



	Experiment title: In situ high pressure EXAFS spectroscopy of zinc polyphosphate	Experiment number: MA-316
Beamline: BM29 and ID24	Date of experiment: from: 11/04/2007 to: 17/04/2007 and 14/05/2007 to: 22/05/2007	Date of report: 25/02/2007
Shifts: 38	Local contact(s): Giuliana Aquilanti	<i>Received at ESRF:</i>
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Report:

ZnDTP is used in engine lubrication to reduce wear. However this additive is at the origin of massive release of sulphured and phosphored emissions, both polluting the environment. The understanding of the lubrication mechanism of this molecule is a key point in order to optimize the lubricant composition.

When it is solicited in a tribological lubricated contact, ZnDTP forms an anti-wear film on metal surfaces, containing zinc phosphates and called "tribofilm". This film protects the surfaces against abrasion caused by the iron oxide particles generated during the friction. Previous studies showed that the structure of the tribofilm in term of length of the phosphate chains is heterogeneous. Long chains (metaphosphate composition) would form on the immediate top surface of the substrate asperities, while shortest (orthophosphate composition) would be located in the vicinity of metal surface. From these considerations, the main question is: i) what is the origin of the phosphate difference in chain length, is there a pressure effect and how does it act? High pressure Raman experiments (performed by us) showed the absence of chains length modification with pressure (up to 17GPa), whatever the type of the considered phosphate. What concern Zinc Metaphosphate and Zinc Orthophosphate, the pressure induces nevertheless phases transition around 3 GPa. Results obtained for these samples showed that the P-O bonds are more sensitive to these transformations. Since the P-O bonds are directly involved in the local environment of the Zinc atom, *in-situ* High pressure XAS experiments at Zn K-edge were performed on different zinc phosphate samples (from the shortest chain length to the longest : Zinc Orthophosphate $Zn_3(PO_4)_2$, Zinc Pyrophosphate $Zn_2P_2O_7$ and Zinc Metaphosphate $Zn(PO_3)_2$). The goal of these synchrotron experiments was to investigate the role of zinc during the compression of each compound. Up to 10 GPa, experiments using the Paris-Edinburgh (PE) press were performed on BM29. For each sample, XAFS spectra up to 10 GPa by 1-2 GPa steps were measured. 18 Shifts were allowed for this part. In the range of 10 to 30 GPa, experiments using a diamond anvil cell were performed on ID24. Data were recorded by 1-2 GPa steps too. Data points were also recorded during the decompression to probe the reversible nature or not of the transition. For this part, 20 shifts were allocated.

Figure 1a shows the evolution of the absorption spectra at the Zn K-edge with the pressure for the Zinc orthophosphate. Near the edge, continuous and irreversible modifications are observed on the spectrum between 0 and 3 GPa. This suggests a rearrangement of the oxygen atoms positions around the Zinc atom. Above 3 GPa and up to 8 GPa, no more modification is then observed. The data are, in this part of the spectrum, quite difficult to interpret. Numerical simulations are necessary. Figure 1b shows the evolution of

the oscillations extracted from absorption spectra at the Zn K-edge, first between 0 and 7 GPa and then during the decompression. A progressive disappearance of high frequency oscillations between 0 and 3 GPa can be observed. This corresponds to a loss of the local order around the Zn atom where the second neighbours are involved. Figure 2 shows the evolution with the pressure of the relative distance between the Zn atom and the first neighbours. The mean Zn-O distance increases in an irreversible way between 0 and 3 GPa and then stabilises until 7 GPa. The modifications observed on the spectra at the absorption edge (figure 1a), the amorphisation observed around the Zinc (figure 1b) and the increase of the Zn-O distance (figure 2) are the signatures of structural changes around the Zn atom in the pressed sample. This effect of the pressure on the Zinc environment occurs in the same pressure range that the phase transitions observed in Raman spectroscopy and which affect the phosphate tetrahedron. The correlation between these two results shows that the structure of the Zinc orthophosphate is strongly affected between 0 and 3 GPa. Nevertheless, it is important to point out that this structural change is irreversible and can not be attributed to a change in the oxidation degree of the Zn but rather to a change of its coordination induced by this phase transition. These preliminary results are extremely important for us since they are in contradiction with some theoretical studies (numerical simulations) published by others authors and which suggest a reversible Zn coordination change with the pressure.

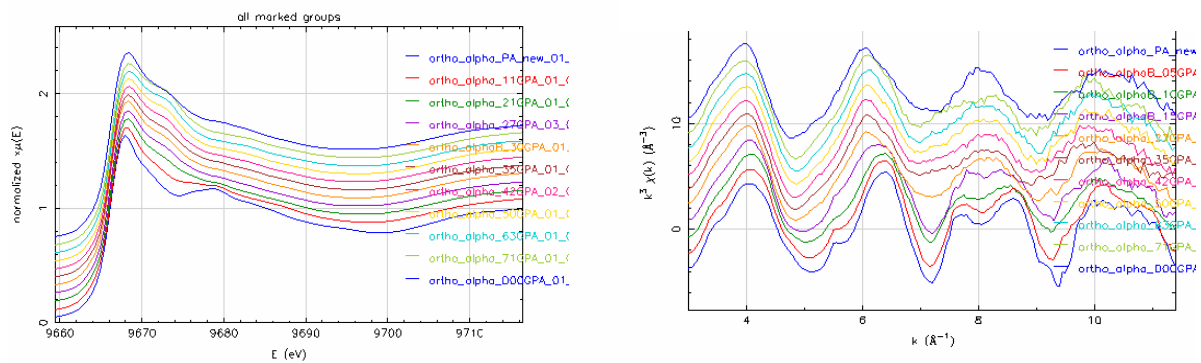


Figure 1: a) Evolution with the pressure of the absorption spectrum at the Zn K-edge for the Zn orthophosphate up to 7 GPa and after decompression – b) Evolution with the pressure of the structure at the Zn K-edge for the orthophosphate up to 7 GPa and after decompression.

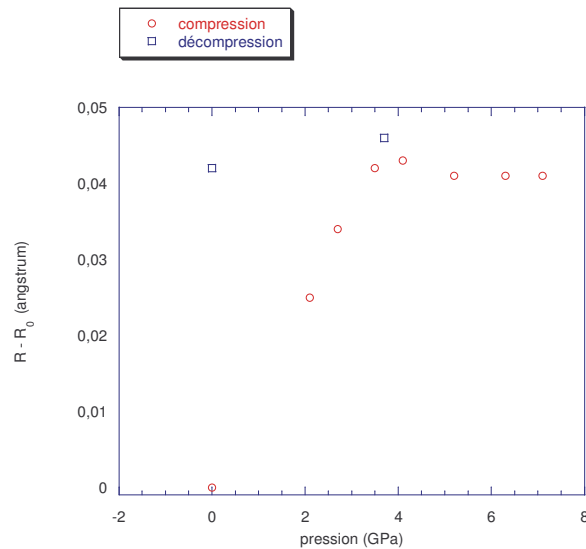


Figure 2: Evolution of the first neighbours distance with the pressure after compression and decompression. The reference ZnO distance is 1.86Å.

The analysis of data recorded from ID24 is still in progress. Nevertheless a first tendency is observed. Above 10 GPa and up to 20 GPa, no further structural change appears in the structure of the orthophosphate. What concern other polyphosphate samples, we can note for the pyrophosphate the absence of structural change whatever the pressure. The interpretation of data recorded for the metaphosphate is still in progress. Data analysis should be achieved within the next 6 months.