



	Experiment title: EXAFS study of pressure-induced local coordination transition in molten ZnCl ₂	Experiment number: HD266
Beamline: BM29	Date of experiment: from: 08/04/2008 to: 16/04/2008	Date of report: 17/10/2008
Shifts: 24	Local contact(s): Giuliana Aquilanti	<i>Received at ESRF:</i>
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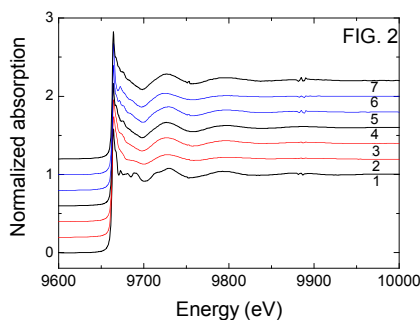
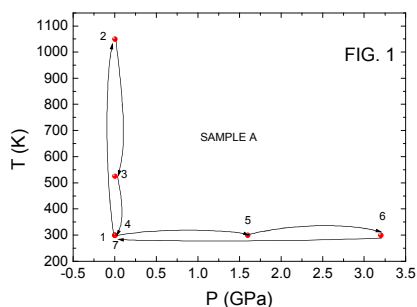
Report:

ZnCl₂ belongs to a class of halides that have a strong “covalent” contribution to the bonding in both the solid and liquid states and, at ambient pressure, the four-fold coordination observed for Zn²⁺ ions in the crystal is retained in the melt [1-3]. The structure of compressed liquid ZnCl₂ has been investigated by using different techniques. For example, a recent x-ray diffraction study at pressures up to 3 GPa indicates a breakdown of the intermediate range order of the network formed by ZnCl₄²⁻ tetrahedra in the low pressure range followed, on further compression, by a sharp structural transformation in the liquid with a possible *increase* in the Zn²⁺ coordination number from four to six [4]. The aim of this experiment was to study the variations of the local structure of molten ZnCl₂, as a function of temperature (*T*) and pressure (*p*), using x-ray absorption spectroscopy (XAS).

Several runs were made on different samples in which a variety of *p-T* paths were followed. The initial sample A gave unexpected results which suggested a reaction between ZnCl₂ and the BN used as a matrix material. Subsequent runs were used to understand the issues encountered for sample A and were designed to test the reaction hypothesis.

SAMPLES A & B

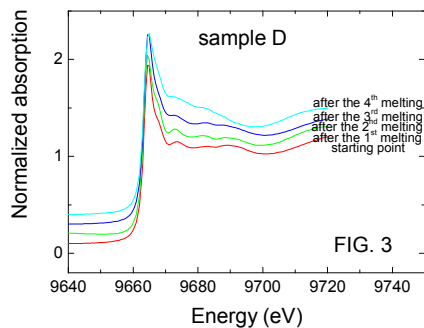
Sample A was press-pelleted from glassy ZnCl₂ which was finely ground and mixed with BN. A ZnCl₂:BN weight ratio of 1:40 was chosen to allow for the need for a cylindrical pellet to be inserted into an annular graphite furnace sitting in a pressure gasket of 7 mm diameter. A gold foil was inserted between the furnace and gasket to cross-calibrate its *p-V-T* equation of state with that of BN and hence determine *p* and *T* for each XAS measurement point. The temperature was also estimated using temperature vs. power curves previously measured for different oil pressures. Although we started with glassy ZnCl₂, the XAS spectrum for ambient conditions showed the typical features of a crystalline material, such as high frequency oscillations embedded



in the main signal. The measured XRD pattern also showed Bragg reflections attributable to ZnCl₂ but the dilution of this material with BN meant that any further investigation of the crystal structure was impossible. The *p-T* path followed for sample A is shown in FIG. 1 and the corresponding spectra

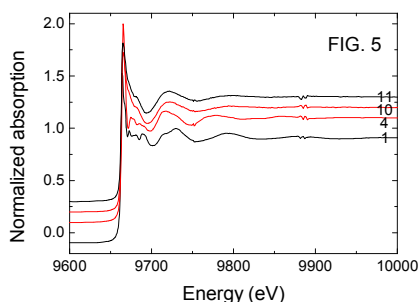
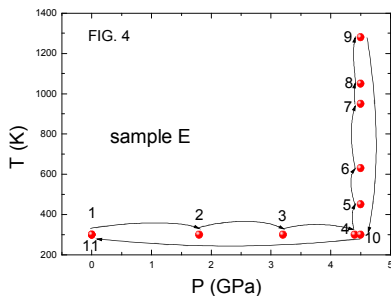
are given in FIG. 2. Spectra 1, 4 and 7 were measured under the same thermodynamic conditions but show different XANES features, suggesting a chemical reaction between ZnCl_2 and BN at high T . The reaction product could not be identified by XRD, partly due to the level of dilution. Sample B comprised ZnCl_2 :BN with a weight ratio of 1:15. The sample was *not* press-pelleted and it was held in a glass capillary. No Bragg peaks were observed *i.e.* the press-pelleting procedure induces crystallization, consistent with our previous diffraction studies (ID27 experiment HD146). At the start of run D (see below) the crystalline phase was confirmed to be a tetragonal red- HgI_2 -type structure.

SAMPLES C & D



For runs C and D the temperature was increased and decreased about the melting point at ambient pressure. Sample C consisted of ZnCl_2 *without* any matrix (BN) material and sample D consisted of a ZnCl_2 :BN mixture with a weight ratio of 1:15. Both samples were held in a glass capillary. Although run C always gave similar XAS features for several temperature cycles, run D gave XANES features that were different to the starting point after the first temperature cycle (see FIG 3). The corresponding XRD patterns could not be attributed to the ZnCl_2 phases encountered in our previous work (experiment HD146) for the same p - T range, consistent with a reaction between ZnCl_2 and BN.

SAMPLE E



Sample E comprised a ZnCl_2 :BN mixture with a weight ratio of 1:15 which was press-pelleted and inserted into a furnace in a high pressure gasket. The measured p - T path is shown in FIG. 4 and several of the spectra are shown in FIG. 5. The data are again consistent with a reaction between ZnCl_2

and BN since different spectra were recorded for equivalent thermodynamic conditions (*e.g.* spectra 4 and 10 in FIG 5). Also we know (experiment HD146) that the ZnCl_2 structures found at pressures above 3-4 GPa are not recoverable to ambient conditions but spectra 10 & 11 in FIG 5 are comparable.

SAMPLE F

Sample F was prepared in the same way as sample E. The temperature was increased and decreased at successively higher pressure points in order to map the melting curve at different pressures. The melting point agreed with the literature value at ambient pressure. However, during the first melting cycle at higher pressure the melting point exceeded the literature value (and the value we measured during experiment HD146) by about 300 K [4]. This is further evidence for a chemical reaction between ZnCl_2 and BN.

In conclusion, we were not able to measure EXAFS spectra for pure liquid ZnCl_2 at any pressure using heavily-diluted ZnCl_2 -BN mixtures. In addition, given the ZnCl_2 :BN weight ratio it was impossible to determine, by diffraction, the different phases of ZnCl_2 under different high p - T conditions or the nature of the compound obtained after the chemical reaction between ZnCl_2 and BN. For these reasons we intend to make a new experiment using a resistively heated diamond anvil cell (DAC). The DAC will allow us to use a *pure* ZnCl_2 powder *i.e.* there will be *no* need to mix it with any matrix material as the typical sample thickness ($\sim 30 \mu\text{m}$) is suitable for XAS at the Zn K-edge, as demonstrated in some of our earlier work [5].

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