ESRF	**Experiment title:** **Pressure-induced modifications of the elastic properties of black-phosphorus**	**Experiment number**: HC-4324
Beamline:	**Date of experiment**: from: 25th November 2020 at 08:00 to: 3rd December 2020 at 16:00	**Date of report**: 28th February 2022
Shifts:	**Local contact(s)**: Alexei Bosak	*Received at ESRF:*

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Due to restriction due to COVID-19 pandemic emergency the experiment was followed in remote mode

Report:

Black phosphorus at ambient conditions has orthorhombic layered structure A17 (Cmce) featuring strong covalent intra-layer bonds and weak van der Waals inter-layer forces, see Fig.1a. By increasing pressure at room temperature, bP undergoes a characteristic phase transition at ~5 GPa from A17 to a layered rhombohedral phase (A7), and to simple-cubic phase (sc) at ~11 GPa, which is stable up to 103 GPa[1]. Interestingly, these structural changes are accompanied by consistent modifications of the electronic properties triggered by a strong electron-phonon interaction, similarly to (Sn,Ge,Pb) systems. In the A17 phase, bP is a narrow-gap (0.3 eV) semiconductor, semimetal in the A7 phase, and metal in the sc phase. The Bardeen–Cooper–Schrieffer superconductivity appearing in the A7 phase has been related to phonon mechanism[2].

The aim of the proposal HC-4324 was to investigate the vibrational precursors in the THz frequency range for the crystal and electronic structure changes of black-phosphorus under high pressure. To reach high pressure we have used a diamond anvil cell with 300-μm culet size diamonds loaded with Ne as pressure-transmission medium which solidifies at 5GPa. A rhenium plate pre-indented to 35-μm thickness was used as the gasket, in which a 150-μm-diameter hole was drilled with an excimer laser. Au was used as the pressure marker. We have focused the beam of 30x30 (horizontal x vertical) μm^2 spot and monochromatize the beam to have incident energy of 17.794 keV (999 reflection of Si monochromator) achieving an energy resolution of 3 meV. Pure single crystal bP samples were synthesized using a chemical vapor transport method placing an evacuated quartz tube containing red phosphorus into a double-zone tube furnace with hot and cold ends at 600°C and 500°C, respectively. The crystals were mechanically cleavaged with a diamond tip and laser cut to achieve ~40 μm thickness in order to work in transmission geometry and cleaned by ethanol. Samples have been characterized by Raman micro-spectroscopy assessing high-crystal purity. **Only one sample survive cell load.**

We first characterized **the phonon dispersions in the orthorhombic phase at ambient conditions along the main crystallographyc directions resolving the 12 phonon branches see Fig. 1b,c from which we extract the full elastic tensor (9 non-zero elastic stiffness coefficients).** Experimental phonon dispersion relations are in good-agreement with ab-initio simulations. **We have prepared and submitted a manuscript reporting the lattice dynamics at ambient condition.**

Having assessed the phonon dispersion relations at ambient pressure, **we have performed inelastic x-ray scattering (IXS) measurements at 4 different pressure points namely P= 0.34, 2.5, 4.5, 11 GPa** going **remarkably beyond the maximum pressure achieved so far by any IXS experiments**, which is 24 kbar (report ESRF-HS3069) thanks to an improved sample quality. **This has allowed to reach for the first time the simple cubic phase.** Unfortunately, intermediate pressure points in rhombohedral phase could not be measured due to twinning as signaled by a broad rocking curve for the reflection 001 and there were not large enough domains to perform the measurements. Annealing treatment could have helped to avoid twinning in the rhombohedral phase and having more than one crystals in the DAC would have increased our chances to have a good sample for characterizing the A7 phase. Due to an unexpected software crash and beam losses, we lost 12hours of measurements while measuring at P=4.5GPa.

We measured 110 longitudinal (LA) and transverse acoustic (TA) polarized, 1-10 and 100 LA+TA in the sc phase and 100,010 and 001 LA+TA in the A17 phase at 3 pressurized points. With the acquired data, we could experimentally observe TA phonons softening increasing pressure, and an anomalous downward-bent dispersion along the [010] direction. We plan to extend and complete the measurements including pressure points, in the range 5 < P < 10 GPa, corresponding to the rhombohedral phase to target the A17-A7 instability, and in the range 10< P< 20 GPa to study the simple cubic phase, where instability at R and X point have been predicted. Possible strategies to circumvent the difficulties that we have experienced include: annealing treatment during pressurization, load more samples in the DAC and increase the focusing.

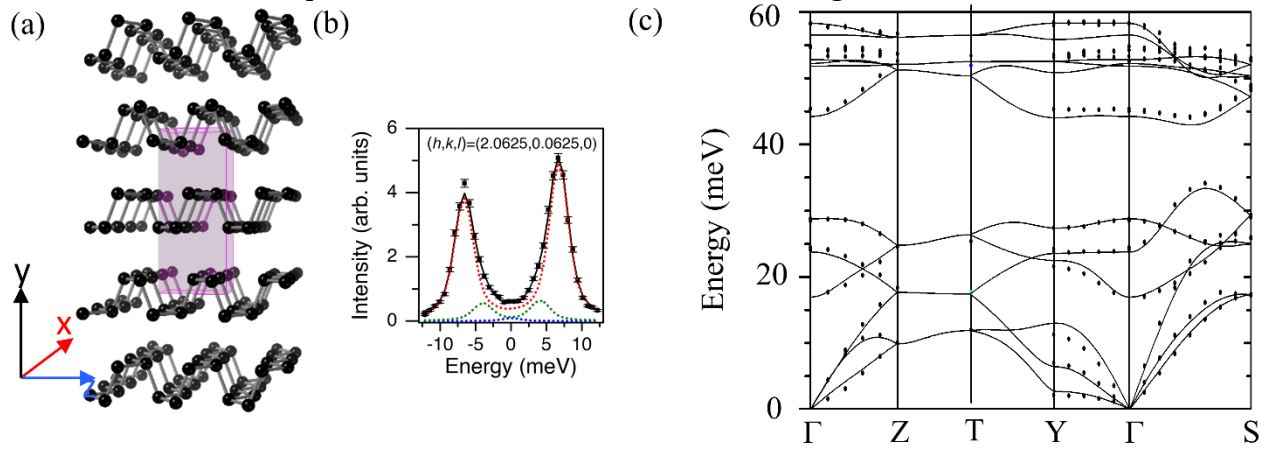

Fig.1 a. Structure of bP in the A17 phase; b) Exemplary IXS spectrum (black symbols) acquired at (h,k,l) together with the best fit (solid black line) including different phonon components (colored dashed line) ; c) Experimental phonon dispersion points (black symbols) compared to ab-initio simulations of bP at ambient conditions (solid lines).

References

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[2] X. Lia, J. Sun, P. Shahi, M. Gao, A. H. MacDonald, Y. Uwatoko, T. Xiang, J. B. Goodenough, J. Cheng, Jianshi Pressure-induced phase transitions and superconductivity in a black phosphorus single crystal PNAS **115**, 9935 (2018).

[3] Y. Yamada et al., Lattice-dynamical properties of black phosphorus under pressure studied by inelastic neutron scattering. *Phys. Rev. B* **30**, 2410 (1984).