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# Local structure of molten polyvalent metal chlorides

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## Introduction

We have studied local structure of molten salt systems by high temperature XAFS technique[1]. It has been reported that many polyvalent metal halides have stable coordination like $(MX_n)^{m-}$ (M=metal and X= halogen) in molten state. We describe the XAFS results of some molten polyvalent chlorides.

## Experimental

The XAFS measurements of molten $YCl_3$(Y K-dege) at 1173K and molten 12%$ZrCl_4$(Zr K-dege) in LiCl-KCl eutectic at 723K were performed at BL27B station in the KEK-PF. The samples were sealed off in the quartz cell under reduced pressure(<$10^{-5}$Torr).

## Results and discussions

### (1)Molten $YCl_3$ systems

The |FT| functions for the molten $YCl_3$ and mixtures with LiCl-KCl are shown in Fig.1. It has been reported[2] that $YCl_3$ has a 6-fold $(YCl_6)^{3-}$ coordinate in molten state. The 1st $Y^{3+}$-$Cl^-$ peak in the |FT| increases by adding LiCl-KCl. It can be simply assigned to decreasing in the Debye-Waller factor, not to increasing in the coordination number, because the peak position does not change by the mixing. The 2nd peak was found around 3.7 Å only in the pure $YCl_3$. This is due to edge-sharing link($Y^{3+}$-$Cl^-$-$Y^{3+}$) of the coordinates. On the other hand, no significant peak was found over the 1st peak in the mixtures. Thus, the link is broken by adding $Cl^-$ donor(LiCl-KCl). It can be expected that the coordinate is stabilized and move freely in the mixture melt.

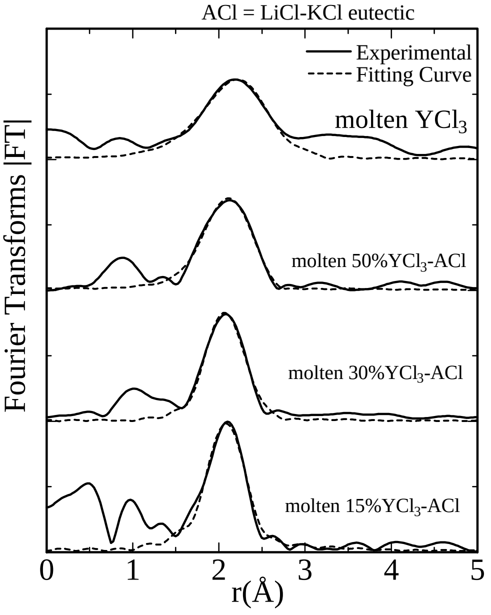

Fig.1 Fourier transform magnitude |FT| of $k^3$-weighed XAFS function for molten $YCl_3$ at 1173K and mixtures with LiCl-KCl eutectic at 973K

### (2)Molten 12%$ZrCl_4$ in LiCl-KCl eutectic

The |FT| functions for the 12%$ZrCl_4$ system is shown in Fig.2, together with that of solid $ZrCl_4$. The 1st peak in the melt is larger than that of the solid $ZrCl_4$. It is assigned to three distinct 1st $Zr^{4+}$-$Cl^-$ distances(2.307, 2.498 and 2.655 Å ) in the solid $ZrCl_4$[3] and single distance 2.51Å in the melt. The latter is close to sum of ionic radii r{$Zr^{4+}$( VI )}=0.72 Å and r($Cl^-$)=1.81 Å . Coordination number from the fitting was also 5.9 ± 0.6. It suggests that the melt has a 6-fold $(ZrCl_6)^{2-}$ coordinate.

## References

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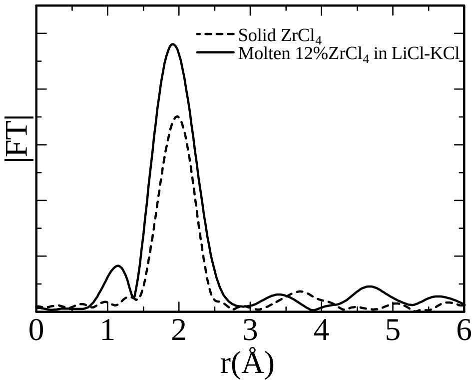

Fig.2 Fourier transform magnitude |FT| for molten 12%$ZrCl_4$ in LiCl-KCl eutectic