

structure [3]. Although S-I has been reported to undergo a gradual transition to an amorphous form on compression at room temperature [4-6], we observe S-I to transform directly to tetragonal S-II [7] at 38 GPa with no evidence of any intermediate amorphous phase. Single-phase diffraction profiles of S-III were observed above 95 GPa, and these revealed that S-III adopts the same incommensurately modulated monoclinic structure as Se-IV and Te-III. Sulfur is thus the first element observed to have an incommensurately modulated structure above 100 GPa. On pressure decrease a previously unreported phase of sulfur can be assigned to the triclinic structure of Se-III and Te-II. In this contribution we describe our most recent results on S-III and Se-II.

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Keywords: high-pressure crystallography, sulfur, phase transition

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Charge-density Wave in the Incommensurate Phase of Metallic Sulfur at Megabar Pressure

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Recent discoveries of incommensurate (IC) host-guest and/or modulated phases in elemental metals at high pressure suggest that aperiodic structures are a common phenomenon among the elements under pressure. However, the driving force for development of the incommensurability and structural modulations in these elemental systems is poorly understood.

Using synchrotron x-ray diffraction and diamond anvil cells, we show that the metallic phase of sulfur stable above 83 GPa, has an IC modulated crystal structure with a monoclinic average cell and a modulation wavevector $q = \langle 0 \ 0.281 \ 0 \rangle$ at 100 GPa. We observe a strong pressure dependence of the modulation up to 135 GPa, where the modulation disappears.

We perform first-principles calculations using the density-functional theory to analyze the average structure of the IC phase. We obtain a simple Fermi surface (FS) that exhibits parallel zones, indicating a nesting, characterized by a wavevector close to the experimental modulation. The phonon dispersion shows a softening with a minimum at the same wavevector as the FS nesting vector. These indicate that the IC structure in metallic sulfur at megabar pressures is due to a charge-density wave.

Keywords: high pressure, incommensurate modulated structures, electronic band structure calculations

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Phase Transitions in the O₂ – H₂O System at High Pressures

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Pressure and temperature induced phase transformations in the O₂ – H₂O system were studied by means of Raman spectroscopy, X-ray powder diffraction and visual observations in diamond anvil cell at high pressure. Ice and liquid oxygen were loaded in high pressure cell simultaneously. Several clathrate hydrate phases in a pressure range 0.5 – 2.8 GPa were detected and assigned to known clathrate hydrate structural types including high-pressure structures recently found for methane and argon clathrate hydrates [1, 2].

Reaction of hydrogen peroxide formation from water and liquid oxygen was found at pressures lower than 1 GPa and room temperature. Brake down reaction of H₂O₂ to H₂O and O₂ was also

studied, for this purpose 30% solution of H₂O₂ was loaded in the diamond anvil cell. Influence of pressure and temperature on the chemical equilibrium $\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{O}_2$ will be discussed.

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Keywords: clathrate hydrates, high-pressure phase transitions, high-pressure X-ray diffraction

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Hexagonal Diamond from Highly Crystalline Graphite Film

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While a compressed graphite transforms to a cubic diamond under high-temperature condition, a high crystalline graphite transforms to a hexagonal diamond under ambient temperature condition. The transition pressure is much affected by the nature of the sample and the compression procedure [1].

We investigated the transition pressure with a highly crystalline graphite film made from a heat-treated poly-imide by Raman spectroscopy and X-ray diffractometry. High pressure was generated by a diamond-anvil cell and Daphne7373 oil was used as a pressure transmitting medium. In Raman spectroscopy, the peaks associate with the hexagonal diamond appeared at 6 GPa and the graphite peaks vanished at 9 GPa. The transition pressure is found to be much lower than that of the previous report. On the other hand, in X-ray diffraction experiment, the transition was detected not at 6 GPa but at 19 GPa same as the previous report [2]. We propose that the transition firstly occurs on the surface at much low pressure with highly crystalline graphite film.

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Chain Melting at HT/HP in Incommensurate Rb-IV

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Rb-IV is the stable high-pressure phase of rubidium between 16 and 21 GPa. The structure of Rb-IV has long been known to be complex, but it is only recently that it has been solved as being an incommensurate host-guest composite structure [1], comprising a tetragonal host framework containing chains of "guest" atoms that form structures incommensurate with the host. While we have observed similar composite structures in a number of other elemental metals [2], these structures all have an 8-atom host framework, while the host structure in Rb-IV contains 16-atoms. Rb-IV is also unique in that on pressure decrease below 16.3 GPa at 300K, the chains of guest atoms become disordered and liquid-like [3]. We have recently investigated the P-T dependence of this "melting" transition, and in this poster we will present the stability field of the disordered chain phase, combining it with previous data on the P-T phase diagram of Rb up to 14 GPa.

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