	Experiment title: Under pressure: HgF_2, the end member of the mercury halides family	**Experiment number**: BM01-02-363
Beamline: BM1A	**Date of experiment**: From: 26-02-02 07:00 to: 28-02-02 07:00	**Date of report**: 04/11/02
Shifts: 6	**Local contact(s)**: Silvia Capelli	*Received at UNIL:*

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Report:

Purpose: Our recent work on the HgX_2 family has shown that very modest change of pressure and temperature (5GPa, 400K) drastically influence the structure of the solid phases. Numerous phase transformations have been observed in this moderate range of p and T. These results lead us to continue our study on HgX_2 compounds by investigating mercuric fluoride. At ambient conditions, HgF_2 is known to be cubic [1], of the CaF_2 type with a = 5.54 Å leading to a density of 9.25 g/cm^3.

Experimental method, part I: HgF_2 powdered sample, as obtained from Fluka, was loaded into a capillary in a glow-box filled of Nitrogen. Its powder diffraction pattern at room temperature was first collected on a MAR detector at a wavelength of 0.702 Å. Powder diffraction pattern were then recorded as a function of temperature, between room temperature and 528 K, at ambient pressure. Using Fit2D [2], the raw images were integrated into 1D powder spectrum.

Results part I: The room temperature powder diagram differs from the diagram simulated with the structural data published in 1933 [1]. Additional peaks are observed with the material acquired from Fluka (fig.1). Moreover, the general shape of the powder diagram reveals a bad crystal quality of the sample: huge background, broadening of several of the peaks (fig.1).
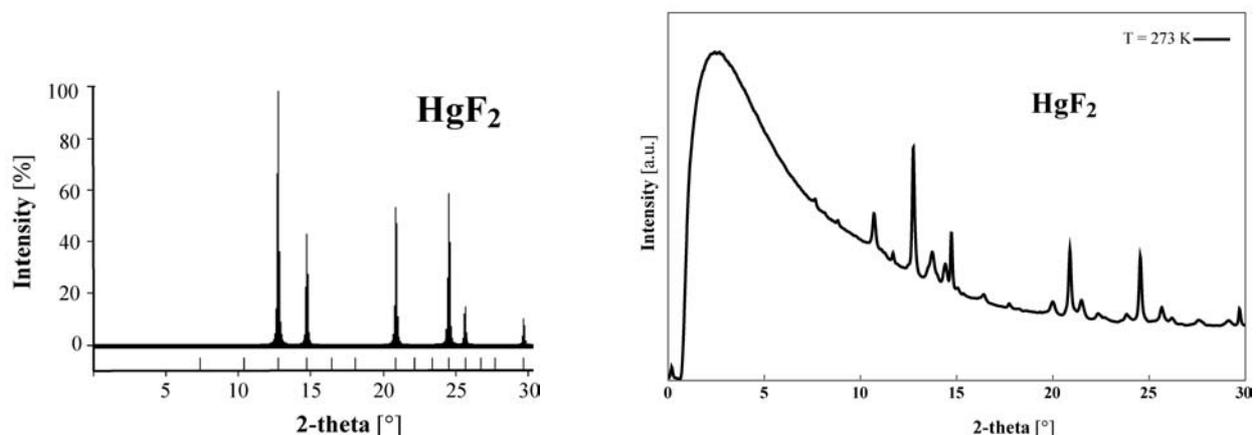

Figure 1. Room temperature powder diagram at a wavelength of 0.702 Å, simulated (left) with the structural data [1] and collected with the commercially available product (right). The much more complex patterns obtained show the possible water contamination of the sample, even a loading of the sample in Nitrogen atmosphere was not enough to prevent its degradation.

The powder diagram collected at room temperature presents the four strongest peak simulated with the structural data published in the literature [1] but show additional peaks that we were unable to explain. The most probable explanation is the hydration of the sample. Due to this problem of sample purity/quality of the available HgF_2 sample we chose to collect data on $HgCl_2$, as a function of pressure.

Experimental method, part II: HgCl$_2$ powdered sample was loaded in a diamond-anvil-cell (DAC) and its powder diffraction pattern collected on the MAR detector at a wavelength of 0.702 Å. Using Fit2D [2], the raw images were integrated into 1D powder spectrum. The pressure was determined from the fluorescence line of a ruby chip. Powder data have been collected between 0-21 GPa at room temperature using silicone oil as pressure medium.

Results, part II: At 0.7 GPa, HgCl$_2$ undergoes a continuous transition to a monoclinic phase, space group $P2_1/m$. This phase results from a slight distortion of the orthorhombic cell, β=91.01(5)° at 1.7 GPa. There are four symmetry independent Cl-Hg-Cl molecules. Their arrangement in the mirror plane is preserved, but they are now bent. The four molecules subtend Cl-Hg-Cl angles of 144.5(7), 147.0(6), 160.1(5) and 171.0(5)°. At 2.1 GPa a first order transition leads to a rhombohedral $R\bar{3}m$ phase with straight molecules. This phase is stable up to 6.0 GPa at which pressure new peaks appear in addition to those of the $R\bar{3}m$ phase. Surprisingly, two phases coexist at least up to 21 GPa.
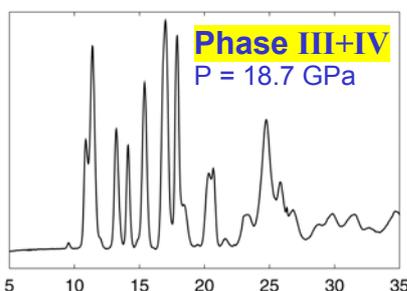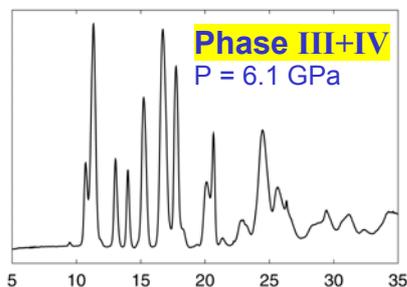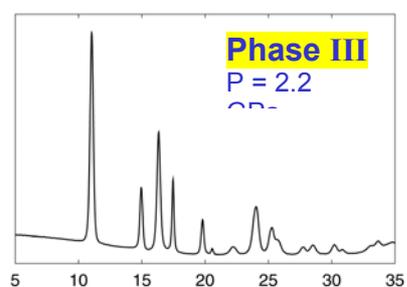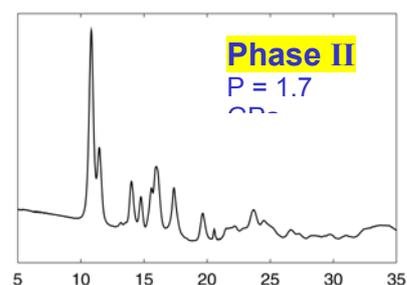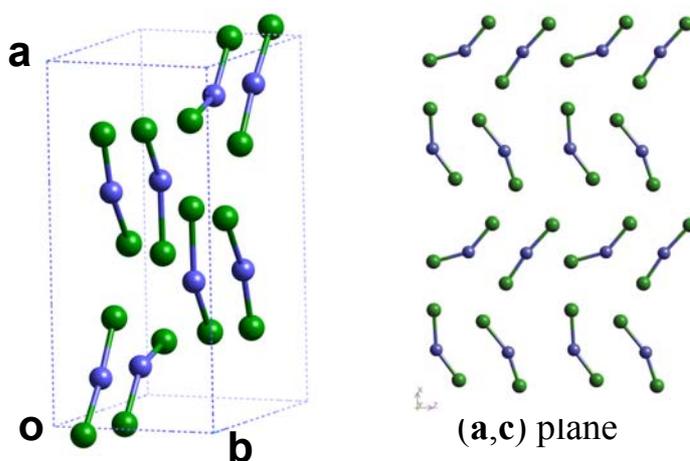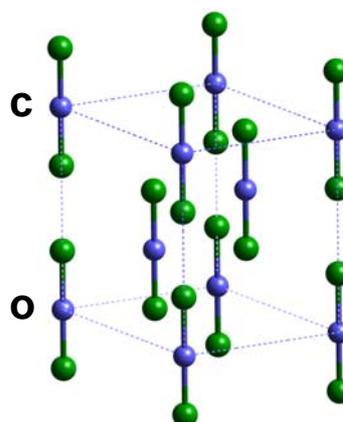

Figure 2. Left: raw powder diagrams collected as a function of pressure for HgCl$_2$, horizontal axis 2-theta in degrees, vertical axis intensity in arbitrary units. Right the two structural models of phase II and phase III, derived from Rietweld refinement.

References

[1] Ebert & Woitinek, *Zeit. Anorg. Allgemeinde Chemie* (1933), 210, p 269-272.

[2] Hammersley, *ESRF Internal Report* (1998), ESRF98HA01T, FIT2D V9.129 Reference Manual V3.1; Hammersley, *et al.*, High Press. Res., (1996), **14**, 235.