ESRF	**Experiment title:** Phase diagram of Li graphite intercalation compound under P-T extreme conditions	**Experiment number:** HS-3138
Beamline: ID27	**Date of experiment:** from: 13/12/2006 to: 18/12/2006	**Date of report:** 21/11/2007
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Report:

The goal of this study was to investigate the phase diagram of light alkaline graphite intercalation compound (GICs) such as LiC_6 at high pressures and high temperatures using a radial geometry. Due to the high air-sensitivity of the sample and difficulties related to the radial geometry, we followed through the HP study with an heavier sample, i.e. CsC_8, in the classical axial geometry available at the ID27 beamline.

High-pressure (HP) XRD of CsC_8 was performed up to 14.0 GPa. A sequence of selected diffraction patterns is displayed in *Figure* **A**. The first pattern recorded at 0.2 GPa matches the hexagonal ambient structure. Inhomogeneous grain size distribution, preferential orientation effects and the identified stacking faults render a Rietveld refinement or even a Le Bail refinement extremely complex. Gradual transformations under increasing pressure is the most eye-catching feature as well as the overall decrease of intensity of the diffraction patterns. At 1.2 GPa, we observe the coexistence of the hexagonal phase with a new phase. This new phase is clearly established at 2.0 GPa. At 3.5 GPa, new changes in the diffraction pattern evidence a new phase transformation. Furthermore, we notice that the number of peaks of this last high pressure phase is lower than in the preceding phases, which could be associated to a higher cell symmetry or to a smaller lattice. As the pressure increases from 7.3 GPa to 14 GPa, the diffraction line broadening becomes more and more pronounced, and the profile becomes highly asymmetric. We deduced a linear compressibility κ_c of 1.079×10^{-2} GPa^{-1} corresponding to a linear bulk modulus B_c of 93 GPa for the hexagonal phase (CsC_8-I). The a lattice parameter was found to be very rigid in this pressure range. We estimated the bulk modulus B_v=94 GPa, close to the linear inter-plane bulk modulus.

Different attempts to determine the crystal structures of the high pressure phases appearing above 1.2 GPa and above 3.5 GPa were carried out. The presence of a diffraction line at very low angle $\sim 2^\circ$ corresponding to a *d*-spacing of 7.69 Å prompted us to look for a larger crystalline cell assuming a new stacking. We propose the space group *C222* as a possible candidate for the first HP phase. This choice corresponds to a space group search procedure with the *Crysfyre Suite* and *Checkcell* softwares. Among the possible space groups obtained, *C222* reproduced best the experimental data. The corresponding orthorhombic lattice is described in term of a supercell with parameters fitted within a Le Bail refinement. The second HP phase, observed between 3.5 and 8.0 GPa was found to be very close to the orthorhombic cell defined in RbC_8 and in CsC_4, a superdense metastable phase of Cs-GICs. We used the same space group *Fddd* and Wyckoff positions as RbC_8 for the refinement model. This supposes a change of the stacking from $\alpha\beta\gamma$ to $\alpha\beta\gamma\delta$ with a corresponding I_c=c/4=5.72 Å (a=4.39 Å b=9.20 Å and c=22.87 Å). *Figure* **B** shows the Le Bail refinement and residuals for the two HP phases using the GSAS analysis software. The two refinements are not completely satisfying: in the 4.8 GPa refinement, essentially broadening is not taken into account as we can see. And in the 2.0 GPa refinement, the position of the peak located around 2° is not well reproduced. In order to check the validity of our proposed lattices and to go deeper into the structural determination, i.e. to determine the atomic positions, better complementary and/or quality data are needed.

We shall mention that this present study reports for the first time HP transformations of the CsC_8 graphite intercalation compound. In addition, we recently carried out Neutron Powder Diffraction at HP. The global results concerning the HP behavior of CsC_8 is the object of a submitted article.

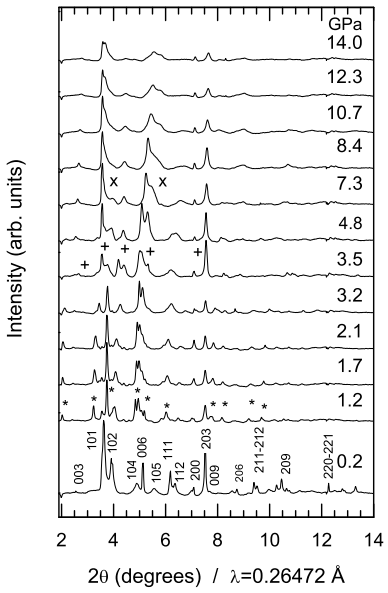

Figure ***A*** *HP-XRD of CsC_8.*

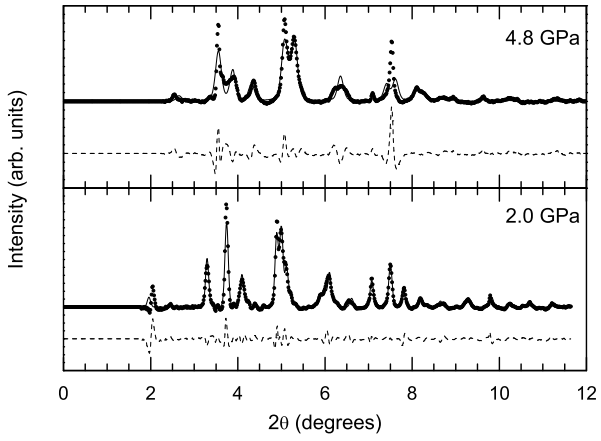

Figure ***B*** *Le Bail refinements at 2.0 GPa and 4.8 GPa.*