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Structural transitions in elemental tin at ultra high pressures up to 230 GPa

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The search for high-temperature superconductivity is one of the major challenges in condensed matter physics and solid-state chemistry. The poly-hydrides of metals, including Sn, are promising candidates for superconductors, which can be obtained at very high pressures of the megabar range. Structural studies of Sn-hydrides using X-ray diffraction (XRD) are valueless without careful investigations of the structure of pure tin as a reference. Moreover, the ^{119}Sn Mössbauer isotope was recently used as a sensor of magnetic field in the search for superconductivity in H_2S compressed to 150 GPa [1]. Therefore, the scientific community addresses the investigation of the tin structure in the multi-megabar pressure region as a very important fundamental problem. There is a lot of literature related to theoretical and experimental studies of phase transitions and high-pressure structural modifications of elemental Sn [2–16]. In our study, the crystal structure of Sn was investigated by synchrotron XRD technique at high-pressures up to a maximal value of ∼ 230 GPa. This is the highest pressure achieved in XRD experiments with tin to date. We used tin foil samples enriched with ^{119}Sn (95 %). High pressures were created in diamond anvil cells (DAC) using different pressure transmitting media (He, H_2, silicon oil PES-5, NaCl) at ambient temperature. Experiments were performed at beam-line ID27 of ESRF (Grenoble, France) [17] and at beam-line P02.2 of PETRA III at DESY (Homburg, Germany) [18]. Five runs of the XRD measurements were performed with different pressure media. In runs

reaching maximal pressures the DACs design similar to [19] were used.

The full set of the experimental XRD data was carefully analysed and we calculated phase composition and $V-P$ equation of state (EOS) of Sn at room temperature in the pressure region of 76–230 GPa (Fig. 1).
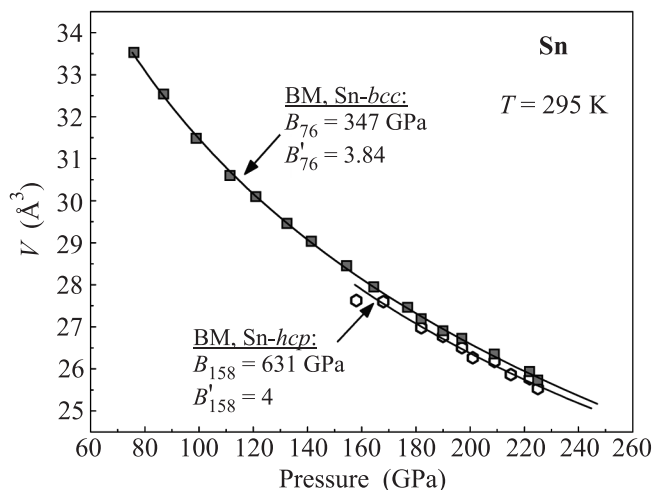

Fig. 1. (Colour online) The room temperature EOS of Sn for the volume of the *bcc* and *hcp* phases at pressure increase in the range from 76 to 230 GPa calculated from the set of XRD measurements with various pressure transmitting media. The symbols are the experimental points. The lines show the fits using a modified 2nd order Birch–Murnaghan equation of state. At pressures higher than the onset of the *bcc-hcp* transition the *bcc* and the *hcp* phases coexist. The difference in cell volumes between the *bcc* and the *hcp* phases at ∼ 168 GPa is about 1.0 %

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We found pure *bcc* phase of Sn above 70 GPa in complete agreement with results observed previously [2, 3, 5]. Upon further compression, the onset of transition into the *hcp* phase at ~ 160 GPa was observed. This is the first experimental acknowledgement up to date of the appearance of the *hcp* phase previously observed in [4]. Thus, our results confirm principal difference between static [4] and dynamic [14] compression on the phase diagram of Sn. At static compression, the *bcc* phase lost stability and transforms into a complicate mixture of *bcc* and *hcp* phases at pressures about 160 GPa, whereas at dynamic compression [14], the *bcc* phase is stable up to 1.2 TPa and there is no evidence of the *hcp* phase. In our experiments, the mixeture of the *bcc-hcp* states was observed at least up to 230 GPa, and it looks like this state could exist even up to higher pressures. In addition to the first observation of the hcp phase [4] in the pressure range of 157–194 GPa, we established that the range of pressures of the coexistence of the *bcc-hcp* phases increases up to ~ 230 GPa. The influence of pressure and pressure medium on the *hcp*-phase content was also revealed and documented.

It was evaluated that in the silicon oil pressure medium, the *hcp* fraction grows up to 90 % at 229 GPa, whereas in CaF_2 medium with a possible small amount of hydrogen it only grows to 30 % at 225 GPa. The lower content of the *hcp*-phase in the later case may be the result of the influence of small amount of hydrogen penetrating to the Sn sample. Most probably, the nucleation of a new phase occurs within the grain boundaries. The fraction of intergrain boundaries increases with pressure, thus increasing the volume of the Sn-*hcp* phase. Hydrogen penetrates most easily and deeper into the volume of metal along grain boundaries, and thus Sn-hydrides can be created. These interesting effects should be investigated in further studies.

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