ESRF	**Experiment title:** Structural studies of solid hydrogen and solid helium under extreme conditions.	Experiment **number:HS140:** HS141; HS191
Beamline: ID09/1D30	**Date of experiment:** from: November 1996 to: April 1997	**Date of** report:20/09/97
Shifts: 60	**Local contact(s):** D.Hausermann and M.Hanfland.	*Received at ESRF.*

Names and affiliations of applicants (* indicates experimentalists):

Paul Loubeyre, Université Paris 6
René LeToullec, Université Paris 6
Frederic Datchi, Université Paris 6.

Report:

Due to the very small scattering power of solid hydrogen and solid helium at high pressure in a DAC, the method to achieve x-ray diffraction from ultra-light elements under high pressure in a DAC involves a combination of single-crystal and energy-dispersive diffraction technique with polychromatic radiation. The high brightness of a third generation synchrotron source is also needed. The lozenge geometry found in fixed-angle energy-dispersive diffraction is usefully exploited to reduce the otherwise dominant background signal from the diamond anvils with the lozenge geometry. On the other hand, the angle dispersive technique with an image plate detector was tried on a large single-crystal of hydrogen: The diffraction peaks were hardly coming out from the background. Hence, it is clear now that this standard technique for high pressure structural studies could not be used for the study of very low-Z elements, H, He, Li and perhaps Be at high pressure. Finally, it should be noted that the single-crystal diffraction technique also gives very high quality structural data at high pressure and should probably be applied to higher-Z systems if one wants to look for fine details(This is exemplified by the study of ice, ESRF Highlights 1995/1996, p. 17).

In 1994 when we started to develop this technique at the ESRF, it was believed that 50 GPa would be a limit for such single-crystal experiments. There were two major obstacles. First, the fragmentation of the single-crystal that reduces the intensity of the single crystal reflections by few orders of magnitude. Second, the design of the cell that should have a large x-ray aperture on both sides, that is x-ray transparent materials have to be used for the diamond seats in a geometry where they are not fully supported. This is a mechanical challenge because of the insufficient bending strength of such materials to hold the massive support of the diamond anvils in the 100 GPa range. A total of 81 shifts were devoted to the hydrogen problem. The breakthrough on this problem originated from the use of helium as a pressure transmitting medium that prevents the fragmentation of the single crystal and the design of a new DAC with boron support of half-sphere geometry. We have now a unique technique worldwide to perform single crystal x-ray diffraction in the Mbar range. Single-crystal x-ray diffraction on H2, He, LiH, H20, Ar(H2)2 have already been performed above IO0 GPa.

When we applied for more beamtime to determine the structure of the high pressure phases of solid H2 or to measure the isotopic shift on the EOS of helium at Mbar pressures, we were quite confident that the single-crystal x-ray technique would be straightforwardly extended in the 200 GPa range. Unfortunately, we were faced to unexpected problems and most of our beamtime was used in sorting out the reasons why we could not go above 120 GPa. it appears that the reach of 200 GPa requires a similar technical jump than the one needed to reach the 100 GPa range but this time in the preparation of the gasket and the choice of initial sample dimensions. Eleven experiments that failed have given us some clues to overcome the problems. Three major causes of failure have been disclosed :

I. Diffusion of hydrogen The quality of the single-crystal is a preliminary condition to reach the. maximum pressure. It can take 2 or 3 days to grow a very good single-crystal of H2 in helium To optimize our probability of success we were coming at the ESRF with 3 DACs and we had grown the single-crystals a mouth in a advance to be sure that everything would be ready in time, That was a mistake. We discovered that the helium surrounding the H2 single crystal was not stopping the slow diffusion of hydrogen in the rhenium gasket and that was destroying the crystal quality with time. The experiments that successfully had reached 120 GPa were prepared just before coming at the ESRF. Somehow, the growing of the single-crystals long is advance has enhanced this parasitic effect. We are now using a liner of gold to make the wall of the sample chamber. That is stopping all diffusion in the gasket. But few samples have been utilized to optimize the geometry of this composite gasket.

2. The fragmentation of the single-crystal. The successful experiments to 120 GPa were performed with 150µm central flat beveled diamonds. In that case, above 40 GPa, it was observed that the thickness of the sample chamber had reached a stable value, **hence limiting** fragmentation of the single-crystal by change of thickness. To reach higher pressures, the central flat had to be reduced to 100µm - 50µm. But this has an important consequence. We observed that the thickness of the sample chamber decreases continuously now to 100 GPa therefore accentuating the fragmentation of the single-crystal. It seems that we have not worked out empirically good initial dimensions for the sample chamber to reduce this effect,

3. Small defects in the diamond anvils. When there is a small defects in the stone, it s revealed and enhanced by diffusion of hydrogen and helium in those defects. Generally, we select our stone for very low luminescence and for very low birefringence since those very good quality stones have a reduced number of defects. It appears that a very bad series of stones was delivered to us last year. Now, we plan to test the quality of the anvils by topography beforehand.

The history of the samples studied during HS140, HS141, HSl91 is summarized in the table below.

The equations of state of hydrogen and helium have been reproducibly measured in those various runs and extended to 125 GPa. The data are presented in figure 1 and figure 2 below. They are very well fitted by a Vinet form, proposed as a quasi-universal EOS at high pressure,

Finally, we want to stress that for each campaign, lasting generally 5 days (15 shifts) we **were** coming with five DACs: 3 loaded with hydrogen, 1 with helium and an other cell loaded with an easier system (H20 or LiH) to use in case some beamtime were left at the end. Because of the many failures, among which some could be diagnosed quite rapidly, we were sometimes **left** with one or two days of beamtime at the end. The extensive single-crystal structural study of ice VII (to be submitted for publication in Nature) and complementary studies on LiD and LiH (submitted for publication to Phys. Rev. Lett.) were performed in this way,

Samples	Flat of the2 diamond anvils	maximum pressure	Reason of failure
Solid H_2 in He	100μm ⊗ 100μm	21 GPa	Diffusion of H in gasket
Solid H_2 in He	75μm ⊗ 100μm	20 GPa	Diffusion of H in gasket
Solid D_2 in He	150μm ⊗ 100μm	18 GPa	Diffusion of H in gasket
Solid H_2 in He	75μm ⊗ 50μm	25 GPa	36 H search, no peaks. Too small sample?
Solid D_2 in He	150μm ⊗ 100μm	35 GPa	Instability of Au liner
Solid D_2 in He	75μm ⊗ 50μm	28 GPa	fragmentation of crystal
Solid He	30μm ⊗ 50μm	50 GPa	Breakage of diamond
Solid He	30μm ⊗ 50μm	56 GPa	Breakage of diamond anvil
Solid H_2 in He	100μm ⊗ 100μm	125 GPa	Breakage of diamond anvil

Table 1: Summary of the experiments that failed.