1}$) should be investigated at the diffraction angles of $2\theta = 5^\circ\text{--}6^\circ$.

At pressure $P \approx 0.6 \text{ GPa}$, the AlCl_3 and ZnCl_2 melts are structurally similar to their respective liquids at atmospheric pressure except for a smaller amplitude of the first pre-peak and a shift of its position into the region of higher wavevectors. At higher pressures the structure of the liquids radically changes; in so doing, the most considerable changes in the pattern of the structure factor affect the pre-peak of the first diffraction maximum, as well as the intensity and form of the second and third maxima. Data in figure 3 present the intensity of the x-ray diffraction from the AlCl_3 and ZnCl_2 melts for small diffraction angles $2\theta = 4^\circ$ of the detector, where it strongly enhances the amplitudes of the pre-peak. In the initial pressure range (up to 2.5 GPa for AlCl_3 and up to 1.8 GPa for ZnCl_2) one can see a dramatic (several-fold!) reduction in the intensity of the pre-peak and a strong shift of its position into the region of higher wavevector values (figure 3). A similar strong weakening of the first sharp pre-peak was earlier observed for some glasses [21] and liquids [7], and has been interpreted as an ‘elimination’ of intermolecular ‘voids’ and a ‘breakdown of intermediate structural correlations’. During further compression (in the range of $2.5\text{--}3.5 \text{ GPa}$ for AlCl_3 and $1.8\text{--}2.5 \text{ GPa}$ for ZnCl_2), the structure of the melts does not undergo any considerable modification. In this case, the diffraction structural patterns for the ZnCl_2 melt become similar to those of such liquid halogenides as CdCl_2 , MgCl_2 , MnCl_2 [14]. These melts are known to have a disrupted intermediate order and a tetrahedral short-range order [10, 14–16].

At pressures $P > 0.5 \text{ GPa}$ in our experiments, quenching from melt at the rates of 10^2 K s^{-1} did not result in the formation of glass. There exists a well known correlation between viscosity of the melt and its glass forming ability [31, 32]. In particular, the viscosity

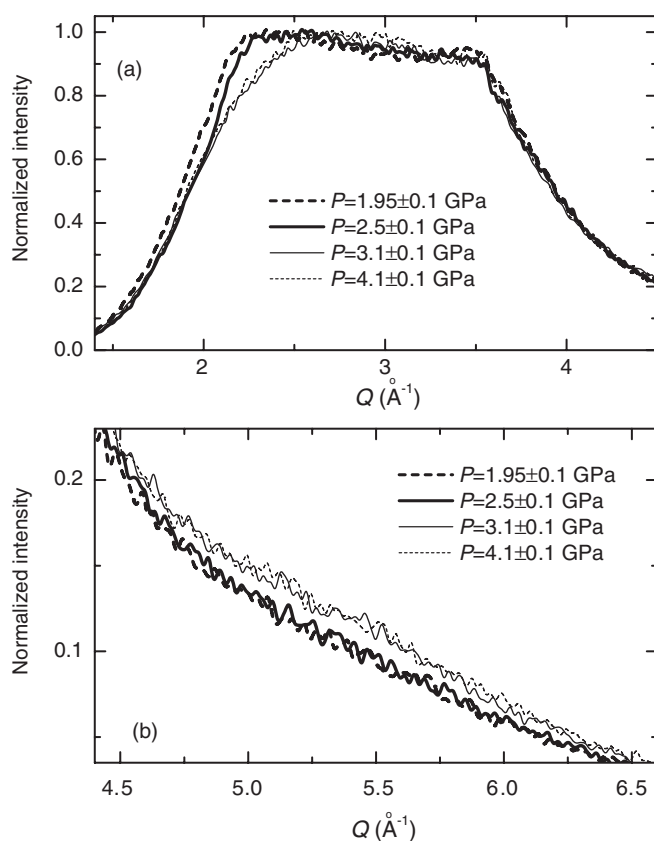


Figure 5. X-ray diffraction data for ZnCl_2 melt, recorded near the melting curve for the angle of the detector $2\theta = 6^\circ$ (smoothed by the Fourier transformation filter). The data are presented for the region of the first and second diffraction peaks (a) and third diffraction peak (b) (the intensity of the third peak is very small for $2\theta = 6^\circ$). The thin and thick lines correspond to the liquid before and after the transition, respectively.

of a slightly undercooled liquid is approximately inversely proportional to the critical cooling rate necessary to get a glass [32]. For viscous oxide and halogenide melts the viscosity is $\nu \sim 10^3\text{--}10^6$ Pa s, while the corresponding critical quenching rate to obtain the glasses is $\dot{T} \sim 10^{-4}\text{--}10^{-2}$ K s $^{-1}$. For nonviscous metallic melts $\nu \sim 10^{-4}\text{--}10^{-2}$ Pa s and $\dot{T} \sim 10^3\text{--}10^7$ K s $^{-1}$. For melts with a moderate viscosity $\nu \sim 10$ Pa s, such as ZnCl_2 , Se, etc, the critical cooling rate is $\dot{T} \sim 1$ K s $^{-1}$. For As_2Te_3 $\nu \sim 1$ Pa s and $\dot{T} \sim 10\text{--}10^2$ K s $^{-1}$. So, with the relation discussed above as quite universal, we can suppose that the ZnCl_2 melt at $P > 0.5$ GPa has the viscosity $\nu \leq 10^{-1}$ Pa s. This means a very rapid decrease of viscosity with pressure, that, in turn, can be indicator of a breakdown of the intermediate order structure of the covalent networked ZnCl_2 liquid.

Variation of the diffraction data under compression in the region of the second and third peaks of the structure factor is shown in figures 4–6. Calculated structure factors for both liquids at different pressures are presented in figures 7 and 8. A minor change of the diffraction pattern in both melts, suggesting the retention of the tetrahedral short-range order, gives way to abrupt changes at $P \approx 4$ GPa for AlCl_3 and around 3 GPa for ZnCl_2 . For AlCl_3 , a substantial decrease in the amplitude and a flattening of the second maximum are observed (figure 4), the

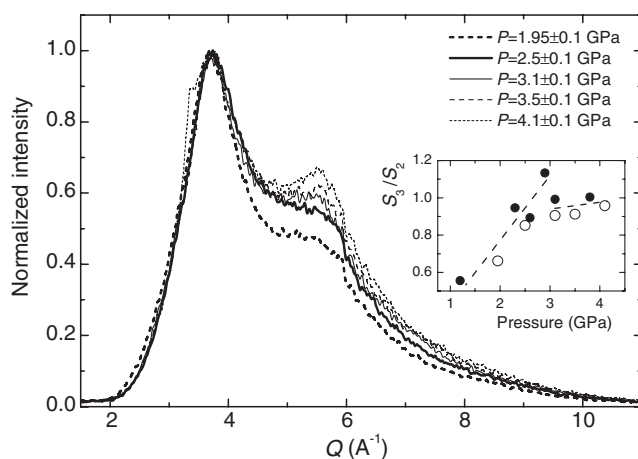


Figure 6. X-ray diffraction data for ZnCl_2 melt, recorded near the melting curve for the angle of the detector $2\theta = 10^\circ$ (smoothed by the Fourier transformation filter). The thick and thin lines correspond to the liquid before and after the transition, respectively. A pressure dependence of the amplitude ratio between the third and second diffraction peaks for two different sets of measurements, distinguished by open and solid symbols, is shown in the inset (dashed lines are guides for eyes).

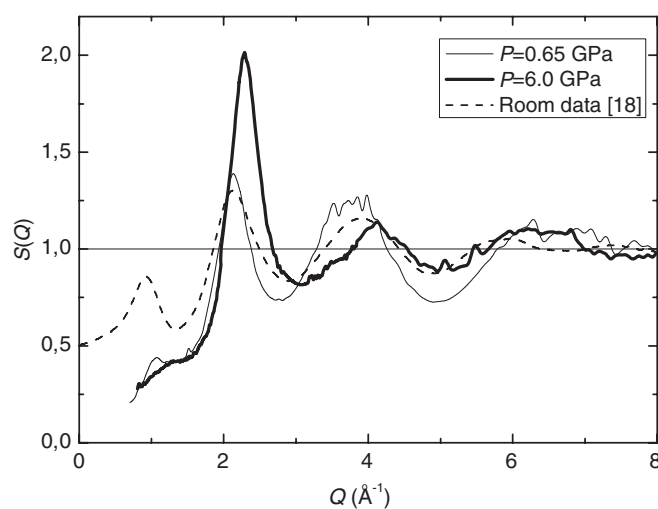


Figure 7. Structure factors of AlCl_3 melt calculated from x-ray diffraction data for the cases of low and high pressure. The structure factor at room pressure, measured by the time-of-flight neutron diffraction, is taken from [18].

structure factor of the AlCl_3 melt at $P \geq 4.3$ GPa resembling the corresponding diffraction patterns for ionic liquid halogenides of LaCl_3 type [8, 12, 13]. This is why we can suppose that the short-range order structure of the AlCl_3 melt changes from the molecular type to the ionic liquid. For ZnCl_2 , the intensity is reduced for the second peak and increased for the third peak and the position of the first peak shifts in a jump-wise manner into the region of higher wavevectors at pressure around 3 GPa (figures 5 and 6). The different experimental sets of liquid ZnCl_2 demonstrate a slightly different behaviour (see the inset in figure 6). However, in

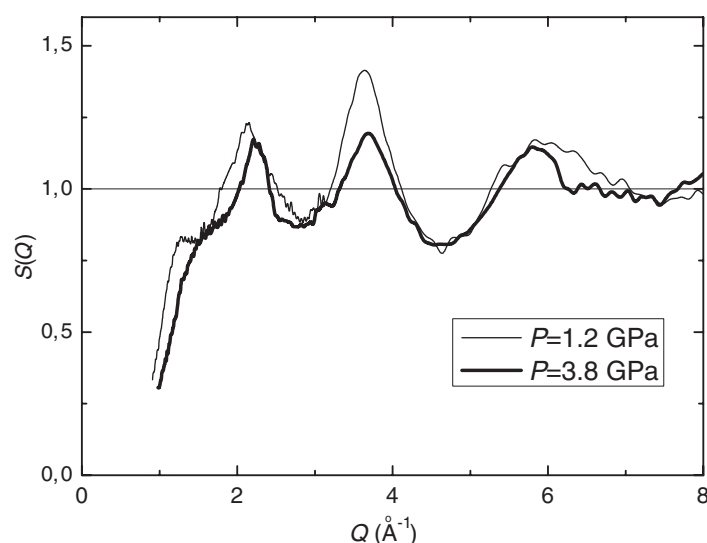


Figure 8. Structure factors of ZnCl_2 melt calculated from x-ray diffraction data for the cases of low and high pressure.

all experimental runs we observed a qualitative change of the melt structure around 3 GPa. One can suppose that the difference in structural data for different experimental runs (figure 6) may be connected with the existence of a critical point for the structural transition in the vicinity of the melting curve. The structure of the ZnCl_2 melt at $P > 3$ GPa becomes similar to the structure of the ionic liquid compounds CaCl_2 and SrCl_2 , whose coordination number is $Z \approx 6$ for the ions of metals [17]. Thus, during compression in both melts a sharp transition takes place; in so doing the short-range order structure changes to the one typical for ionic melts (see figures 7 and 8). The anomalous behaviour of the structure of the melts correlates with the rather sharp bends in the melting curves at $P \approx 4$ GPa for AlCl_3 and $P \approx 3$ GPa for ZnCl_2 , which is indicative of the volume anomalies in the liquids during compression (see figures 1 and 2).

4. Conclusion

In summary, we have found that AlCl_3 and ZnCl_2 are the first substances to demonstrate in their melts at compression two striking phenomena: first, a breakdown of intermediate correlations in the AlCl_4^- and ZnCl_4^{2-} tetrahedral network in the initial pressure range, and, second, a sharp structural transformation in the liquids with the possible change of the coordination number during further compression. Experimental evidence of either of these phenomena had been rare to date [2, 3, 7]. The transition, accompanied by an increase of the coordination number, in the liquid (from a pseudo-covalent melt to an ionic one) is connected with the reduction, as compared to the Coulomb interaction, of a relative contribution of ‘polarization energy’ during compression. Since intermolecular interaction in the ZnCl_2 and AlCl_3 melts can be easily simulated [8–10], it is interesting to study theoretically the coordination change in the melt by a computer simulation.

An anomalous behaviour of the melt structure and anomalies of other physical properties should be observed at compression for many pseudo-covalent halogenides. In comparison with covalent oxide melts, significant changes in the structure of liquid halogenides should occur at lower pressures and temperatures, which makes halogenides attractive objects for an experimental study. For instance, a behaviour similar to that of AlCl_3 at compression can be

expected for the FeCl₃ melt. For such pseudo-covalent halogenides as GaCl₃ and AlBr₃, one should expect a transition during compression to ionic structure both from the crystalline state and from the melt. A tetrahedral short-range order in the CdCl₂, MnCl₂, and MgCl₂ melts could change to the octahedral one at relatively low pressures of 1–2 GPa. For the BeF₂ network melt, one should expect the phenomena similar to the effects observed for ZnCl₂, but probably at higher temperatures and pressures. As in the BiCl₃ melt, all these liquids under compression should demonstrate an increase of ionic conductivity.

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