# Ionic Conduction and Molecular Structure of Molten $FeCl_3$

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Former experiments on molten $FeCl_3$ have shown that, as for $AlCl_3$, melting is accompanied by a transition from sixfold to essentially fourfold coordination. However, in contrast to $AlCl_3$, the $FeCl_3$ melt near freezing has an appreciable ionic conductivity. We propose a model for the structure of $FeCl_3$ melt as consisting of closely packed $Fe_2Cl_6$ bitetrahedral molecules in equilibrium with $(Fe_2Cl_5)^+$ and $(Fe_2Cl_7)^-$ ionised species.

*Key words:* Melting; Liquid Structure; Molecular Liquids

## 1. Introduction

In metal halides, the ionic character of the crystalline bond is usually preserved on melting. $AlCl_3$ has long been known to be an exception to this general rule [1]. This material crystallises in a layer-type structure, which is formed from a slightly distorted cubic close packing of chlorines accommodating the trivalent metal ions inside every second (111) plane of octahedral sites. On melting the coordination of the metal ions becomes essentially fourfold. The anomalous nature of the melting transition of $AlCl_3$ is signalled by the truly enormous values of the relative volume change ($\Delta V/V_l = 47\%$) and entropy change ($\Delta S$ = 18.14 e.u.) and by the very low value of the electric conductivity of the melt ($\sigma = 5{\times}10^{-7}\ \Omega^{-1}$ cm$^{-1}$). These properties and a variety of observations from diffraction and Raman scattering experiments on the $AlCl_3$ melt and its mixtures with alkali halides are generally explained by viewing the melt as composed of $Al_2Cl_6$ bitetrahedral molecules with substantial intermolecular correlations. $AlBr_3$ possesses such a molecular type of structure already in the crystalline state.

$FeCl_3$ has been proposed as a further example of ionic-to-molecular melting [2]. Its crystal structure differs from that of $AlCl_3$ primarily in the interlayer correlations, being based on an almost perfect hexagonal (rather than cubic) close packing of the chlorines with each metal ion at the centre of an almost perfect octahedron. The values of the melting parameters are anomalously large ($\Delta V/V_l = 39\%$ and $\Delta S$ = 17.80 e.u.). There is evidence from Raman scattering [3, 4] and diffraction [2, 5] that the coordination of the metal ions changes to essentially fourfold on melting. Yet the ionic conductivity of the melt, though relatively small, is still appreciable ($\sigma = 4{\times}10^{-2}$ $\Omega^{-1}$ cm$^{-1}$ [4]).

We propose a model to account for the coexistence of ionic conduction with a molecular liquid structure in molten $FeCl_3$ near freezing. It is based on our studies of neutral and ionised states for molecular monomers and dimers *in vacuo* [6–8]. A full account of our model will be given in [9].

## 2. Molecular Units Relevant to Molten Trihalides

A relatively sophisticated model of polarisable ions can account for the presence of molecular local structures in these melts and assess their stability against fluctuations into ionised states. Such a model was proposed in early work on bond-bending in alkaline-earth dihalide molecules [10] and on tetrahedral halocomplexes of polyvalent metal ions [11]. A crucial aspect is the electronic polarisation of the halogens. Through a suitable extension of the shell model in lattice dynamics, each halogen ion is viewed as composed of an outer shell of valence electrons which is coupled to a rigid inner core: therefore, relative displacements of neighbouring ions are accompanied by the creation of electronic dipoles due to changes in the state of closed-shell overlap, in addition to induction by the electric field.

Table 1 reports a comparison of the structural parameters calculated [8] for $Al_2Cl_6$, $Fe_2Cl_6$ and $Al_2Br_6$ molecules by the ionic model (IM) with those determined from

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Table 1. Structure of $M_2X_6$ molecular dimers (bond lengths in Å, bond angles in degrees).

| Dimer | $M\text{-}X^B$ | $M\text{-}X^T$ | $M\text{-}M$ | $X^B\text{-}X^B$ | $X^T\text{-}X^T$ | $X^B\hat{M}X^B$ | $X^T\hat{M}X^T$ |
|---|---|---|---|---|---|---|---|
| $Al_2Cl_6$: | | | | | | | |
| IM | 2.27 | (2.065) | 3.22 | 3.19 | 3.60 | 89.5 | 121.3 |
| ED | 2.25 | (2.065) | 3.21 | 3.16 | 3.64 | 91.0 | 123.4 |
| $Fe_2Cl_6$: | | | | | | | |
| IM | 2.32 | 2.15 | (3.20) | 3.37 | 3.72 | 93.0 | 120.1 |
| ED | 2.33 | 2.13 | (3.20) | 3.37 | 3.72 | 92.9 | 122.1 |
| $Al_2Br_6$: | | | | | | | |
| IM | 2.41 | 2.22 | (3.34) | 3.48 | 3.84 | 92.3 | 120.0 |
| ED | 2.41 | 2.22 | (3.34) | 3.48 | 3.90 | 92.3 | 122.8 |

electron diffraction (ED) on the vapour phase. A minimal adjustment of model parameters to the data is needed: Table 1 reports in parentheses the values of the bond lengths which have been fitted to the ED data. The agreement between model and experiment is of similar quality as for refined quantum-chemical calculations at the Hartree-Fock level and for refined first-principles calculations by the density functional method.

The vibrational motions of these molecular dimers and the halogen-transfer reaction

$$2\,(M_2X_6) \Leftrightarrow (M_2X_7)^- + (M_2X_5)^+ \qquad (1)$$

have been evaluated by the same model. The $(M_2X_7)^-$ anion is known to be formed by two $MX_4$ tetrahedra sharing a single halogen bridge [12]. For the $(M_2X_5)^+$ cation we have found two mechanically stable structures: a symmetric one built from two $MX_4$ tetrahedra by face sharing, and an asymmetric one (at somewhat higher energy) which is obtained by direct stripping of a terminal halogen from the $M_2X_6$ dimer. The activation energy for the halogen transfer reaction in (1) is estimated to be 4.5 eV *in vacuo* for the three dimers of present interest. This value does not include the Coulomb energy gain from the interaction between the two ionised products, which have been taken to lie an infinite distance apart.

## 3. A Model for Ionic Conduction in Molten $FeCl_3$

Ionic conduction can arise in these molecular melts from fluctuations allowing transfer of halogen ions between neighbouring molecular units. We propose that it is associated with a partial ionisation equilibrium being present according to (1) in the dense liquid medium [9].

The first step in establishing this equilibrium is envisaged to be the transfer of a terminal halogen from a neutral dimer to a neighbouring neutral dimer, leaving behind on a short time scale the $(M_2X_5)^+$ cation in its partly relaxed double-bridged configuration and forming a single-bridged $(M_2X_7)^-$ anion. The activation energy for this ion transfer in the liquid medium is vastly reduced by the Coulomb attraction between the two neighbouring charged species.

On a longer time scale, the $(M_2X_5)^+$ cation relaxes to its triple-bridged equilibrium configuration with an energy release of about 0.6 eV, fostering the transfer of a halogen ion from the $(M_2X_7)^-$ anion to neighbouring neutral dimers. Further migration is helped by the high flexibility of the $(M_2X_7)^-$ anion and by the gains of polarisation energy and of entropy as the halogen migrates away from the $(M_2X_5)^+$ cation. Notice that the highly favoured tetrahedral coordination of the metal ions is preserved throughout the proposed mechanism of conduction.

On the above basis the different conduction behaviours of the $FeCl_3$ and $AlCl_3$ melts near freezing are naturally explained by assuming that the partial ion-transfer equilibrium is already present in the former melt. There should therefore be subtle structural differences between the two melts near their respective freezing points, corresponding to differences in the relative concentrations of double-bridged relative to single- and triple-bridged tetrahedra. Of course, the equilibrium in (1) would shift to the right with increasing temperature, with an accompanying increase in ionic conductivity.

Finally, it is relevant to recall that Voyiatzis [4] reported Raman evidence for $(Fe_2Cl_7)^-$ in liquid $(FeCl_3)_x \cdot (CsCl)_{1-x}$ mixtures at $x \cong 0.66$ and an order-of-magnitude increase in the ionic conductivity of molten $AlCl_3$ over a temperature range of ≈100 K. He also associated a Raman peak at 452 $cm^{-1}$ in molten $FeCl_3$ to the presence of the $(Fe_2Cl_5)^+$ ion. However, we believe that it is important to realise that between jumps the released chlorine is not in a free state inside the melt: it is instead part of a $(M_2Cl_7)^-$ anion. The stripping of a chlorine ion from a single $M_2Cl_6$ dimer requires a much higher activation energy.

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