Interlayer bond formation in arsenic at high pressure

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Abstract

The high-pressure behavior of arsenic has been explored in literature up to 250 GPa. Upon room temperature compression, ambient pressure hexagonal As-I (A7), commonly known as gray arsenic, transforms into simple cubic (sc) As-II, then into host-guest incommensurately modulated As-III and ultimately into bcc As-IV [1]. The first transformation from A7 As-I to sc As-II represents a prototypical phase transition in structural chemistry, which is particularly relevant for group 15 elements, inherently featuring the characteristic ns^2np^3 outer shell orbital electronic configuration. This transformation represents indeed the transition from a layered structure (A7 As-I), in which As atoms exhibit three first-neighbor distances in the same layer and three second-neighbor distances in the adjacent layer, highlighting trigonal-pyramidal coordination, to a non-layered structure (sc As-II), featuring six equivalent nearest-neighbor distances and octahedral atomic coordination. Nevertheless, after several decades of investigations, the A7 to sc transformation in As still remains elusive and debated, essentially due to the lack of conclusive experimental studies [2-4]. Here we report the results of single-crystal structure determination of As by synchrotron X-ray diffraction during room T compression up to 38 GPa, using a membrane diamond anvil cell for the generation of pressure and He as pressure transmitting medium. Our experiments enabled to finely and unambiguously track the pressure dependence of the lattice parameters, atomic positions and interatomic distances across the full pressure range of the transformation. Our data highlight a two-step pressure-induced inter-layer bonding mechanism, underlying the increase of the As coordination number, and reveal the existence of a pseudo-simple cubic (p-sc) structure between A7 As-I and sc As-II, which demonstrates structural consistency with lighter P in group 15 [5]. The results are interpreted according to literature theoretical studies and supported by additional data analysis, which adds focus on the key-role of *s-p* orbital mixing. While finally solving the long-standing debate on the elusive A7 to sc transformation in As, implications concern fundamental bond theory in pnictogens and the synthesis of As-based materials.

References

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