ESRF

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Report:
Black phosphorus (BP) is a 0.2 eV band gap semiconductor with orthorhombic layered structure (A11-Cmca) at ambient pressure that metallizes upon application of pressure at 15 kbar and remains semimetallic with increasing pressure up to the transition to a rhombohedral phase (A7-R$\overline{3}$m) at 47 kbar [1]. Inelastic neutron scattering measurements performed on BP showed a softening of the longitudinal acoustic (LA) branch upon application of pressure up to 15 kbar [2], an indication of an instability of the crystal structure that may have two different origins, namely the insulator-to-metal transition and the phase transformation to the rhombohedral phase. Unfortunately these studies did not reach higher pressure values, thus leaving open the question concerning the mechanism responsible for the softening.

We report here inelastic x-ray scattering (IXS) measurements of the acoustic phonon dispersion relations of BP as a function of pressure. To this aim, we employed a diamond anvil cell and a focused beam of 40×60 (horizontal×vertical) μm^2 and incident energy of 17.794 keV (999 reflection of Si monochromator), achieving an energy resolution of 3 meV. Single crystalline samples were obtained via the high-temperature high-pressure growth method in a Paris-Edinburgh cell. The quality of the samples was very variable and was tested at ID27 at the time of the IXS measurements. The obtained rocking curves for the 200 reflection of the investigated samples varied between 1 and 3 degrees, mainly due to bending of the layers, and it changed significantly upon application of pressure. Due to the insufficient quality of the samples available (up to 10 samples were tested), the acquisition rate was slower than expected, and some of the results expected could not be addressed in a conclusive manner. Despite these limitations, we found that the

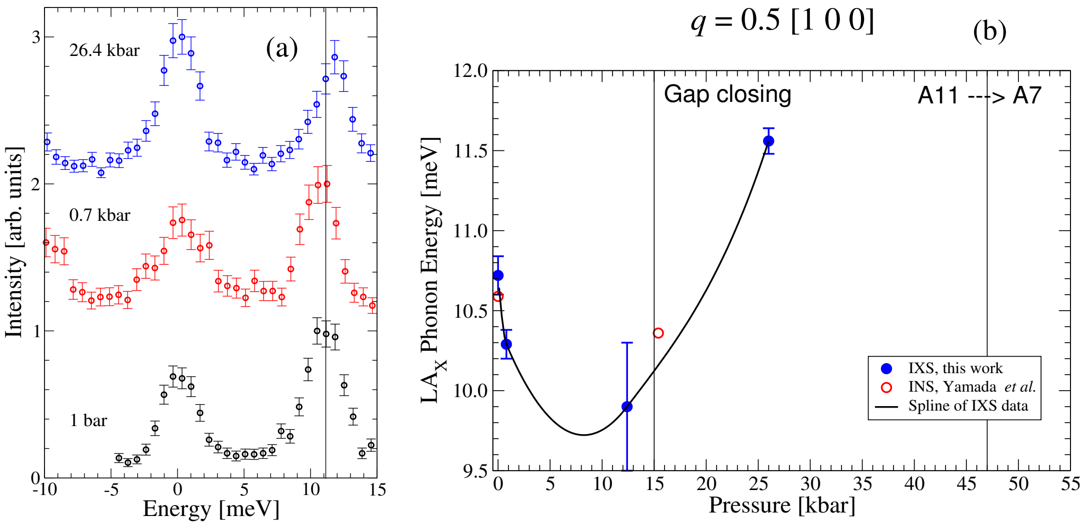

Fig. 1: IXS data of BP as a function of pressure for the LA modes along the [100] direction. (a) IXS spectra corresponding to longitudinal acoustic modes at q = (0.500) as a function of pressure. (b) Softening and hardening of the LA branch represented by q = (1/2 0 0), as a function of pressure.

LA branch along the [100] direction, not only softens as predicted by Yamada *et al.* [2], but it hardens when increasing the pressure up to 26.4 kbar, the maximum pressure achieved in the present measurements. Figure 1 displays the IXS spectra corresponding to the longitudinal branch for $q = (0.500)$ as a function of pressure, together with the elastic line. A softening of ≈ 0.5 meV is observed, followed by a blue shift of the longitudinal mode at higher values of pressure. Unfortunately we could not obtain reliable data at intermediate values of pressure. The theoretical calculations predict the hardening of the LA modes along [100] at a pressure of 40 kbar and a softening of an infrared active mode at 16 meV that will be a subject of separate investigations using infrared spectroscopy. Simultaneous single-crystal x-ray diffraction measurements performed at ID27 on the change of the lattice parameters in BP under pressure yielded also a significant change in the compressibility of a/a_0 at 15 kbar, contrary to the data reported in [1].

We can conclude from these two data sets that the softening observed for the LA modes along the [100] direction is a fingerprint of the closing of the electronic gap. However, additional pressure points would be highly desirable in order to pinpoint the trend softening-to-hardening for this mode, shown in Fig. 1(b), and to explore other possibilities for soft modes pointed out in the literature [2], such as the (1/2 1/2 1/2) and the (0 0 1/2) q-points, which could not be investigated due to a lack of beam time. Future experiments will benefit very much from a post-annealing treatment of the samples after growth in order to increase the crystal quality, and the increased focus capabilities achieved at ID28 during the commissioning performed after the summer shutdown. Some elastic constants can be readily obtained from the IXS data taken at [100] and [010] directions, though a complete set requires also further IXS measurements.

References

[1] T. Akai *et al.*, “The crystal structure and oriented transformation of black phosphorus under high pressure”, High Press. Res. **1**, 115 (1989).

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