ESRF	**Experiment title:** **Study of Phase Properties of Intercalates by SWAXS**	**Experiment number**: SC-1364
Beamline: BM26B	**Date of experiment**: from: 3. 12. 2003 to: 5. 12. 2003	**Date of report**: 27.2.2004
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Report:

Intercalation represents a reversible insertion of mobile atomic or molecular guest species into solid layer host lattice. Intercalates of zirconium phosphate (α-$Zr(HPO_4)_2 \cdot H_2O$, hereafter ZrP) [1] belong among largely studied compounds. In our previous measurements on ZrP-liquid alcohol systems [2], we have observed a phase transition induced by temperature changes. In this phase transition the bimolecular film of alkanols intercalated undergoes a change from an *all-trans* conformation to a conformation in which the O-C1-C2-C3 torsion angle changes from 180 to 136° during cooling the samples. This leads to the change of the alkyl chain inclination from 59.6° to 47.1°. Consequently, the interlayer distance, that is a distance of ZrP layers, decreases. From the macroscopic point of view, the changes of the interlayer distance result in the change of the thickness of crystals of the sample. On the other hand, we can presume that a force exerted to the crystal would decrease its thickness and thus the interlayer distance. The change of the interlayer distance in our case could lead into the change of the conformation of alkanol chains. The force exerted on the crystal can be applied using hydrostatic pressure in a system consisting of a suspension of the solid sample in a liquid medium.

Recently, we have studied the dependence of the interlayer distance of intercalates of 1-nonanol, 1-octanol and 1-decanol on pressure [3]. The phase transitions of the ZrP intercalates with other 1-alkanols

(heptanol, undecanol and dodecanol) were studied at ESRF in Grenoble. Similarly as in the case of the 1-nonanol intercalate, there is a gradual linear decrease of the interlayer distance of intercalates of alkanols with odd number of carbon atoms with increasing pressure at constant temperature up to a certain value of pressure, under which the second phase appears. The interlayer distance of this second phase also decreases with increasing pressure. Both phases are present in the area of the phase transition. The dependence of the interlayer distance of the heptanol intercalate is given in Figure 1. For dodecanol intercalated ZrP (Fig. 2), the interlayer distance vs. pressure dependence is different, similarly as in the case of ZrP intercalated with octanol or decanol. At first, this dependence is linear. The phase transition occurs in broad range of pressures, where the interlayer distance decreases slowly. Coexistence of both phases was not observed.

In intercalates containing a bimolecular film of the guest molecules with aliphatic chains which are not perpendicular to the host layers an even-odd effect can take place [4]. This effect is given by different orientations of the terminal methyl groups of the chains for even and odd numbers of the carbon atoms in the guest chains. Therefore, we can presume that the distinctly different dependence of the interlayer distance on pressure in the case of the ZrP intercalate with alkanols with odd number of carbon atoms in the chain compared to the intercalates with alkanols with even number of carbon atoms is probably connected with the even-odd effect.

We also conducted preliminary time resolution measurements of hydrothermal synthesis of hydrotalcite-like compounds which have the general chemical formula $Mg_xLa_{1-x}(OH)_2(C_6H_5COO)_x \cdot yH_2O$, where $x<0.45$ and $y<1$. The results are illustrated in the Figure 3. It is evident that under the conditions of the experiment the reaction can be traced and the intermediate products are easily visible. Due to the lack of beam-time, the hydrothermal reaction was not completed.

References

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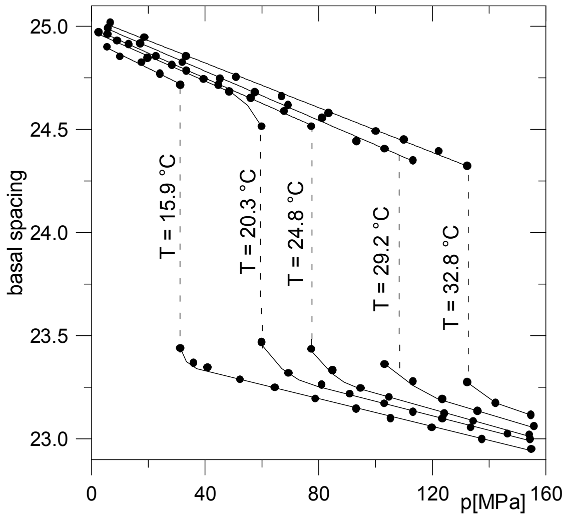

Figure 1. Dependence of the interlayer distance of the $Zr(HPO_4)_2 \cdot 2C_7H_{15}OH$ intercalate on pressure measured at various temperatures.

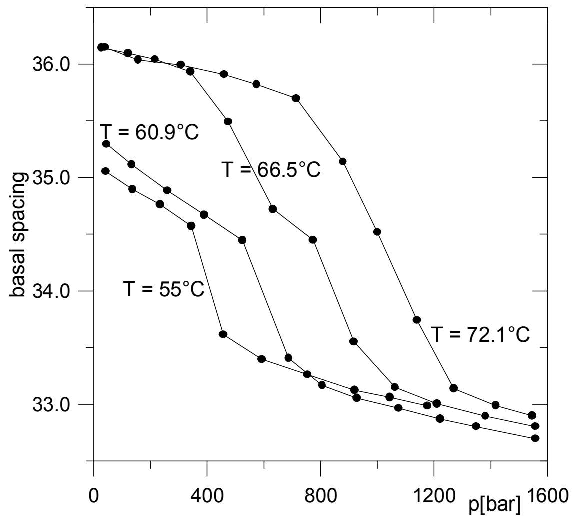

Figure 2. Dependence of the interlayer distance of the $Zr(HPO_4)_2 \cdot 2C_{12}H_{25}OH$ intercalate on pressure measured at various temperatures.

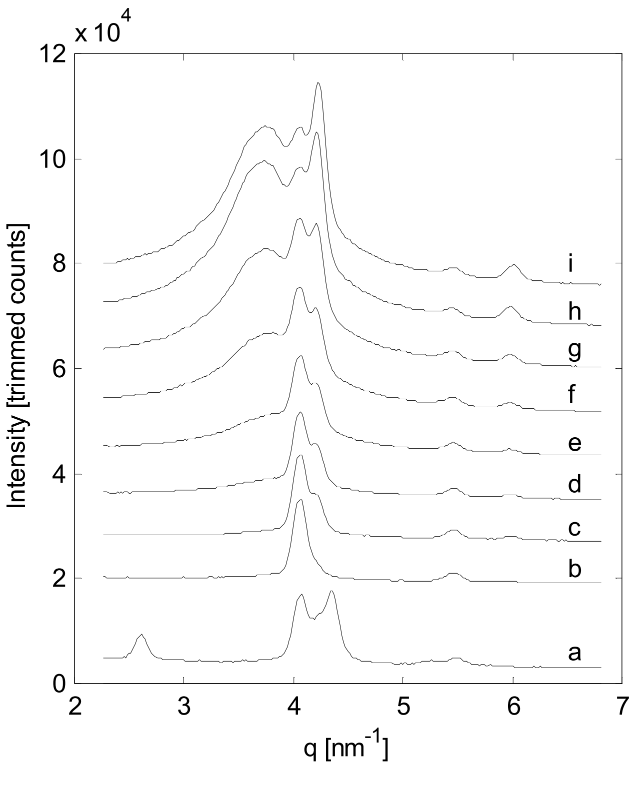

Figure 3. Selected diffractograms from the hydrothermal synthesis measurements: a) starting compound at ambient and b) at the reaction conditions. Synthesis after c) 1 hour, d) 2 hours, e) 4 hours, f) 6 hours, g) 8 hours and h) 11 hours, i) after the reaction back at ambient conditions.