



	Experiment title: Local order in liquid zinc halides at high pressure and high temperature	Experiment number: HS 1634
Beamline: ID24	Date of experiment: from: 6/03/2002 to: 10/03/2002	Date of report: 30/10/2002
Shifts: 12	Local contact(s): Sakura Pascarelli	<i>Received at ESRF:</i>
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Report: The structural properties of liquids and glasses of tetrahedral oxides, including the degree of short-range and intermediate order, and the dependence of these properties on pressure and temperature is of fundamental and technical interest. Structural models based on an open network of corner shared tetrahedra have been used to explain many of the physical properties of the liquid and glassy phases of such systems. However, disruption of this tetrahedral framework has an important effect on the physical properties of these network liquids and glasses. Pressure increase, leading to modifications of the short-range order and coordination changes, is a method to obtain such a disruption. Direct *in situ* observations of coordination changes in MO₂-type oxides has been difficult to obtain, in opposite to the same changes in the analogous crystalline materials. Observing possible pressure-induced coordination changes inside the liquid phase of MO₂-type oxide with tetrahedral network requires temperature much too high for the diamond anvil cell experiments. Therefore, in order to make it more accessible, we have proposed to substitute the oxide by the zinc chloride, a glass forming material which melting point and glass transition temperature are relatively low ($T_m = 593\text{K}$, $T_g = 375\text{K}$).

The aim of the project was to follow by X-rays methods the local organisation around the zinc cation with varying temperature and pressure.

Experimental method

The sample was pure anhydrous crystalline ZnCl₂ powder finely ground in order to be loaded in a diamond anvil cell together with a pressure marker (ruby). The pressure and temperature ranges explored were from ambient conditions up to 5GPa and 420°C. Glitches due to the Bragg peaks of the diamond have been rejected from the energy range of interest by taking advantage of the ID24 beamline facilities.

Experiments were performed at the zinc K-edge (9659 eV).

First run : We monitored the change in the structure at constant pressure (~1.3GPa) increasing temperature up to 400°C. Then pressure was increased keeping temperature constant equal to 400°C. And we went back at ambient.

Second run : Same sample. Pressure was kept constant (~3.5GPa) and temperature is increased step by step from room temperature to 420°C. Then pressure was decreased at constant temperature.

Third run : New sample. We followed the change of the structure at room temperature, increasing pressure up to 3.5GPa. Then temperature was increased up to 420°C and pressure decreased until 2GPa.

First results

Three phases of zinc chloride had been observed during the runs (fig.1) : a low pressure crystalline phase with a tetrahedral structure, at high pressure one with an octahedral structure and a liquid phase with a tetrahedral framework.

The EXAFS spectra are analysed using the gnxas software package. The coordination numbers but also the atomic distances are obtained for the first two shells (fig.2 is an example of a fit).

The transition between the two crystalline phases happens around 2.5 GPa on compression, at room temperature. And at 420°C, transition happens at the same pressure. The atomic distances for the first two shells, i.e. the distance between the Cl atoms at the corners of the tetrahedron and the central Zn atom (first shell), and the Zn-Zn distance, are the same in the low pressure crystalline phase and the liquid phase and don't change with temperature, in the studied range, which is consistent with previous results [7], [8], [9], [10]. Furthermore, the distances seem to be pressure independent too, which shows a strong covalent character of the bonds.

With more accurate analyses we expect to have more information about the solid-solid transition and the solid-liquid one, and also about the third shell in the two crystalline phases.

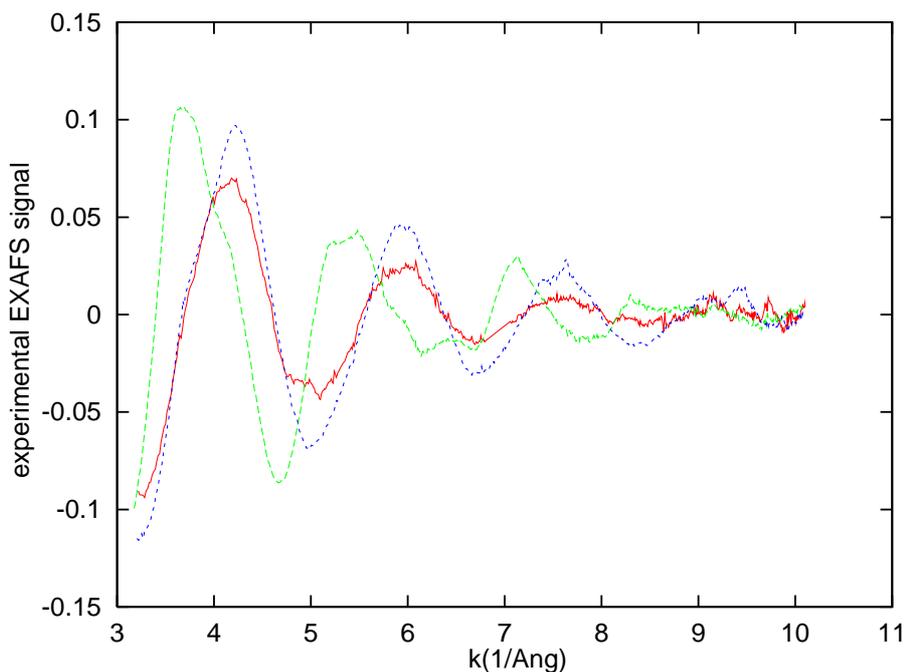


Figure 1 : EXAFS signals of three phases of ZnCl₂

Low pressure crystalline phase (blue curve), high pressure crystalline phase (green curve), liquid phase (red curve)

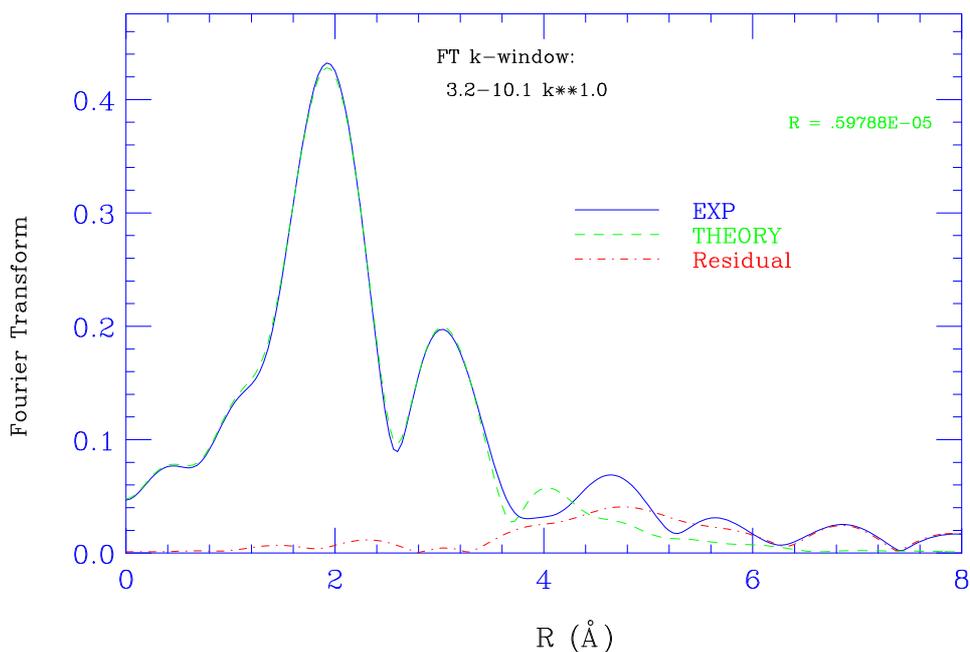


Figure 2 : Fit of the Fourier transform of the EXAFS signal, for the high pressure phase of crystalline ZnCl_2 (only the two first shells around the zinc atom are considered)

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