

MS22 P06

Simple metals at high pressure: the Hume-Rothery argument Valentina F. Degtyareva, *Institute of Solid State Physics, Russian Academy of Sciences, Chernogolovka, Moscow district, Russia*. E-mail: degtyar@issp.ac.ru

Keywords: high-pressure structures, phase stability, crystal structure and properties

Under compression, simple s-bonded alkali metals pass through the sequence of phases characterized by lowering in symmetry, coordination number and packing density [1]. 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 Li-*cI16*, 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 [2]. Upon compression up to ~0.4 of initial volume, Cs and Rb form a very open structure *tI4* with coordination number 4+4 and packing density ~0.56. The transition to Cs-*tI4* is accompanied by an approximately 12% reduction in the atomic radius compared with Cs-fcc. 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 up to ~4 [2]. In the *tI4* structure the loss in the electrostatic energy compared with fcc should be compensated for by the gain in electronic energy that can occur by increase in the number of valence electrons due to the core overlap. The *tI4* and *oC16* structures in heavy alkalis Rb and Cs are similar to those in polyvalent group IV elements (Si, Ge and Sn) implying the similarity in the valence electron configurations in these two groups metals and supporting an assumption of core ionization in alkalis at much lower pressures than predicted by theory [3].

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MS22 P07

Origin of unexpectedly high bulk modulus of Au and Ag nanoparticles Qinfen Gu^a, Guenter Krauss,^a Fabian Gramm,^b Antonio Cervellino,^c Walter Steurer^a
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Keywords: high pressure, nanocrystalline, gold and silver

We studied commercially available gold (30 nm, *n*-Au) and silver (10 nm, *n*-Ag) nanoparticles at high pressures up to 30 GPa using X-ray diffraction (XRD) and a diamond-anvil cell. Unexpectedly for that particle size, the nanoparticles show significantly higher bulk modulus than the corresponding bulk materials, i.e. about 60 % for *n*-Au and 20 % for *n*-Ag. The bulk modulus of *n*-Au, $K_0 = 277(5)$ GPa, even surpasses that of ceramic materials such

as B₄C (254 GPa), SiC (203 GPa), Al₂O₃ (257 GPa) or TiB₂ (240 GPa). The structural characterization of both kinds of nanoparticles by XRD using a whole pattern-fitting method [1] and high-resolution electron microscopy (HRTEM) identified polysynthetic domain twinning and lamellar defects as described in [2] as the main origin of the strong decrease in compressibility. Free-surface effects do not play a significant role.

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MS22 P08

Single crystal neutron diffraction R. J. Nelves, J.S.Loveday, C.L.Bull, M.Guthrie, K.Komatsu and H. E. Maynard, SUPA, School of Physics and Centre for Science at Extreme Conditions, University of Edinburgh, Mayfield Road, Edinburgh, EH9 3JZ, UK
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Keywords: High-Pressure, Neutron Diffraction, Hydrogen Bonding

Although the pressures achieved routinely in high pressure neutron diffraction studies have reached to 30 GPa and beyond for almost twenty years this limit has applied only to powder diffraction studies. The limit for single crystal studies has remained at ~3 GPa which was achieved in the 1980's. This has meant that the advantages of neutrons for the study of problems like multisite disorder and anharmonic thermal motion have not been fully exploited beyond 3 GPa.

In this paper we will present developments made using the new VX Paris-Edinburgh cells which have extended the limit for neutron single crystal studies to almost 10 GPa. We will illustrate the power of high (real-space) resolution in studies of hydrogen bond centring in potassium dihydrogen phosphate and squaric acid as well as studies of multi-site disorder in ice VII.

MS22 P09

Sixfold coordinated phosphorus by oxygen in AlPO₄ quartz homeotype under high pressure. Alain Polian¹, Julio Pellicer-Porres², Antonino Marco Saitta¹, Jean Paul Itié^{1,3}, and Michael Hanfland⁴
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Keywords: high-pressure, phase transitions, X-ray diffraction, berlinite

AlPO₄ belongs to the berlinite quartz homeotype family, with potential applications as piezoelectric materials. We performed new angle dispersive x-ray diffraction experiments under high pressure combined with laser heating to relax the deviatoric stresses, complemented with *ab initio* calculations. We observed two phase transformations, and the structures were determined through Rietveld refinements. It is shown that AlPO₄

shares the same two stage densification mechanism as quartz. The first one from berlinite to a CrVO_4 type structure where Al is six-fold coordinated and P still four-fold occurs around 14 GPa. In the final compression step, phosphorous becomes sixfold coordinated by oxygen. This previously unknown phosphorous coordination is of great importance from a fundamental point of view and opens new possibilities on the high pressure chemistry of phosphorus

MS22 P10

The high pressure behaviour of gypsum: a single crystal X-ray study Comodi P., Nazzareni S., Zanazzi P.F., Dept. of Earth Sciences, Università di Perugia, Italy
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Keywords: Gypsum, High-pressure, X-ray single crystal diffraction

Gypsum is the most common sulphate mineral with molecular water which may be easily removed from the structure by heating. This can affect the pore pressure inside the rocks, greatly enhancing the probability of large-scale over thrusts. Most studies on gypsum were devoted to understand the dehydration mechanism, while its baric behaviour was less studied as well as the nature of phase transitions observed at different pressures by X-ray powder diffraction [1] and infrared and Raman spectroscopy [2].

A gypsum crystal was loaded at different pressures up to 5 GPa in a Merrill-Bassett DAC with ethanol: methanol mixture as hydrostatic fluid. Both quartz and Sm^{+2} : Ba FCl chips were used to monitor the pressure. Single-crystal X-ray diffraction experiments were performed by using a Xcalibur Oxford diffractometer (with a CCD detector for intensity data collection and a point detector for accurate cell parameters measurements).

The bulk modulus determined by fitting the volume-pressure data with a third order Birch-Murnaghan equation-of-state is 44 (1) GPa with $K' = 3.3$ GPa, and 43(1) GPa when K' is fixed to 4. The principal linear compression coefficients calculated by STRAIN program [3] up to 4 GPa were $\varepsilon_1 < \varepsilon_2 < \varepsilon_3$, with ε_2 parallel to the b axis and ε_3 forming an angle of 55° with the a axis.

The structural refinements indicate that the SO_4 volume and the average S-O bond distance remain almost unchanged from room pressure to 3.9 GPa: (in the range 1.64\AA^3 - 1.66\AA^3 ; 1.473\AA - 1.481\AA) while they undergo a sensible distortion: the smaller distance decreases (from 1.473\AA to 1.45\AA) and the larger increases (from 1.474\AA to 1.51\AA). On the other hand the calcium polyhedra show a normal high-pressure behaviour, becoming more regular and reducing the volume (from 25.84\AA^3 at room P to 24.67\AA^3 at 3.9GPa). The largest variations are observed in the interlayer region where the water molecules are located. The two hydroxyls of the water molecule, under room conditions, form weak hydrogen bonds with the

oxygens of Ca and S polyhedra. Increasing pressure, the weakest hydrogen bond becomes the strongest one.

These structural results indicate that the water remain in the structure also at HP condition and explain raman and infrared spectra. In fact the distortion of sulphate tetrahedra explains the splitting of raman mode and the different compressibilities of the two hydrogen bonds explain the coalescence of the Raman stretching mode observed at HP (Knittle et al. 2001)

The diffraction pattern above 4 GPa changes. Indexing with the $C2/c$ space group, some $h+k$ odd reflections appear, the a and b lattice parameters, as well as the cell volume, show a discontinuity, while the c lattice parameter and the β angle, vary linearly.

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MS22 P11

In situ diffraction study of high-pressure transformation of C_{60} to disordered sp^2 -carbon L. Marques^a, M.Mezouar,^b J-L.Hodeau,^c ^aDepartamento de Física and Cicco, Universidade de Aveiro, Portugal. ^bE.S.R.F., Grenoble, France. ^cC.N.R.S., Grenoble, France.
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Keywords: C_{60} , high-pressure phases, in-situ diffraction

C_{60} -2DR polymer amorphisation under high pressure has been studied by in situ diffraction techniques employing the Paris-Edinburgh press. The initial interest of this study was to find structural signatures of the so-called magnetic carbon phase, which would be formed by the C_{60} -2DR polymer phase close to the molecular collapse. Evolution of the transformation process was followed by 2D angular-dispersive diffraction. The recorded diffraction patterns show that the C_{60} polymer phase gradually amorphises into a disordered sp^2 -carbon phase. Changes in the diffraction pattern of the 2DR C_{60} polymer during the amorphisation transition, which would be indicative of the magnetic phase, were not perceived. This must be confirmed by detailed data analysis, under way.

Samples quenched at different levels of transformation were recovered in order to perform x-ray diffraction and complementary magnetization measurements. Diffraction patterns of the partial amorphised samples show that both the amorphous sp^2 carbon and the 2DR C_{60} polymer are highly oriented. This indicates an orientational relationship between the parent polymeric structure and the amorphous transformed structure: the graphitic planes and C_{60} polymerized planes have a defined orientational relationship typical of martensitic transformations. Therefore C_{60} molecules amorphise in a way that does not involve the complete collapse of the cage structure, in contrast to what one would expect. Detailed data analysis is under way in order to obtain the full orientational relationship between parent and transformed structures.