— Communication —

Extended X-Ray Absorption Fine Structure Spectroscopic Study of PbCl₂ Molten Salt

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The structural parameters of molten PbCl₂ have been re-examined by EXAFS spectroscopy. The analysis of the experimental results has been performed, by using a combination of molecular dynamic (MD) simulations and multiple scattering code (FEFF). It is found that in molten PbCl₂ each Pb atom is surrounded by near six Cl atoms at an average distance of 0.283 nm.

Key Words : EXAFS Spectroscopy, Molecular Dynamic (MD) Simulations, Molten Salt

1 Introduction

Extended X-ray absorption fine structure (EXAFS) study allows to confirm directly a local coordination in melts by an analysis of the EXAFS function $\chi(k)$ which is defined as follows

$$\chi(k) = (\mu - \mu_0) / \mu_0 \quad (1)$$

where μ and μ_0 , in our case, refer to the absorption by Pb atom in the specimen and in the free state, respectively.

The structural data of the molten PbCl₂ system have been reported previously but they reveal the significant discrepancies. Ohno *et al.*¹⁾ have found out, by using CuK α radiation in X-ray diffraction analysis, that in molten PbCl₂, each Pb atom is surrounded by about eight Cl atoms at the distances of 0.292 nm. Morikawa *et al.*²⁾ have carried out X-ray measurements by using MoK α irradiation. According to them, each Pb atom is surrounded by three Cl atoms at an average distance of 0.263 nm as well as four Cl atoms of 0.314 nm, and the coordination number of the Pb atom is seven.

In the present paper we attempt to re-examine structural data of molten PbCl₂ at 873 ± 0.5 K by using EXAFS spectroscopy beyond the PbL₃-edge. Although the EXAFS experiments of molten salts have scarcely been made due to the experimental difficulty, it is very powerful tool to know very short-range configuration around ions in question. The commercially available code FEFF has been used to analyze EXAFS data, however, it is not clear whether it works well for our system. Then we examined effectiveness of this code for the solid PbCl₂ whose structure is well defined.³⁾ The MD simulations of liquid PbCl₂ with 3 kinds of ionic radii of Pb²⁺ were carried out to obtain the function $\chi(k)$ with the FEFF code. The obtained $\chi(k)$ functions were compared with the experimental one to know the coordination

number of Cl⁻ around Pb²⁺.

2 Experimental

Anhydrous PbCl₂ (Merck, 99.98 % of purity) was pre-dried in an argon atmosphere and, then, placed into the quartz cell for the measurements inside a furnace (Fig.1). The sample thickness should be defined accurately, in order to get enough EXAFS signal beyond its absorption edge, with $\mu d \cong 2.5$ -3.0, thus, the sample thickness (d) was maintained about 10 μ m.

The EXAFS measurements have been carried out by using the EXAFS spectrometer (Rigaku Corp.) with the rotating molybdenum target. Tube voltage and tube current were of +25 kV and 250 mA, respectively, within a scanning energy range of 12.800 keV-13.600 keV. The Ge (400) monochromator crystal and the slits were chosen to get a better possible energy resolution and an observed sharpness near the PbL₃ edge region. Figure 2 shows the measured EXAFS spectra after background removal.

3 Data Analysis

In order to extract $\chi(k)$ from the experimental

Fig. 1 The quartz cell with PbCl₂ melt (schematically) for EXAFS measurements.

Fig. 2 The experimental EXAFS spectra for the solid and the molten PbCl_2 after background removal.

spectrum several steps should be done. The first step is a background subtraction, which avoids, by using Victoreen fit, an excitation on the low-energy side before the edge. The second step is a spline technique when the absorption spectrum above the edge is divided and fit by the third-order polynomials and then the EXAFS function, $\chi(k)$, can be extracted at the observed region. Further, the Fourier transform of $\chi(k)$ yields a radial structure function $\phi(r)$, while, in our case, we are estimating structural parameters directly from a radial pair distribution plot, since values of phase shifts and back-scattering amplitudes are not available for PbCl_2 melt.

In the case of melts or liquids the EXAFS spectrum should be constructed as a function of separation distance for pairs of ions. Thus, we attempt herein to generate the EXAFS spectrum directly from ion trajectories by using molecular dynamics (MD) simulations proposed by Nose.⁴⁾ The pair-potentials used for the simulation were of Born-Mayer-Huggins type ;

$$\phi_{ij}(r) = z_i z_j e^2 / r + A_{ij} b \exp \{ (1/\rho) (\sigma_i + \sigma_j - r) \} \quad (2)$$

where z is the number of ionic charge; e , a unit charge; A_{ij} , Pauling factor; b , a constant; ρ , a constant called the "softness parameter"; σ , a parameter representing the ionic radius and r is the distance between ion i and ion j . These parameters for the case of PbCl_2 melt, when coordination number is 6, are listed in Table 1.

Configurations taken from MD simulations, after running by 3000 steps each time, were used then, as the input parameters to the multiple scattering code FEFF (version 7.02),⁵⁻⁷⁾ which produces an EXAFS spectrum for each ion complex. After a combining these spectra the averaged spectrum was obtained and compared with the experiment.

The effectiveness of FEFF code was demonstrated

by defining $\chi(k)$ for the PbCl_2 crystal at room temperature. Figure 3 shows a good agreement between the experimental curve and the calculated ones which were obtained at Debye temperature of 600 K but one of them is, additionally, considered to be with an energy shift and a broadening caused by error in Fermi level.⁵⁻⁷⁾

4 Results and Discussion

Figure 4 is the plot of the experimental and the simulated $\chi(k)$ as a function of a Δk -space range which, in our case, is limited by 50 nm^{-1} . One curve corresponds to the experimental result and the other three are the simulated curves obtained after a run-

Table 1 The parameters used in MD simulations for PbCl_2 melt at 873 K for coordination number 6.

A_{ij}	b (J)	ρ (nm)	σ (nm)
1.500 _(Pb Pb)	0.338×10^{-19}	0.033	0.123 _(Pb)
1.125 _(Pb Cl)			0.180 _(Cl)
0.750 _(Cl Cl)

Fig. 3 The experimental (solid) and the calculated $\chi(k)$ for the PbCl_2 crystal at room temperature. (Debye temperature is 600 K; dotted line is with error corrections, dashed line is without)

Fig. 4 The experimental (solid line) and calculated $\chi(k)$ for PbCl_2 at 873 K for various coordination numbers:

- — coordination number is 6,
- ▲ — coordination number is 7,
- — coordination number is 8.

ning of MD and FEFF programs by changing the calculated values of ionic radii on different coordination numbers. We have simulated here three states of Pb ion surroundings corresponded to the about 8, 7, and 6 coordination numbers, respectively.⁸⁾ The function of $\chi(k)$ is defined as follows⁹⁾

$$\chi(k) = \sum_j \frac{N_j f_j(k)}{kr_j^2} \sin(2kr_j + \varphi_{ij}(k)) \quad (3)$$

where $f_j(k)$ is the back scattering amplitude of atomic species j , N_j is the coordination number of atom j , and $\varphi_{ij}(k)$ is the total phase shift. The Eq. (3) shows that periodicity of $\chi(k)$ is determined by r_j . The mean ionic separation distance r_j depends on the coordination number, that is, the larger the coordination number becomes, the longer the mean ionic separation distance becomes.

The plot clearly reveals that the curve of about 6 coordination number tends to be in a closer agreement with the experimental one, while the others do not. For the case of 6 coordination number the radial pair distribution functions, $G(R)$, for the Pb-Cl, Pb-Pb, and Cl-Cl distances, were calculated from the simulations and are shown in Fig. 5. The curve for Pb-Cl distance clearly demonstrates a sharp peak centered at about 0.283 nm. The curves of the running coor-

Fig. 5 The calculated radial distribution functions $G(R)$ of PbCl_2 melt for the case when the coordination number is 6.

Fig. 6 The curves of the running coordination numbers $N(R)$ calculated from $G(R)$ functions: solid line is for Pb-Cl, dashed line is for Cl-Cl and dotted line is for Pb-Pb combinations.

dination numbers $N(R)$ calculated from the $G(R)$ functions are shown in Fig. 6 and all parameters, together with those reported before, are summarized in Table 2.

In the case of PbCl_2 crystal each lead atom has about two chlorine atoms at 0.267 nm, one each at 0.305 nm, 0.308 nm, and 0.288 nm, and two each at 0.313 nm and 0.329 nm.³⁾ Thus a cell of the PbCl_2 crystal is usually presented so as each Pb atom is surrounded by nine Cl atoms, six of which lie at the apices of a trigonal prism and the remaining three beyond to the centres of the three prism faces. As it was mentioned above, in the case of melt, a decreasing of the coordination number, in spite of a decrease in density, was every time observed. In ref. ²⁾ the last was explained, on a base of the distorted CaF_2 -type model, as a changing of the Cl atom coordination. The authors interpret that half of the Cl atoms form ClPb_4 tetrahedra and the rest form ClPb_3 pyramids, therefore each Pb atom should be surrounded by seven Cl atoms. In our case, we have observed a decreasing of the coordination number to six and, meanwhile, a number of chlorine-chlorine neighbors increases while a distance decreases. Although from the data available, it is difficult to develop a cell model of the PbCl_2 melt, the last two points are an evidence of a cell distortion which might be caused, for example, by a formation of some high ionic $\text{Pb}\cdots\text{Cl}$ complexes in the melt. However, Maroni¹⁰⁾ has observed no bands after Raman spectroscopy measurements in pure molten PbCl_2 that means PbCl_2 melt appears to have very little bonded structure

Table 2 The nearest-neighbor numbers and the nearest distances for PbCl_2 melt at 873 K.

Peak position/nm	Coordination number
Pb-Cl 0.283; (0.292 ¹⁾ ; 0.263, 0.314 ²⁾	6.2; (8.0 (7.4) ¹⁾ ; 7.0 ²⁾
Pb-Pb 0.506; (0.485 ¹⁾)	11.1; (8.0 ¹⁾)
Cl-Cl 0.382; (0.390 ¹⁾)	12.4; (10.0 ¹⁾)

Numbers in parenthesis are the data from the references 1) and 2)

Fig. 7 The calculated angular distribution function of Cl-Pb-Cl and a probable schematic image of the distorted PbCl_2 sub-cell of molten PbCl_2 .

which correlates with our results. Figure 7 shows the calculated angle distribution function and a probable schematic image of Pb-Cl cell of molten PbCl_2 . The plot shows two peaks which correspond to the distortion angles of about 78° and 168° .

5 Conclusion

EXAFS measurements of the PbCl_2 at 873 K were carried out in this work. The experimental geometry and, especially, the defined optimal thickness of the melt sample have allowed us to get the sufficiently resolved EXAFS spectrum.

The data analysis shows that a combination of molecular dynamic simulations with multiple scattering (FEFF) calculations is a useful tool to interpret EXAFS results, particularly in the case, when data of phase shifts and back-scattering amplitudes are not available.

The data analysis reveals that in molten PbCl_2 a number of the chlorine neighbors of Pb atom tends to six at an average distance of 0.283 nm. This signifi-

cant decreasing in a coordination number, compare with a crystalline state, we consider, might be a cause of a bond breaking in PbCl_2 melt which distorts a Pb-Cl local structure.

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