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X-RAY STRUCTURAL ANALYSIS OF MOLTEN LiF-KF EQUIMOLAR MIXTURE

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The structure of molten LiF-KF equimolar mixture at 545 °C was studied by X-ray diffraction analysis. From the analysis of RDF, the nearest neighbour distance and coordination number of Li^+-F^- pair in the mixture were found to be 1.85 Å and 3.0, respectively.

The molten eutectic mixture of LiF-KF is interesting as solvent and heat transfer medium, because of its solvent properties, thermal stability, and extended liquid range. There are numerous studies$^{1)}$ on the thermodynamic and transport properties of this melt. The studies on the structure, however, have not yet been made. The information of the structure is essential in elucidating microscopically the physical properties and in comparing with those obtained from computer simulations such as MD and MC.

For simplifying the analysis, the equimolar composition instead of the eutectic one(LiF:KF=52.2:47.8 mol%) was chosen, and the structure of the molten mixture at 545 °C was analysed by X-ray diffraction method.

Prescribed amounts of LiF and KF of analytical reagent grade dried under reduced pressure were melted in a platinum crucible under Ar atmosphere. After mixing for 30 min., the melt was quenched to prevent the segregation.

X-ray diffraction measurememts were performed on a θ-θ X-ray diffractometer using the step-scanning technique. The observable range of scattering angle(θ) was $3° \leq \theta \leq 45°$, corresponding to the range $0.93 Å^{-1} \leq Q \leq 12.5 Å^{-1}$ ($Q=4\pi \sin\theta/\lambda$, $\lambda=0.7107$ Å). Several runs were made in order to accumulate to 2×10^4 counts per datum point in the low scattering angles and 4×10^4 counts in the high scattering angles. The temperature of the melt was controlled within 545 ± 5 °C throughout the experiments. The intensity data were corrected and normalized by the usual method.$^{2)}$ The density used in the calculation of RDF was 2.054 g cm^{-3}.$^{3)}$

The correlation function G(r) is shown in Fig. 1, which has peaks at r=1.85, 2.75, 5.45, and 7.85 Å and has a shoulder at r=3.4-4.0 Å.

The position of the first peak is close to the sum(2.07 Å) of ionic radii$^{4)}$ of Li^+ and F^- ions and the number of F^- ions around an Li^+ ion calculated from the first peak area of RDF according to the method (a) in Ref.2 is 3.0. These results reveal that the first peak corresponds to the nearest neighbour Li^+-F^- interaction. Okada et al.$^{5)}$ have reported that the first peak positions of Li^+-Cl^- and K^+-Cl^- pairs in the molten eutectic LiCl-KCl mixture from the studies of MD simulation and

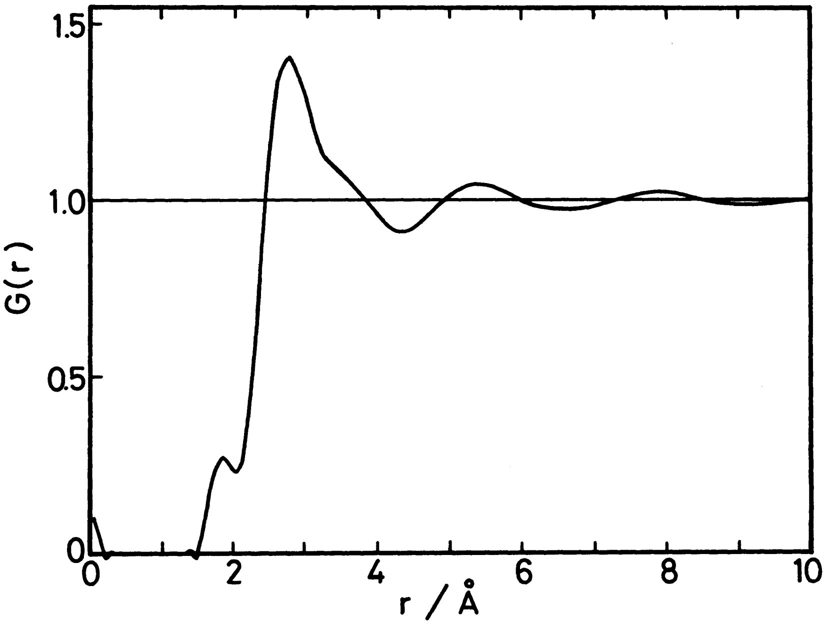

Fig. 1. Correlation function G(r) of molten LiF-KF equimolar mixture at 545 °C.

X-ray diffraction analysis are almost the same as those of the molten pure salts and have concluded that the first peak positions of unlike ion pairs may not change on mixing two pure ionic melts. In the present study, the first peak position and coordination number of Li^+-F^- pair in the mixture obtained from the analysis of RDF were found to be nearly equal to those in the molten pure LiF at 875 °C analysed by Vaslow and Narten.6) The first peak as seen in Fig. 1 is separable evidently from the second peak at 2.75 Å. Since the radius of F^- ion is less than that of Cl^- ion, the fall between the first and second peaks seems to be somewhat larger than that of the molten LiCl-KCl mixture.

As expected, the second peak at 2.75 Å is close to the distance, 2.65 Å, of the nearest neighbour K^+-F^- pair in the molten pure KF analysed by Zarzycki.7) The area of this peak, however, is much larger than that obtained by assuming the same coordination number as the first one in the pure melt. The nearest ion pairs with similar distances to the K^+-F^- pair, e.g., F^--F^- pair, will contribute to this peak. Based on the conclusion by Okada et al., further examinations using the Debye equation are now in progress.

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