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

\[
\chi(k) = \frac{\mu - \mu_0}{\mu_0}
\]

where \( \mu \) and \( \mu_0 \), 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 CuKα 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 MoKα 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 \( \mu d \approx 2.5-3.0 \), thus, the sample thickness (\( d \)) was maintained about 10 \( \mu m \).

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

![Diagram of quartz cell with PbCl₂ melt](image)
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 $\Delta k$-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>
<thead>
<tr>
<th>$A_{ij}$</th>
<th>$b$ (J)</th>
<th>$\rho$ (nm)</th>
<th>$\sigma$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.508 (Pb)</td>
<td>0.338 $\times 10^{-19}$</td>
<td>0.033</td>
<td>0.123 (Pb)</td>
</tr>
<tr>
<td>1.125 (Pb, Cl)</td>
<td></td>
<td></td>
<td>0.180 (Cl)</td>
</tr>
<tr>
<td>0.750 (Cl, Cl)</td>
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</tbody>
</table>

The effectiveness of FEFF code was demonstrated

![Figure 3](image3.png)

**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.)

![Figure 4](image4.png)

**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. The function of $\chi(k)$ is defined as follows:

$$\chi(k) = \sum_{j} \frac{N_j f_j(k)}{kr_j^3} \sin(2kr_j + \varphi_j(k))$$

(3)

where $f_j(k)$ is the back scattering amplitude of atomic species $j$, $N_j$ is the coordination number of atom $j$, and $\varphi_j(k)$ 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 coordination 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. 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. 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 CIPb$_4$ tetrahedra and the rest form CIPb$_3$ 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 Pb…Cl complexes in the melt. However, Maroni 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.

<table>
<thead>
<tr>
<th>Peak position/nm</th>
<th>Coordination number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb-Cl 0.283; 0.292$^{11}$; 0.263, 0.314$^{11}$</td>
<td>6.2; (8.0; 7.4)$^{11}$; 7.0$^{11}$</td>
</tr>
<tr>
<td>Pb-Pb 0.506; 0.485$^{11}$</td>
<td>11.1; (8.0)$^{11}$</td>
</tr>
<tr>
<td>Cl-Cl 0.382; 0.390$^{11}$</td>
<td>12.4; (10.0)$^{11}$</td>
</tr>
</tbody>
</table>

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

![Fig. 5](image5.png)  The calculated radial distribution functions $G(R)$ of PbCl$_2$ melt for the case when the coordination number is 6.

![Fig. 6](image6.png)  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.

![Fig. 7](image7.png)  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 significant 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.

References