

FA5-MS07-P01**Dissolution of Boron in Diamond under High Pressures: Experimental Evidences.**

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The discovery of superconductivity in polycrystalline boron-doped diamond (BDD) synthesized under high pressure and high temperatures [1] has raised a number of questions on the origin of the superconducting state. It was suggested that the heavy boron doping of diamond eventually leads to superconductivity. To justify such statements more detailed information on the microstructure of the composite materials and on the exact boron content in the diamond grains is needed. For that we used high-resolution transmission electron microscopy and electron energy loss spectroscopy. For the studied superconducting BDD samples synthesized at high pressures and high temperatures the diamond grain sizes are about 1–2 μm with a boron content between 0.2 (2) and 0.5 (1) at %. The grains are separated by 10- to 20-nm-thick layers and triangular-shaped pockets of predominantly (at least 95 at %) amorphous boron [2]. These results render superconductivity caused by the heavy boron doping in diamond highly unlikely. A comparison of these results with those for the B-C system recently reported in literature will be given in the presentation.

[1] Ekimov E., *et al. Nature*, **2004**, 428, 542. [2] Dubrovinskaia N., *et al. PNAS*, **2008**, 105, 11619.

Keywords: boron compounds; diamond-like structures; transmission electron microscopy and diffraction

FA5-MS07-P02**High-pressure Behaviour of Inorganic Oxide Materials with Tl^{1+} and Te^{4+} Cations.**

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In this contribution, we will review our work on the high-pressure behaviour of inorganic oxide materials containing Tl^{1+} and Te^{4+} cations with lone non-bonded electron pairs using single-crystal x-ray diffraction in diamond anvil cells.

At atmospheric pressure, the coordination numbers (CNs) in TlO_n and TeO_n polyhedra range from 3 to 12 and from 3

to 7, respectively [1-3]. Low CNs are associated with the pronounced stereoactivity of the lone electron pair, with typically a few short bonds lying to one side of the cation and with very long bonds on the other side.

In the materials with low CNs around the Tl^{1+} and Te^{4+} cations, the compression mainly takes place in the region of the structure where the lone pairs are located. The long distances to oxygen atoms decrease, while the short ones are constant or even become slightly longer. The CNs usually increase, not necessarily being associated with a phase transition. This implies the pressure-induced suppression of the stereochemical effect of the lone electron pairs [4,5].

On the other hand, the presence of the lone pairs does not influence the high-pressure behaviour of the materials in which the cations have high coordination numbers. For instance, the effect of pressure on the crystal structure of Tl_2SeO_4 (*Pmcn*, $Z = 4$) with two non-equivalent Tl^{1+} cations surrounded by nine and eleven oxygen atoms results in the compressibility mechanism already observed in other compounds with the $\beta\text{-K}_2\text{SO}_4$ type structure [6].

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Keywords: oxides; inorganic stereochemistry; high pressure

FA5-MS07-P03**Stability of Xenon Oxides and Xenon Silicates at High Pressures.**

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Xenon is a noble gas and is quite inert at ambient conditions. Although a few compounds of xenon fluorides have been found, experimental and theoretical high pressure studies on the systems Xe-C and Xe-F did not find a tendency of xenon to form alloys. Two xenon oxides (XeO_3 , XeO_4) are known at atmospheric pressure. Both of these compounds are unstable and decompose explosively at room temperature. There is growing evidence that noble gases, especially Xe, may become reactive under pressure. The possibility of formation of stable xenon oxides and silicates could explain the “missing xenon” paradox, i.e. that the amount of Xe in the Earth’s atmosphere is an order of magnitude below predictions based on a model assuming that noble gases cannot be retained in the deep Earth. In fact, there is new

experimental evidence that xenon reacts with SiO₂ at high pressures and temperatures [1].

The evolutionary algorithm USPEX [2,3], used here for predicting new stable structures, searches for the structure with the lowest free energy at the given P-T conditions and is capable of predicting the stable structure of a compound knowing just the chemical composition. The underlying *ab initio* structure relaxations were performed using density functional theory (DFT) with the generalized gradient approximation (GGA) together with the all-electron projector augmented wave (PAW) method, as implemented in the VASP [4] code.

Using the *ab initio* evolutionary algorithm USPEX, we investigated the stability of Xe-O compounds at high pressures. Present results clearly show that Xe loses its chemical inertness under pressure and that charge transfer plays an essential role in chemical bonding in Xe compounds and stability of these compounds is largely determined by electronegativity differences.

XeO (space group *Pbcm*) and XeO₂ (space group *Pnma*) have been found to be thermodynamically stable at pressures above 89 GPa and 102 GPa, respectively, with xenon adopting increasingly more oxidized states on increasing pressure. Extending our calculations to the Xe-Si-O system, we found no stable xenon silicates at pressures relevant to the Earth's mantle (<136 GPa). However, energetically favoured structural analoga to the xenon oxides were found in the silicon oxides, pointing to a preferred Xe coordination, which could be found in a possible stable xenon silicate.

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Keywords: *ab-initio* calculations; crystal structure prediction; xenon oxides

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Combining synthetic multilayer mirrors with microfocus X-ray sources (rotating or stationary target) has, over the past years, become standard in home lab X-ray sources for single crystal diffraction and for certain applications in powder diffraction [1]. In contrast to multilayer mirrors for Cu sources, the maximum angles of incidence at which a multilayer mirror reflects higher energy radiation, such as Mo-K_α or Ag-K_α radiation, are significantly smaller than for Cu radiation. With today's deposition technology, however, high quality multilayer mirrors can be produced which have a small *d*-spacing and reflect higher energy radiation at larger angles of incidence [2, 3]. Together with the latest developments of microfocus sealed tubes, this makes way for new high-performance low-power X-ray sources for

shorter wavelengths.

We will present selected results on the use of microfocusing sealed tube X-ray sources with high-performance focusing multilayer mirrors for Mo-K_α and Ag-K_α radiation applied in small molecule and high-pressure crystallography.

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Core Ionization in Compressed Alkali and Alkali-Earth Metals. Valentina Degtyareva. *Institute of Solid State Physics, Russian Academy of Science, Chernogolovka, Russia.*

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Under compression, simple s-bonded alkali and alkali-earth metals pass through the sequence of phases characterized by lowering in symmetry, coordination number and packing density [1,2]. Structural transformations in these metals are controlled by the combined effects of electrostatic (Madelung) and electronic (band-structure) contributions to the crystal energy. The latter term increases with pressure yielding low-symmetry complex structures, such as cI16 in Li and Na, Rb-oC52 and Cs-oC84. Stability of these structures can be supported by a Hume-Rothery argument when new diffraction plains appear close to the Fermi level [3].

Upon further compression heavy alkalis Cs and Rb form a very open structure tI4 with coordination number 4+4 and packing density ~0.56. Considering the Brillouin zone configuration with respect to the Fermi sphere one can conclude that the Hume-Rothery mechanism is effective if the number of valence electrons increases from 1 up to 2 and higher values implying the transition of the outer core electrons into the valence band.

Similar changes in the valence state are expected for compressed Na at the transition from cI16 to oP8 at pressures above 117 GPa [2]. Observations of the simple cubic structure in Ca (above 32 GPa) and the beta-tin structure in Sr (above 25 GPa) imply the increase in the number of valence electrons resulting from the core ionization [3].

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