Isostructural phase transformations (ISPhTs) are particular cases of isosymmetric transformations and include discontinuous isostructural transitions and crossovers. They are rare, intriguing phenomena in solids often associated with a significant volume collapse, giant magneto-elastic coupling, or negative thermal expansion. So far ISPhTs were reported for heavy elements and their compounds with complex electronic and/or magnetic structures. We have studied the high-pressure boron phase γ-B_{28} by means of *in situ* single-crystal X-ray diffraction in diamond anvil cells at ID09a above and Raman spectroscopy at megabar pressure range. The discontinuous behavior of the Raman modes and the abrupt changes in the compressional behavior of γ-B_{28} are manifestations of the isostructural phase transformation at about 40 GPa (Fig. 1). The combined experimental and *ab inito* theoretical analysis of the structural and vibrational properties of γ-B_{28} suggest that the ISPhT under compression is due to the weakening of the polarity of the covalent bonds between the boron atoms in the complex quasimolecular structure of γ-B_{28}.

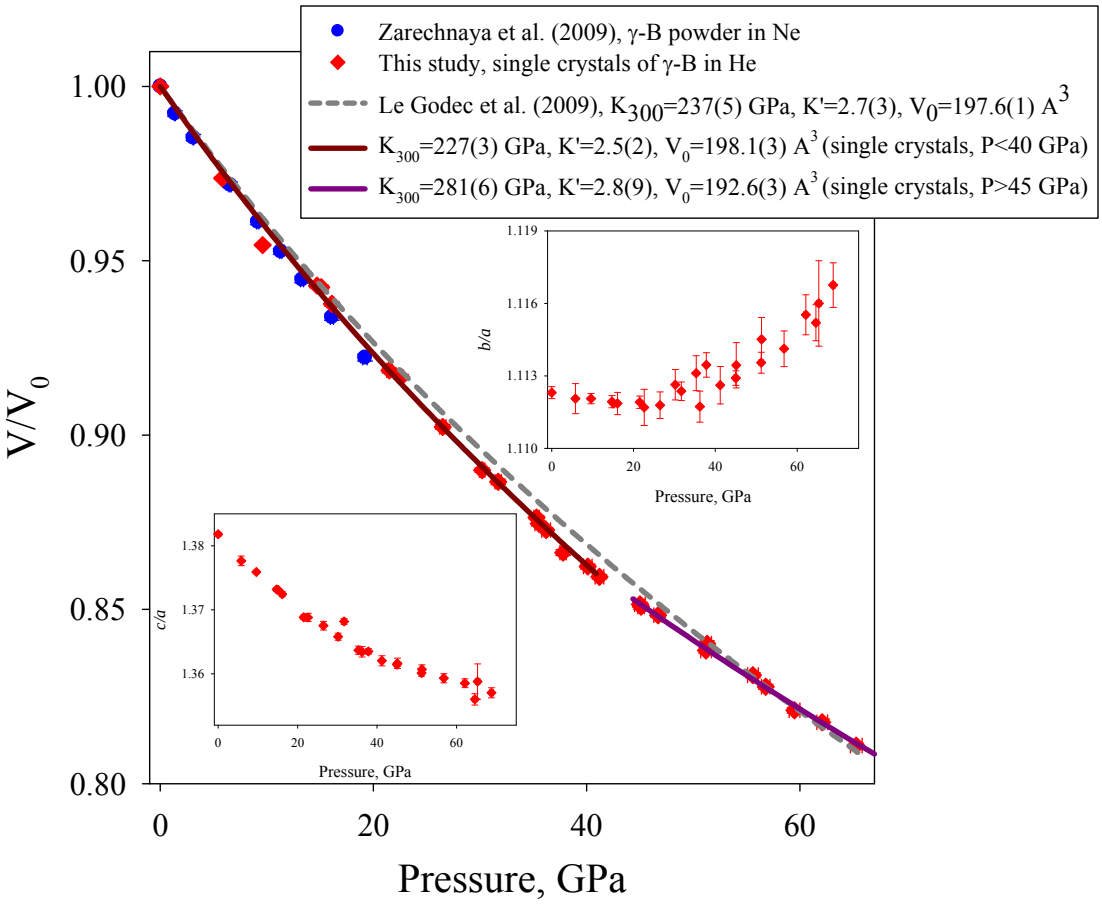

Fig. 1. The relative unit cell volume of γ-B as a function of pressure (red diamonds – single crystal data from this study; blue circles – powder diffraction data form Zarechany et al. (2009); lines are fits with the 3rd order Birch-Murnaghan (BM3) equation of state: dark-red for single crystal data below 40 GPa, dark-purple for single crystal data above 45 GPa, and dashed line as reported by Le Godec et al. (2009) based on powder x-ray diffraction data to 70 GPa). Inserts show the variations of the ratios of the lattice parameters *c/a* and *b/a* as a function of pressure.