

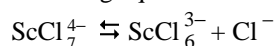
Network and Cluster-Like Structures in ScCl₃-CsCl Melts

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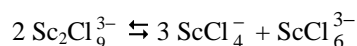
The present work concerns with a systematic Raman spectroscopic investigation of the structural properties of molten mixtures of ScCl₃-CsCl in the complete composition range. The temperature and composition effects on the Raman spectra have been carefully measured and used to identify the possible structural entities present.

In dilute ScCl₃ melts and at compositions up to 25 mol% ScCl₃ the following equilibrium is established:



which shift to the right with increasing temperature and/or ScCl₃ mole fraction. At intermediate compositions with $0.25 < X_{\text{ScCl}_3} < 0.7$ the Raman spectra indicate (e.g.

Fig. 1) a multispecies equilibrium involving at least three species:



Both tetrahedral (ScCl₄⁻) and octahedral (ScCl₆³⁻) species are formed by dissociating a species formed by two octahedral bound by a face.

For compositions rich in ScCl₃ and for pure ScCl₃ the data indicate to some extent a loose-network structure of bridged octahedral similar to that proposed for YCl₃ melts⁽¹⁾. On the other hand a variety of physicochemical measurements (molar volumes, vapor pressures, electrical conductivity)⁽²⁾ as well as recent computer simulation⁽³⁾ and neutron diffraction⁽⁴⁾ studies require a model structure that fulfils the following contradictable properties for pure molten ScCl₃ (a) an average coordination number less than six (b) a loose network structures connecting coordination polyhedra through chloride bridging and (c) large molar volume changes upon melting (i.e. “molecular” melt) but appreciable electrical conductivity (i.e. “ionic” melt).

The model proposed (Fig. 2) is based on the formation of cluster structures which is composed of “inner” fragments of “octahedral” network-like structures which terminate with “surface” fragments of scandium in “tetrahedral” coordination. The clusters are not considered stationary. Their life time is longer than the time for vibration but continuous fluctuations in size may occur by splitting or merging clusters or by rearrangements between the inner and outer fragments.

References

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3. P.A. Madden, M. Wilson and F. Hutchinson, *J. Chem. Phys.* **120**, 6609 (2004)
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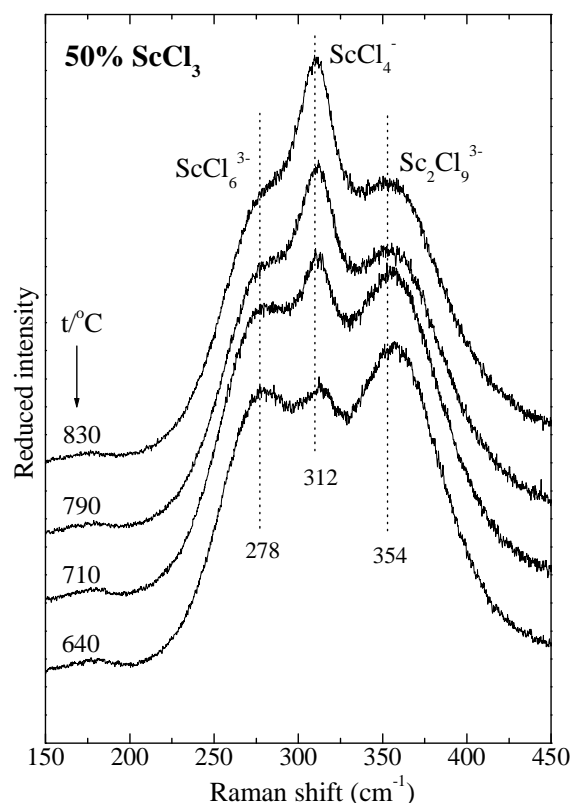


Fig. 1. Temperature dependence of the Raman spectra of molten ScCl₃-CsCl mixtures

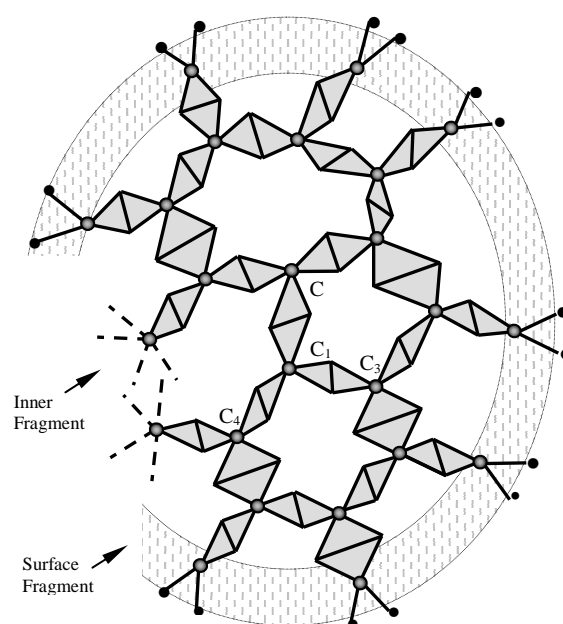


Fig. 2. Network-cluster-like model of molten ScCl₃; the inner fragment is composed of edge bridged octahedra. The outer (surface) fragment involves tetrahedral bridged to the inner fragment and having two terminal chlorides.